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^{13}C NMR Study of a Co_2Ni Tetrahedral Cluster. Preferential π-Orbital Overlap and Reorientational Dynamics in $Co_2NiCp(CO)_6(\mu_3\text{-}CPh)$

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Received April 25, 1991

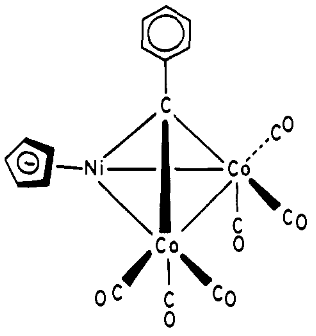
Carbon-13 spin-lattice relaxation times of the phenyl and cyclopentadienyl nuclei in $Co_2NiCp(CO)_6(\mu_3\text{-}CPh)$ were measured as a function of temperature in the solvent chloroform. Additionally, T_1's were determined for the carbonyl ^{13}C nuclei at two magnetic field strengths. The results were used to determine the cluster's overall reorientational diffusion coefficients, $D_\perp$ and $D_\parallel$, and the internal rotation rates of the phenyl [R(Ph)] and cyclopentadienyl [R(Cp)] rings. The net phenyl spinning rates, $D_s = D_\parallel + R(\text{Ph})$, were found to significantly below values observed earlier in the isolobal cluster $Co_3(CO)_9(\mu_3\text{-}CPh)$. The slowed internal rotation has been attributed to a barrier created by the Ni heteroatom, which splits the degeneracy of the metals' 2e orbitals, inducing an asymmetric electronic interaction between the ring and the metal framework. In contrast, the spinning rate of the Cp group is quite facile, indicating that there is no appreciable barrier to internal rotation of this ring.

Introduction

The construction of mixed-metal clusters derived from $RCCo_3(CO)_9$ has been assisted greatly through the isolobal mapping of organometallic fragments. The theoretical foundation for many of the isolobal analogies rests with the work of Hoffmann,[2] while the majority of the experimental achievements stems from work originating with the Vahrenkamp and Stone groups.[3,4]

Interestingly enough, while the tricobalt clusters $RCCo_3(CO)_9$ have been studied extensively, comparatively little data exist concerning the corresponding heterometallic analogues. Of interest to us were the reports of Hoffmann[5] and Stone[6] on $PhCCo_3(CO)_9$, which predicted a subjacent HOMO of e symmetry. Furthermore, the degeneracy of the 2e SHOMO is lifted upon the replacement of one (or two) of the $Co(CO)_3$ vertices with an isolobal equivalent. One direct manifestation of such an isolobal replacement is the preferential stabilization of the phenyl π system in the molecular mirror plane of the cluster.[7] Stone et al.[6] were the first to observe this interaction in the tetrahedral cluster $Fe_2Co(\mu_2\text{-}CO)(CO)_9(\mu_3\text{-}CC_6H_4Me\text{-}4)$. More recently, we have also presented data that support the existence of an extended benzylidyne–cluster orbital overlap in $Cp_2Co_3(\mu_2\text{-}CO)(CO)_3(\mu_3\text{-}CPh)$[8] (**1**) and in $FeCo_2(CO)_9(\mu_3\text{-}PPh)$.[9]

In the above studies[8,9] and other recent investigations from these laboratories,[10,11] we have demonstrated the utility of NMR relaxation[12] to probe the electronic and steric factors affecting phenyl group internal rotation in benzylidyne- and phosphinidene-capped metal carbonyl clusters. In order to determine whether the observed cluster–aryl orbital overlap in $Fe_2Co(\mu_2\text{-}CO)(CO)_9(\mu_3\text{-}CC_6H_4Me\text{-}4)$[6] and $FeCo_2(CO)_9(\mu_3\text{-}PPh)$[9] is, indeed, a general phenomenon associated with heterometallic tetrahedrane clusters, we have utilized temperature and magnetic field dependent carbon-13 relaxation time measurements to investigate the barrier to internal rotation and reorientational dynamics of the isolobally related complex $Co_2NiCp(CO)_6(\mu_3\text{-}CPh)$[13] (**2**).



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Experimental Section

Dicobalt octacarbonyl and $[CpNi(CO)]_2$ were purchased from Pressure Chemical and used as received. $Co_2NiCp(CO)_6(\mu_3\text{-}CPh)$ was prepared according to the procedure of Vahrenkamp[13] by using $Co_3(CO)_9(\mu_3\text{-}CPh)$.[14] $CDCl_3$ was distilled from P_2O_5 under argon by using Schlenk techniques.[15] The NMR sample was prepared in a 5-mm NMR tube contained 0.07 g (0.14 mmol) of $Co_2NiCp(CO)_6(\mu_3\text{-}CPh)$ dissolved in 0.7 mL of $CDCl_3$ (0.2 M) and was freeze–pump–thaw degassed two times prior to flame sealing.

The ortho, meta and para phenyl (at δ = 128.6, 127.9 and 127.2 ppm downfield from TMS) and cyclopentadienyl (at δ = 91.0 ppm) carbon-13 relaxation times and nuclear Overhauser enhancements (NOE's) of **2** were measured at various temperatures between 215 and 303 K on a Varian VXR-300 FT-NMR spectrometer at a magnetic field of B_0 = 7.05 T. In addition, the carbonyl (at δ = 199.0 ppm) ^{13}C T_1's were determined at the three lowest temperatures at B_0 = 7.05 T and B_0 = 4.70 T (on a Varian Gemini-200 spectrometer); the latter measurements were prohibited at higher temperatures due to spectral broadening resulting from ^{59}Co – ^{13}C scalar coupling.[16,17] Details of the relaxation

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[2] (a) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711 and references therein. (b) See also: Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

[3] (a) Vahrenkamp, H. *Philos. Trans. R. Soc. London, A* **1982**, *308*, 17. (b) Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169. (c) Schacht, H. T.; Vahrenkamp, H. *J. Organomet. Chem.* **1990**, *381*, 261 and references therein.

[4] (a) Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89. (b) Stone, F. G. A. *Pure Appl. Chem.* **1986**, *58*, 529.

[5] Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456.

[6] Evans, D. G.; Howard, J. A. K.; Jeffery, J. C.; Lewis, D. B.; Lewis, G. E.; Grosse-Ophoff, M. J.; Parrott, M. J.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1986**, 1723.

[7] (a) The molecular mirror plane is defined as the plane that bisects the metal–metal bond of the two identical groups. (b) For example, see: Sutin, K. A.; Faggiani, R.; McGlinchey, M. J. *New J. Chem.* **1988**, *12*, 419.

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[9] Yuan, P.; Richmond, M. G.; Schwartz, M. *Inorg. Chem.* **1991**, *30*, 588.

[10] Schwartz, M.; Richmond, M. G.; Chen, A. F. T.; Martin, G. E.; Kochi, J. K. *Inorg. Chem.* **1988**, *27*, 4698.

[11] Wang, S. P.; Chen, A. F. T.; Richmond, M. G.; Schwartz, M. *J. Organomet. Chem.* **1989**, *371*, 81.

[12] Relevant reviews on applications of NMR relaxation to rotational dynamics include: (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) Boeré, R. T.; Kidd, R. G. *Annu. Rep. NMR Spectrosc.* **1982**, *13*, 319. (c) Versmold, H. *NATO ASI Ser., Ser. C* **1984**, No. 135, 309.

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[14] Nestle, M. O.; Hallgren, J. E.; Seyferth, D. *Inorg. Synth.* **1980**, *20*, 226.

[15] Shriver, D. F. The *Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969.

[16] (a) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: New York, 1981. (b) Aime, S.; Milone, L. *Prog. NMR Spectrosc.* **1977**, *11*, 183. (c) Aime, S.; Milone, L.; Valle, M. *Inorg. Chim. Acta* **1976**, *18*, 1.

[17] (a) Gates, R. A.; D'Agostino, M. F.; Sutin, K. A.; McGlinchey, M. J.; Janik, T. S.; Churchill, M. R. *Organometallics* **1990**, *9*, 20 and references therein. (b) See also ref 25.

Table I. ^{13}C NMR Relaxation Times in $Co_2NiCp(CO)_6(\mu_3\text{-}CPh)^{a-c}$

T, K	$T_{1M}(Ph)$, s	$T_{1O}(Ph)$, s	$T_{1P}(Ph)$, s	$T_1(Cp)$, s	$T_1^A(CO)$,[d] s	$T_1^B(CO)$,[e] s
215	0.85 (0.03) [0.79]	0.80 (0.04) [0.79]	0.31 (0.04) [0.28]	1.3 (0.1) [1.37]	1.20 (0.05)	1.97 (0.02)
220	1.02 (0.04) [1.00]	0.97 (0.03) [1.00]	0.39 (0.03) [0.35]	1.8 (0.1) [1.64]	1.46 (0.03)	2.4 (0.2)
228	1.24 (0.09) [1.34]	1.28 (0.04) [1.34]	0.46 (0.01) [0.47]	2.2 (0.1) [2.08]	1.75 (0.08)	2.64 (0.01)
248	2.4 (0.3) [2.17]	2.23 (0.07) [2.17]	0.70 (0.05) [0.76]	3.1 (0.1) [3.17]		
268	3.1 (0.1) [3.01]	3.00 (0.0) [3.01]	1.04 (0.03) [1.05]	4.1 (0.2) [4.27]		
283	3.3 (0.2) [3.63]	3.30 (0.07) [3.63]	1.15 (0.03) [1.27]	2.8 (0.2) [5.08]		
303	4.7 (0.2) [4.47]	4.6 (0.1) [4.47]	1.7 (0.1) [1.56]	6.50 (0.02) [6.18]		

[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 $B_0^A = 7.05$ T ($\nu_0 = 75.44$ MHz). [e] Measured at $B_0^B = 4.70$ T ($\nu_0 = 50.29$ MHz).

Table II. Diffusion Coefficients in $Co_2NiCp(CO)_6(\mu_3\text{-}CPh)^a$

T, K	$D_\perp$, ns^{-1}	$D_\parallel$,[b] ns^{-1}	D_s, ns^{-1}	$R(Ph)$, ns^{-1}	$R(Cp)$, ns^{-1}
215	1.1	3.0	8.4	5.4	19
220	1.3	3.8	11	7.2	20
228	1.8	5.0	14	9.1	22
248	2.9	8.2	23	15	30
268	4.0	11	32	21	38
283	4.8	14	38	24	44
303	5.9	17	48	31	52
E_a, kcal/mol	2.5 (0.3)[c]	2.5 (0.3)[c]	2.5 (0.3)[c]	2.5 (0.3)[c]	1.5 (0.1)[c]

[a] Values in the table are presented to two significant digits. However all calculations were performed prior to round off. [b] $D_\parallel = 2.85D_\perp$. See text. [c] Quantities in parentheses are 95% confidence limits.

time and NOE experiments and of temperature regulation and measurement have been presented elsewhere.[8-11,18]

Results

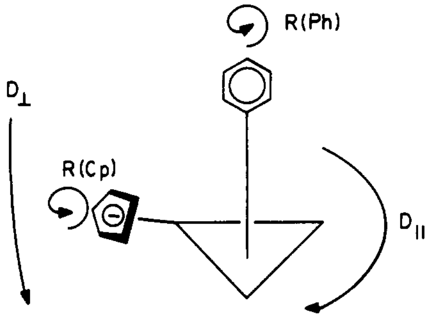
The various relaxation times as a function of temperature are displayed in Table I. All measurements were performed at least two times; values in the table are the average of the runs and quantities in parentheses represent the mean deviation. The numbers of square brackets are the relaxation times calculated by a semilogarithmic Arrhenius fit of the data. These values, which, generally, are close to the individual experimental results, were used in all further calculations in order to minimize the propagation of error from scatter in the measurements.

NOE's of both the phenyl and Cp carbons were found to be complete [$\eta = \eta_{max} = 2.0$] at all temperatures, indicating that dipole–dipole relaxation by the attached protons is the sole operative mechanism.[19]

The last two columns in the table are the carbonyl ^{13}C T_1's at 7.05 and 4.70 T, respectively. The increase in T_1 with diminishing field strength reveals that, as expected, chemical shift anisotropy (CSA) is the predominant relaxation mechanism.[20,21]

Discussion

Although $Co_2NiCp(CO)_6(\mu_3\text{-}CPh)$ is an asymmetric top molecule, from its structure,[22] the two semiaxis lengths of its volume ellipsoid in the $NiCo_2$ plane are almost identical ($b = 5.52$ Å and $c = 5.54$ Å), and slightly longer than the unique axis, perpendicular to the plane ($a = 5.26$ Å). Thus, the molecule may be treated as a pseudosymmetric top, requiring only two diffusion coefficients, $D_\perp$ and $D_\parallel$, to characterize the tumbling and spinning motions of the molecule in solution. To completely specify its rotational dynamics, one must introduce, in addition, two internal rotational diffusion coefficients. $R(Ph)$ represents the rate of rotation of the phenyl group about its C_2 axis and $R(Cp)$ is the rate of spinning of the cyclopentadienyl group about its C_5 axis.



The calculations required to determine these diffusion constants are similar to those performed in our earlier study of $Cp_2Co_3(\mu_2\text{-}CO)(CO)_3(\mu_3\text{-}CPh)$. Therefore, in the interest of brevity, we shall cite the appropriate equations and computational methods detailed in earlier papers.[8,10]

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(18) Martin, M. L.; Delpuech, J. J.; Martin, G. J. *Practical NMR Spectroscopy*; Heyden: London, 1980; Chapters 6 and 7.

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

(20) Becker, E. D. *High Resolution NMR: Theory and Chemical Applications*, 2nd ed.; Academic: New York, 1980; Chapter 9.

(21) Wang, S. P.; Yuan, P.; Schwartz, M. *Inorg. Chem.* **1990**, *29*, 484.

(22) (a) The structure of $Co_2NiCp(CO)_6(\mu_3\text{-}CPh)$ has not yet been reported. Dimensions were calculated from the crystal structure of the similar complex, $Co_2NiCp(CO)_6(\mu_3\text{-}CCO_2Me)$, together with standard CPh bond lengths and angles. (b) See: Blumhofer, R.; Fischer, K.; Vahrenkamp, H. *Chem. Ber.* **1986**, *119*, 194.

Molecular Reorientation. The C–H vector of the phenyl ring's para carbon lies along the principal molecular axis (a). Therefore, the correlation time, τ_c, determined from ^{13}C–H dipolar relaxation depends solely upon $D_\perp$, the tumbling diffusion coefficient.[23] We have used the measured values of T_{1p}(Ph) to calculate $D_\perp$ as a function of temperature.[24] The results are displayed in Table II.

The perpendicular diffusion constants in this complex are somewhat greater than found in the earlier investigation of the tricobalt cluster (**1**).[8] For example, the results at 25 °C are $D_\perp$(**2**) = 6.1 ns^{-1} (interpolated) and $D_\perp$(**1**) = 4.2 ns^{-1}, respectively. This difference may be understood by the fact that the unique semiaxis length (a), is longer (6.14 vs 5.26 Å) and, hence, the rotation slower in the latter complex. Indeed, the classic Gierer–Wirtz (GW) microviscosity model[25,26] of molecular reorientation yields calculated diffusion constants that are in near-quantitative agreement with experiment; e.g. at 25 °C, one finds that $D_\perp$(GW) = 6.2 ns^{-1} in **2** and $D_\perp$(GW) = 3.5 ns^{-1} in **1**.

The dependence of $D_\perp$ on temperature is the same in **2** and **1**; $E_a(D_\perp)$ = 2.5 kcal/mol in both clusters. This activation energy is also within experimental error (±0.3 kcal/mol) of the value predicted by the Gierer–Wirtz model (and other hydrodynamic theories);[12b,27] E_a(GW) = 2.3 kcal/mol.[28]

Calculation of the parallel diffusion coefficient, $D_\parallel$, requires determination of the rotational correlation time of a second vector, anchored on the molecular skeleton, at a finite angle relative to the unique axis.[10,29] The contribution to relaxation of the carbonyl carbons by chemical shift anisotropy is governed by rotation of the vector along the MCO bond; the angle of this vector differs for the three nonequivalent CO's.[30] However, due to their rapid exchange, which results in a single carbonyl resonance,[31,32] one measures the mean relaxation rate which, in turn, depends upon the average correlation time.[8] Using methods described earlier,[8-10,33] we have used T_1^A(CO) and T_1^B(CO) (Table I) to calculate τ_c (av) and, thence, $D_\parallel$ at the three lowest temperatures.[34,35] As noted above, measurement at higher temperature was not possible due to extensive ^{59}Co–^{13}C scalar coupling. It was found that the average ratio of the parallel to perpendicular diffusion coefficients is $D_\parallel/D_\perp$ = 2.85 ± 0.14. Therefore, we have used this ratio to estimate the parallel diffusion constant at the various temperatures; the results are given in Table II.

On the basis of its overall dimensions, one would expect the molecular reorientation to be close to isotropic [$D_\parallel \approx D_\perp$], since $a \approx b \approx c$. However, a similar motional anisotropy, $D_\parallel/D_\perp$ = 2.2, has been observed in the tricobalt complex **1**,[8] which is also close to spherical in shape. The comparatively rapid parallel rotation in these two clusters probably reflects the fact that spinning of these molecules about their principal axes, unlike their tumbling, requires little or no displacement of solvent. Indeed, in the "slip" limit of rotation,[36] it is this factor alone that determines the magnitude of the frictional forces impeding molecular reorientation.

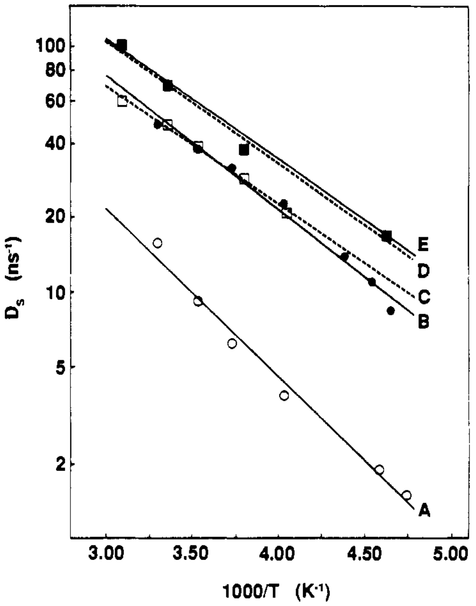

Figure 1. Temperature dependence of the phenyl spinning diffusion coefficient in metal carbonyl clusters: (A) $Co_3Cp_2(\mu_2\text{-}CO)(CO)_3(\mu_3\text{-}CPh)$ [open circles and solid line]; (B) $Co_2NiCp(CO)_6(\mu_3\text{-}CPh)$ [filled circles and solid line]; (C) $FeCo_2(CO)_9(\mu_3\text{-}PPh)$ [open squares and dashed line]; (D) $Co_3(CO)_9(\mu_3\text{-}CPh)$ [filled squares and dashed line]; (E) benzene [solid line].

Internal Rotation. The C–H vectors of the ortho and meta phenyl carbons lie at (equivalent) angles of 120 and 60° relative to the principal axis. It has been shown[10,29] that the ratio $\chi = T_{1O}/T_{1P} = T_{1M}/T_{1P}$, is a function of θ (the angle between the vector and the axis), $D_\perp$, and D_S; $D_S = D_\parallel + R$(Ph) is the coefficient representing the net spinning rate of the phenyl ring. We have used these ratios to determine D_S and R(Ph) as a function of temperature;[37] the results are shown in Table II. D_S is also plotted in Figure 1 (line B). In passing, we note that, unlike the earlier study of **1**, the values of T_{1M} and T_{1O} in **2** are generally quite close (Table I), verifying the validity of the assumption that this molecule is a pseudosymmetric top.[23]

Also shown in Figure 1 are the spinning diffusion constants, D_S, for a number of other trinuclear metal carbonyl clusters,[8-11] and the rate of the equivalent rotation of benzene in chloroform (line E).[38] One observes immediately that the rate of spinning of the aryl ring in **2** (line B) is much greater than that in **1** (line A); e.g. at 298 K, D_S(**2**) = 49 ns^{-1} ≫ D_S(**1**) = 9 ns^{-1}.[8] This provides further substantive evidence that, as suggested earlier,[8] the slowed internal rotation in $Cp_2Co_3(\mu_2\text{-}CO)(CO)_3(\mu_3\text{-}CPh)$ results from electronic orbital interactions between the phenyl group and the bridging carbonyl in the latter complex.

D_S in $Co_2NiCp(CO)_6(\mu_3\text{-}CPh)$ is not as large, however, as observed in an earlier investigation of the analogous homonuclear benzylidyne-capped cluster, $Co_3(CO)_9(\mu_3\text{-}CPh)$ (line D),[11] in which it was found that the phenyl ring rotation is as rapid as that of free benzene in the same solvent.[38] Rather, the spinning rates found here are virtually identical at all temperatures as are results reported for a bimetallic phosphinidene-capped trinuclear cluster, $FeCo_2(CO)_9(\mu_3\text{-}PPh)$ (line C).[9] In the latter system, the slowed internal rotation was attributed to a barrier created by the heteroatom, which splits the degeneracy of the metals' 2e orbitals, inducing an angle-dependent electronic interaction between the

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(23) (a) Levy, G. C.; White, D. M.; Anet, F. A. L. *J. Magn. Reson.* **1972**, *6*, 453. (b) Levy, G. C.; Cargioli, J. D.; Anet, F. A. L. *J. Am. Chem. Soc.* **1973**, *95*, 1527.

(24) See eq 3 in ref 10.

(25) Gierer, A.; Wirtz, K. *Z. Naturforsch., A* **1953**, *8*, 532.

(26) The GW microviscosity model was originally derived to describe the reorientation of spherical molecules. It has been shown that its application to determine $D_\perp$ in symmetric top molecules yields the most accurate results if one uses half the length of the principal axis rather than the mean radius. See, for example: Gillen, K. T.; Griffiths, J. E. *Chem. Phys. Lett.* **1972**, *17*, 359.

(27) (a) Debye, P. *Polar Molecules*; Dover Press: New York, 1929. (b) Perrin, E. *J. Phys. Radium* **1934**, *5*, 497.

(28) See discussion on page 84 of ref 11.

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

(30) From the structure,[22] one finds that θ_1 = 71.4°, θ_2 = 82.4°, and θ_3 = 169.3°.

(31) (a) Richmond, M. G.; Kochi, J. K. *J. Organomet. Chem.* **1987**, *323*, 219 and references therein. (b) Aime, S.; Gobetto, R.; Nicola, G.; Osella, D.; Milone, L.; Rosenberg, E. *Organometallics* **1986**, *5*, 1829.

(32) (a) Richmond, M. G.; Kochi, J. K. *Inorg. Chem.* **1986**, *25*, 1334 and references therein. (b) Richmond, M. G.; Kochi, J. K. *Organometallics* **1987**, *6*, 254.

(33) (a) Schwartz, M. *Chem. Phys. Lett.* **1980**, *73*, 127. (b) Brownlee, R. T. C.; O'Connor, M. J.; Shehan, B. P.; Wedd, A. G. *J. Magn. Reson.* **1985**, *61*, 22. (c) Spiess, H. W.; Schweitzer, D.; Haeberlen, U.; Hausser, K. H. *J. Magn. Reson.* **1971**, *5*, 101.

(34) The chemical shift anisotropy ($\Delta\sigma$), required to determine τ_c(avg) was calculated to be $\Delta\sigma$ = 415.8 ppm by using the approximation method outlined in ref 33.

(35) See discussion and equations on p 681 in ref 8.

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

(37) See eq 4 in ref 10.

(38) See footnote 38 in ref 8.

ring and metal framework. From the results found in this investigation, one concludes that an equivalent internal rotation barrier exists in $Co_2NiCp(CO)_6(\mu_3\text{-}CPh)$. Additional NMR studies are clearly required before any quantitative comparison can be made between the aryl spinning rates in different tetrahedral clusters.

Unlike the phenyl ring, the internal rotation axis of the cyclopentadienyl group is not coincident with the principal axis of the molecular framework. Therefore, the correlation time governing rotation of the Cp's C–H vectors is a somewhat more complex function of θ,[39] $D_\perp$, $D_\parallel$, and R(Cp); $\tau_c = f[\theta, D_\perp, D_\parallel, R(\mathrm{Cp})]$.[40] However, with values of τ_c [from T_1(Cp)], one may still solve the equation[35] for R(Cp). The results are given in the final column of Table II.

One sees that rotation of the Cp group about its C_5 axis is quite facile, with values of R(Cp) somewhat greater than found in the earlier investigation of **1**; e.g. at 298 K, $R(\mathbf{2}) = 50\ \mathrm{ns}^{-1}$ (interpolated) and $R(\mathbf{1}) = 33\ \mathrm{ns}^{-1}$.[8] The rapid internal rotation of the Cp ring provides evidence that there is little or no phenyl/cyclopentadienyl inter-ring interaction. This is not surprising, since the distance of closest approach of protons on the two groups is ~2.3 Å, which is approximately equal to the sum of the van der Waals radii ($2R_H = 2.4$ Å).[41]

Finally, we note that the activation energy determined for R(Cp), $E_a = 1.5$ kcal/mol, is quite similar to that found in **1** (1.6 kcal/mol), and substantially less than the activation energy for R(Ph). This probably results from the fact that, unlike the phenyl ring rotation about its C_2 axis, spinning of the Cp group about its C_5 axis does not require displacement of solvent. Thus, there is less of an intermolecular barrier retarding rotation of the latter ring.

Acknowledgment. We thank the Robert A. Welch Foundation [Grants B-1039 (M.G.R.) and B-657 (M.S.)] and the UNT Faculty Research Program for financial support.

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(39) From the structure,[22] the angle between the Cp axis and the principal axis is $\theta = 99.2°$.

(40) 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 $R_2 = D_\perp$.

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

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Solvent Effects on the Linkage Isomerization of the N1-Bonded Pentaamminecobalt(III) Complex of 5-Methyltetrazole

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Received January 23, 1991

A study of linkage isomerization for the five-membered cyclic CN_4 tetrazole ligand system from the carbon-adjacent-N1-bonded (5-methyltetrazolato)pentaamminecobalt(III) to its N2-bonded form in 11 different solvents is reported. The solvents include both protic and aprotic solvents as well as the hydroxylic solvents water and methanol. Rate constants in the various solvents were successfully correlated to solvent properties by using Reichardt's acceptor parameter E_T and Gutmann's donor parameter D_N in the equation $\ln k = \ln k_0 + \alpha E_T + \beta D_N$ with $\alpha = 0.0557$, $\beta = 0.0794$, and $\ln k_0 = -18.70$. Alternatively, the equation $\ln k = \ln k_0 + a\alpha + b\beta + c\pi^*$ due to Kamlet and Taft can be used to model the solvent effects. Here α measures the ability of a solvent to act as a hydrogen-bond donor, β measures the solvent's hydrogen-bond-accepting ability, and π^* measures the solvent's dipolarity/polarizability and its ability to stabilize a charge dipole. The fit to these solvent parameters was also successful for all 11 solvents with $\ln k_0 = -17.35$, $a = 0.92$, $b = 2.16$, and $c = 1.98$. These fits are discussed in terms of specific solvent interactions with the complex, and solvent effects on the rate constants for linkage isomerization of the tetrazolato system are compared to solvent effects in the nitrito system.

Introduction

Linkage isomers have drawn a great deal of attention because they enable us to determine which factors are important to the stability of transition-metal coordination compounds and to determine rearrangement mechanisms. Hence, frequent reviews have appeared in the literature.[1] The overall hardness of the metal center as determined by its oxidation state and the hard/soft nature of the other ligands is of primary importance. Hard metal centers are believed to prefer hard donor atoms while softer metal centers will favor softer donor atoms. However, steric effects can also determine which isomer is more stable. When donor atoms are similar or when bulky alkyl or aryl groups are used, the less sterically hindered isomer will be favored. An ever increasing variety of ligands which undergo dynamic linkage isomerization processes have been identified recently, primarily by Jackson and co-workers.[2]

Many studies have been conducted in order to determine the solvent's effect on linkage isomerization reactions. Although electronic effects dominate, the solvent can have a minor influence on isomer stability. It has been found that hard metal centers will coordinate to soft donor atoms in solvents of low dielectric constant but will coordinate to hard donor atoms in solvents of high dielectric constant. Soft metal centers show the opposite effect.[1]

The solvent will also have an impact on the rate of isomerization. This effect can often be modeled successfully on the basis of the solvent's physical and chemical properties. However, in most cases, it is not possible to predict this effect by using only one solvent parameter, and consequently, a multiparameter approach is necessary.[3] In order for the solvent to affect the reaction rate, it must interact specifically with the reacting species. Empirical parameters used to model the solvent effect are direct measures of these interactions. As the number of specific interactions increases, the number of solvent parameters necessary to model the solvent effect will also increase.

Jackson et al. studied the isomerization of $Co(NH_3)_5ONO^{2+}$ to $Co(NH_3)_5NO_2^{2+}$.[4] They showed that the rate of spontaneous isomerization was dependent on two factors. The isomerization is catalyzed by the ability of the solvent to donate electron density to the ammine hydrogens. This weakens the ammine hydrogen

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0020-1669/91/1330-3707$02.50/0