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Carbon-13 relaxation and phenyl group rotation in a benzylidyne-capped tricobalt cluster

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Abstract

^{13}C spin-lattice relaxation times of the protonated carbons in $Co_3(CO)_9(\mu_3\text{-}CPh)$ were measured as a function of temperature in the solvent chloroform. The T_1's were used to calculate the phenyl group's tumbling ($D_\perp$) and spinning (D_s) rotational diffusion constants. It was observed that the ratio, $D_s/D_\perp \gg 1$, revealing extremely facile internal rotation of the phenyl ring. This result is in direct contrast to earlier data on the bicapped tetracobalt cluster $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$, and indicates a complete lack of steric or electronic interaction between the aromatic ring and the tricobalt nonacarbonyl skeleton. Theoretical diffusion constants calculated by the Gierer–Wirtz Microviscosity model are in excellent agreement with experimental values of $D_\perp$.

Introduction

The internal rotational mobility of capping groups (i.e., μ_3-CPh, μ_3-PPh, and μ_4-PPh) in tri- and tetra-nuclear metal clusters is expected to be dependent on the magnitude of both steric and electronic interactions between the capping ligand and the cluster polyhedron. The rotation of such ligands may be easily examined by the use of spin-lattice relaxation times (T_1) which have also afforded data related to molecular structure and bonding [1]. However, while proton (hydride) and carbonyl (^{13}C and ^{17}O) spin-lattice relaxation times (T_1) of many organometallic systems have been measured, there have been virtually no investigations of internal ligand rotation in capped metal clusters [2,3]. In a recent publication [4], we reported the results of a ^{13}C spin-lattice relaxation time study of phenyl group rotation in the phosphinidene-capped tatracobalt cluster $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$. It was observed

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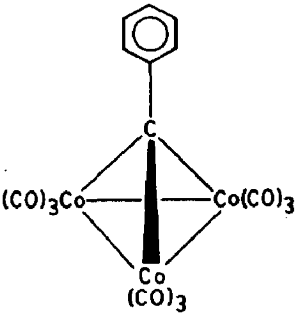

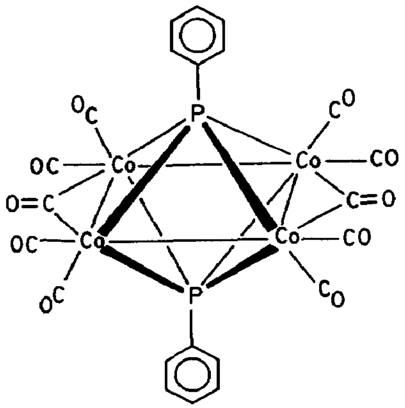

that the phosphinidene caps appear to be immobile on a molecular rotation timescale ($\tau_c \approx 50$ picoseconds); i.e., the aryl rings do not undergo internal rotation relative to the tetracobalt skeleton. This observation was totally unexpected and could not be rationalized strictly on the basis of steric repulsions inherent within the molecular frame of the cluster. Therefore, it was conjectured that an additional factor such as electronic interactions between the benzene π system and the *d*-orbitals on the phosphorus might explain the immobility of the rings.

In order to determine the relative importance of various parameters which may affect the internal mobility, we have utilized NMR relaxation time measurements to investigate phenyl group rotation in the benzylidyne-capped tricobalt cluster $Co_3(CO)_9(\mu_3\text{-}CPh)$. In direct contrast to the tetracobalt system, one expects (a) very little steric repulsion between the benzylidyne ligand and the cluster polyhedron based on recent X-ray diffraction data [5] and (b) no electronic interaction between the aryl ring and the apical carbyne atom, unlike the phosphorus, due to the absence of low lying carbon *d*-orbitals. Finally, the results of this and our earlier study [4] should establish the accessible range of rotational rates in phenyl-capped polynuclear clusters .

Results and discussion

Shown in Table 1 are the relaxation times of the protonated phenyl carbons of the tricobalt cluster, dissolved in chloroform-d_1 (ca. 0.32 *M*) at several temperatures spanning a 100°C range. Chemical shifts are given relative to TMS, and are referenced to $\delta(^{13}CDCl_3) = 77.0$ ppm. The *para*-carbon is easily assigned to the singlet at 127.9 ppm on the basis of its lower integrated intensity and shorter relaxation times. The singlets at 128.4 and 128.5 ppm (designated as A and B) arise from the *ortho*- and *meta*-carbons. The near magnetic degeneracy of the *ortho*- and *meta*-carbons has previously been observed by Milone and coworkers [6]. While the unequivocal assignment of the *ortho*- and *meta*-carbons can, in principle, be established by a tedious three-bond optimized $^1H\text{-}^{13}C$ 2D NMR experiment [7], it is not required for analysis since the two carbons' T_1's exhibit the same temperature dependence on the rotational dynamics.

Table 1

Temperature dependence of relaxation times and rotational diffusion constants [a]

T (K)	T_{1P}^{b} (s)	T_{1A}^{c} (s)	T_{1B}^{d} (s)	χ	σ	$D_{\perp}$ (ns^{-1})	D_s (ns^{-1})
216	0.25	1.33	1.21	5.08	18.0	0.9	17
263	0.77	3.17	2.97	3.99	13.0	2.9	38
298	1.29	5.52	5.42	4.24	14.1	4.9	69
323	1.78	6.99	6.99	4.47	15.1	6.7	102

[a] Each relaxation time represents the average of two measurements. [b] *Para*-carbon, at 127.9 ppm (relative to TMS). [c] *Meta*- (or *ortho*)-carbon, at 128.4 ppm. [d] *Ortho*- (or *meta*)-carbon, at 128.5 ppm.

The NMR relaxation time technique is particularly well suited for the characterization of the reorientation of molecules which contain phenyl groups [8,9]. The ^{13}C T_1 of the *para*-carbon (T_{1P}) depends solely upon $D_{\perp}$, which is the rotational diffusion constant characterizing the rate of overall 'tumbling' of the molecule. Relaxation times of the *ortho*- and *meta*-carbons (T_{1A} and T_{1B}) depend both on $D_{\perp}$ and on D_s, the 'spinning' diffusion coefficient. The latter quantity measures the rate of phenyl rotation about the bond connecting it to the molecular framework (C–Ph). D_s must be distinguished from $D_{\parallel}$ which, conventionally, is taken to represent the spinning rate of the molecular skeleton. Generally, $D_s = D_{\parallel} + R$, where R is the internal rotation diffusion constant.

The tumbling diffusion constant, $D_{\perp}$, may be determined from T_{1P} by the relation [10];

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

To calculate D_s, it is convenient to express the relaxation time ratio $\chi = (T_{1A})/(T_{1P}) = (T_{1B})/(T_{1P})$, as a function of $\sigma = D_s/D_{\perp}$ [10]:

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

It is straightforward to determine σ from the experimental value of χ using a simple iterative algorithm. Then, with $D_{\perp}$ from eq. 1, one may obtain D_s from σ.

The results of this analysis are presented in Table 1 and in Fig. 1 (lines [A] and [B]). One observes immediately that $D_s \gg D_{\perp}$ at all temperatures. This is in dramatic contrast to our earlier data on the tetracobalt cluster, where $\sigma = (D_s/D_{\perp}) \approx 1.5$–$2.1$ (e.g. at 298 K, $D_{\perp} = 2.6$ ns^{-1} and $D_s = 4.9$ ns^{-1}) [4]. The latter low ratio is expected only if the phenyl ring does not undergo significant internal rotation.

The crystal structure of $\mathrm{Co_3(CO)_9(CPh)}$ has recently been reported [5]. From the molecular structural parameters (i.e., $a = 6.1$ Å and $b = c = 5.3$ Å) it is observed that the cluster has a nearly spherical shape. From this data it is expected that $D_{\parallel} \approx D_{\perp}$. Hence, the very large ratios, $\sigma = 13$–18, observed here show quite clearly that the benzene ring is undergoing extremely facile internal rotation about the C–Ph bond. Indeed, the spinning rates, D_s, determined for this cluster are substantially higher than values reported in most other investigations of phenyl groups to date [9]. Finally, we estimate that the closest approach distance of the *ortho*-proton

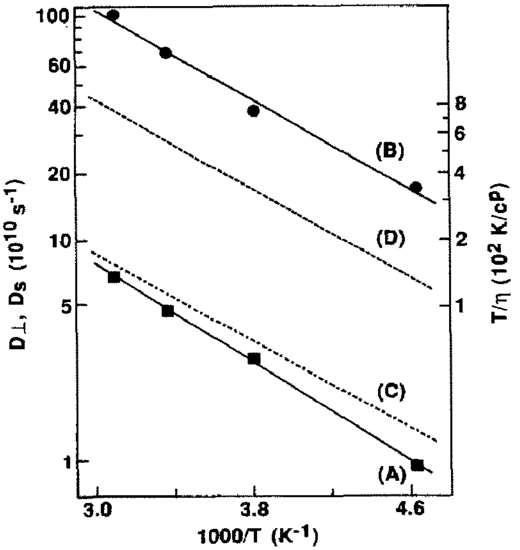

Fig. 1. Temperature dependence of rotational diffusion constants: (A) $D_\perp$(exp); (B) $D_\parallel$(exp); (C) $D_\perp$(theor); (D) T/η(right axis).

and the equatorial carbonyl oxygens is approximately 2.6 Å. This distance is only slightly less than the sum of the two atoms' Van der Waal's radii ($r_H + r_0 = 1.2 + 1.5$ Å), indicating the unimportance of steric repulsion between the aryl capping ligand and the tricobalt cluster core.

It is very informative to compare our results for D_s with the rates of rotation of the free benzene molecule about its C_2 axis. For C_6H_6 in $CDCl_3$, Tanabe [11] has reported that this diffusion constant is 72 ns^{-1} at room temperature, which is virtually identical to our result, $D_s = 69$ ns^{-1} at 298 K. The temperature dependence of the diffusion constant for benzene in chloroform was not measured. However, one expects its activation energy to equal that of T/η, where T is the temperature and η is the viscosity [12]. For chloroform, one finds that $E_a(T/\eta) = 2.27$ kcal/mol, which compares well with $E_a(D_s) = 2.3$ kcal/mol. The close equivalence of the two activation energies is also seen from the parallel behavior of the lines [B] (D_s) and [D] (T/η) in Fig. 1. (Note, we use the activation energies solely to compare the relative dependence on temperature of these two quantities; E_a should not be taken to represent the kinetic barrier to a specific transition state.)

Thus we find that in both magnitude and dependence on temperature, the measured spinning rate, D_s, of the phenyl ring in this cluster is quite close to that observed for the equivalent rotation of benzene in the same solvent. These results show clearly that, in complete contrast to the previous data on $Co_4(CO)_{10}(PPh)_2$, there is no measurable hindrance to rotation of the phenyl group about the C–Ph bond in $Co_3(CO)_9(CPh)$.

As noted above, unlike in the tetranuclear cluster, one expects little or no steric or electronic interactions between the ring and the skeletal framework in the tricobalt complex studied here. Therefore, we see from this pair of very distinctive results that the spinning rate of the capping group may serve as a sensitive measure of the magnitude of these intramolecular forces in capped polynuclear clusters. Further experiments on additional systems are underway to elucidate the relative effects of steric and electronic factors on internal rotation rates in metal carbonyl clusters.

Finally, it is of interest to compare the measured tumbling rates, $D_\perp$, of this cluster to values predicted by the Microviscosity theory of Gierer and Wirtz [8b,13]. As observed in Fig. 1, the theoretically calculated diffusion coefficients (line [C]) are in quite good agreement with experiment (line [A]). As an example, at 298 K, $D_\perp(\text{theor}) = 5.4\ \text{ns}^{-1}$, which is very close to $D_\perp(\text{exp}) = 4.9\ \text{ns}^{-1}$. Thus, as observed in earlier studies [8b], the relatively simple Microviscosity model furnishes relatively accurate semi-quantitative estimates of the rotational diffusion constant of quasi-spherical molecules in solution.

Experimental

$Co_3(CO)_9(\mu_3\text{-CPh})$ was prepared using the method of Seyferth [14], and purified by sublimation. A sample containing 0.58 g (1.12 mmol) of the cluster was dissolved in 3.5 ml of $CDCl_3$ (ca. 0.32 *M*) and placed in a 10 mm NMR tube. The solution was degassed by three freeze-pump-thaw cycles prior to flame sealing the tube.

All experiments were performed on a Varian VXR-300 NMR spectrometer (75.5 MHz for ^{13}C). Details of the spin-lattice relaxation and nuclear Overhauser enhancement measurements were presented in our earlier paper [4]. The observed enhancements were complete ($\eta = \eta_{max} = 2.0$) for all three carbons at all temperatures. Therefore, ^{13}C-^1H dipole–dipole is the sole operative relaxation mechanism.

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