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^{13}C NMR Study and Observation of Restricted Phenyl Rotation in the Alkyne Complex $Co_2(CO)_6(\mu\text{-PhC}\equiv\text{CH})$

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We have recently reported the application of ^{13}C NMR relaxation time analysis to investigate the phenyl group internal rotation in benzylidyne- and phosphinidene-capped metal carbonyl clusters[2-6] with the goal of elucidating the factors affecting electronic interactions between the aryl ring and molecular skeleton.

The experimental results have ranged from unhindered phenyl group rotation in $Co_3(CO)_9(\mu_3\text{-CPh})$ (**1**) to complete immobility in $Co_4(CO)_{10}(\mu_4\text{-PPh})_2$ (**2**) and $Cp_2Co_3(\mu\text{-CO})(CO)_3(\mu_3\text{-CPh})$ (**3**). The arrested ring rotation observed in the latter complex was attributed to a strong electronic interaction between the bridging carbonyl's π^* orbital and the phenyl π system through the metal 2e and carbynyl 2p orbitals. The same phenomenon has been observed by Stone et al.[7] in their low-temperature NMR study of the μ-bridged cluster $Fe_2Co(CO)_{10}(\mu_3\text{-C}_6H_4Me\text{-}4)$.

More recently, we observed in studies of two mixed-metal trinuclear clusters, $FeCo_2(CO)_9(\mu_3\text{-PPh})$ (**4**) and $Co_2NiCp(CO)_6(\mu_3\text{-CPh})$ (**5**), that the phenyl group rotational rates are slowed relative to that observed in **1**, due possibly to a preferential phenyl π–metal 2e orbital overlap. This result is the direct effect of the introduction of the heterometal into the cluster core, which induces an asymmetry in the 2e molecular orbitals. The phenyl spinning rates, however, are more rapid than in **2** or **3**, indicating that the internal rotation barriers in the non-carbonyl-bridged heterometallic clusters are comparatively small.

In order to establish the accessible range of aryl–metal orbital interactions in isolobally related benzylidyne-capped clusters, we have undertaken an NMR relaxation time investigation of the barrier to internal rotation in $Co_2(CO)_6(\mu\text{-PhC}\equiv\text{CH})$ (**6**). To our knowledge, no ^{13}C spin–lattice relaxation studies have been reported for perpendicular alkyne complexes, $M_2(CO)_6(\mu\text{-alkyne})$.

Experimental Section

The synthesis of $Co_2(CO)_6(\mu\text{-PhC}\equiv\text{CH})$ was carried out according to the procedure of Wender et al.[8] The complex was isolated by using air-free chromatography and stored in a drybox until needed. The NMR sample was prepared in the drybox using 0.12 g (~0.32 mmol) of $Co_2(CO)_6(\mu\text{-PhC}\equiv\text{CH})$ and 0.6 mL of $CDCl_3$ (~0.53 M). After the NMR tube was removed from the drybox, the sample was freeze–pump–thaw degassed prior to flame sealing.

Temperature-dependent ^{13}C spin–lattice relaxation times, T_1, and nuclear Overhauser enhancements (NOE), η, of the phenyl (ortho, meta, and para) and alkynyl carbons were acquired at ν_0 = 50.29 MHz on a Varian Gemini-200 FT-NMR spectrometer using the procedures detailed in earlier investigations.[3,4] The relaxation times, which represent the average of two runs at each temperature, are presented in Table I.

Results

NOE's of the phenyl carbons were found to be complete ($\eta = \eta_{max}$ = 2.00), indicating that relaxation is due solely to dipolar interaction with the attached proton.[9] In contrast, enhancements of the alkynyl carbon (C–H) were substantially less than the maximum, which probably results from the contribution of ^{59}Co–^{13}C scalar coupling to the relaxation of this nucleus; the values were approximately independent of temperature with η_{av} = 1.34. The standard formula[10] was used to extract the contribution from dipole–dipole interaction (T_{1DD}(CH) in Table I).

As shown in previous work,[3] metal clusters' perpendicular (tumbling) diffusion coefficients can be obtained directly from the relaxation times of the para carbons. The ratio $\chi = T_{1O}/T_{1P}$ (or T_{1M}/T_{1P}) yields values for the phenyl group's net spinning rate, $D_s = D_\parallel + R$, where $D_\parallel$ is the diffusion constant which characterizes rotation of the skeleton about the unique axis and R is the rate of *internal* rotation of the ring relative to the molecular framework.[3] It may be seen from Table I that $T_{1O} \approx T_{1M}$ at all temperatures, indicating validity of the assumption (required for the analysis) that this molecule approximates a symmetric top with its unique axis parallel to the vector connecting C_1 and C_4 of the capping group. In order to minimize propagation of error due to scatter in the relaxation times, least-squares values interpolated from Arrhenius plots (shown in square brackets in Table I) were used in all calculations. The coefficients $D_\perp$ and D_s are presented in the second and fourth columns of Table II.

Determination of the rate of internal rotation, R, requires a knowledge of the parallel diffusion coefficient, $D_\parallel$. This quantity can be calculated from the rotational correlation time, τ_c, of a vector at a finite (non-zero) angle, θ, relative to the principal axis. From the structure of a related complex,[11] the angle of the C–H vector of the alkynyl carbon is θ = 103.2°. With τ_c(CH) [from T_{1DD}(CH)][9] and $D_\perp$ [from T_{1P}], $D_\parallel$ may be obtained from Woessner's standard equation[12] relating τ_c to θ, $D_\perp$, and $D_\parallel$. The results are shown in the third column of Table II. As found in earlier investigations of cluster reorientation in solution,[3,4,6] $D_\parallel$ is substantially greater than $D_\perp$ at all temperatures. The derived internal rotation diffusion constants, R ($=D_s - D_\parallel$), are given in the last column of the table.

Discussion

It is informative to compare the phenyl spinning rate in $Co_2(CO)_6(\mu\text{-PhC}\equiv\text{CH})$ with results obtained in earlier investigations involving related isolobal complexes.[2-6] Presented in Table II and Figure 1 are values of D_s measured for complexes **1** (line E in the figure and fifth column of the table), **3** (line A and seventh column), and the two bimetallic clusters, **4** (line D and sixth column) and **5** (line C).[13]

One observes that $D_s[\mathbf{6}] \ll D_s[\mathbf{1}]$, by a factor of 2–4. The spinning rate in **1** is predicted to be quite rapid, due to the symmetrical interaction of the phenyl π system with both of the metals' degenerate 2e orbitals (through the carbyne's p_x and p_y

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(13) Values of D_s for other complexes, presented in Table II, were interpolated to the temperatures used in this study by semilogarithmic fits of the original results to the Arrhenius equation.

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Table I. NMR Relaxation and Correlation Times in $Co_2(CO)_6(\mu\text{-}PhC{\equiv}CH)^{a-c}$

T, K	T_{1O}(Ph), s	T_{1M}(Ph), s	T_{1P}(Ph), s	T_1(CH), s	T_{1DD}(CH), s	τ_c(CH), ps
216	0.56	0.58	0.33	0.44	0.65	79.8
	(0.01)	(0.01)	(0.03)	(0.02)	(0.03)	(3.7)
	[0.49]	[0.49]	[0.30]	[0.37]	[0.55]	
223	0.68	0.72	0.41	0.48	0.71	56.6
	(0.03)	(0.03)	(0.03)	(0.00)	(0.00)	(0.0)
	[0.75]	[0.75]	[0.43]	[0.53]	[0.78]	
245	1.24	1.23	0.71	0.90	1.33	29.5
	(0.00)	(0.02)	(0.03)	(0.07)	(0.10)	(2.2)
	[1.56]	[1.56]	[0.85]	[1.00]	[1.49]	
266	2.01	2.20	1.17	1.40	2.07	20.3
	(0.04)	(0.02)	(0.02)	(0.03)	(0.04)	(0.4)
	[2.34]	[2.34]	[1.25]	[1.46]	[2.17]	
295	3.79	3.85	1.92	2.11	3.13	14.2
	(0.10)	(0.03)	(0.05)	(0.07)	(0.10)	(0.5)
	[3.41]	[3.41]	[1.80]	[2.09]	[3.11]	
319	4.26	4.19	2.27	2.69	3.99	11.3
	(0.12)	(0.08)	(0.05)	(0.03)	(0.04)	(0.1)
	[4.30]	[4.30]	[2.26]	[2.62]	[3.89]	

[a] Relaxation times are the average of two measurements at each temperature. [b] Quantities in parentheses represent the mean deviation between runs. [c] Quantities in square brackets were obtained from semilogarithmic fits of the data to the Arrhenius equation. These values were used in all further calculations.

Table II. Diffusion Coefficients in $Co_2(CO)_6(\mu\text{-}PhC{\equiv}CH)$ and Related Clusters

T, K	$D_\perp$,[a] ns^{-1}	$D_\parallel$,[a] ns^{-1}	D_s[**6**],[a] ns^{-1}	D_s[**1**],[b] ns^{-1}	D_s[**4**],[c] ns^{-1}	D_s[**3**],[d] ns^{-1}	R,[a] ns^{-1}
216	1.1	3.9	3.6	16	11	1.7	~0
223	1.6	5.4	5.7	19	13	2.1	0.3
245	3.2	10	12	30	21	3.7	2.4
266	4.7	14	19	44	30	5.7	4.3
295	6.8	20	27	68	45	9.5	7.1
319	8.6	25	35	91	60	13	9.4

[a] Diffusion coefficients in $Co_2(CO)_6(\mu\text{-}PhC{\equiv}CH)$. This work. [b] D_s in $Co_3(CO)_9(\mu_3\text{-}CPh)$. Reference 2. [c] D_s in $FeCo_2(CO)_9(\mu_3\text{-}PPh)$. Reference 5. [d] D_s in $Cp_2Co_3(\mu\text{-}CO)(CO)_3(\mu\text{-}CPh)$. Reference 4.

orbitals).[14] Indeed, D_s[**1**] is as large as the same rotation of free benzene in chloroform (line F in the figure).

D_s[**6**] is also seen to be significantly slower than the spinning rate in either of the bimetallic clusters, D_s[**4**] or D_s[**5**], indicating that the barrier to ring rotation in the former complex, V_0[**6**], is greater than that in either of the mixed-metal species. In contrast, the phenyl spinning rate of **6** is observed to be more rapid than that of **3**, indicating a lower internal rotation barrier here than in the latter carbonyl-bridged complex.

One may obtain a semiquantitative estimate of V_0[**6**] through analysis of the internal rotation diffusion constant, R, by application of the equation $R = R_0e^{-V_0/R_GT}$.[15] In this expression, R_G is the gas constant and R_0 represents the diffusion coefficient of a benzene molecule rotating freely about its C_2 axis; the latter quantity may be obtained from $R_0 = (5/3)(k_BT/I)^{1/2}$,[16] where k_B is Boltzmann's constant and $I = 1.48 \times 10^{-38}$ g·cm^2.[17]

Application of the above equation with values of R at the four highest temperatures[18] yields V_0[**6**] = 3.5 ± 0.1 kcal/mol. We note that the barrier results entirely from ring–skeleton electronic interactions, since the closest approach distance of the ortho ring protons and terminal CO's, r_{min} = 2.8 Å, is greater than the sum of the oxygen and hydrogen van der Waals radii.[19]

Consistent with the observation (vide supra) that D_s[**6**] > D_s[**3**], the calculated barrier to phenyl rotation in this complex, **6**, is less than that obtained for the carbonyl-bridged cluster, **3**, where it has been estimated that 5 kcal/mol < V_0[**3**] < 9 kcal/mol.[4]

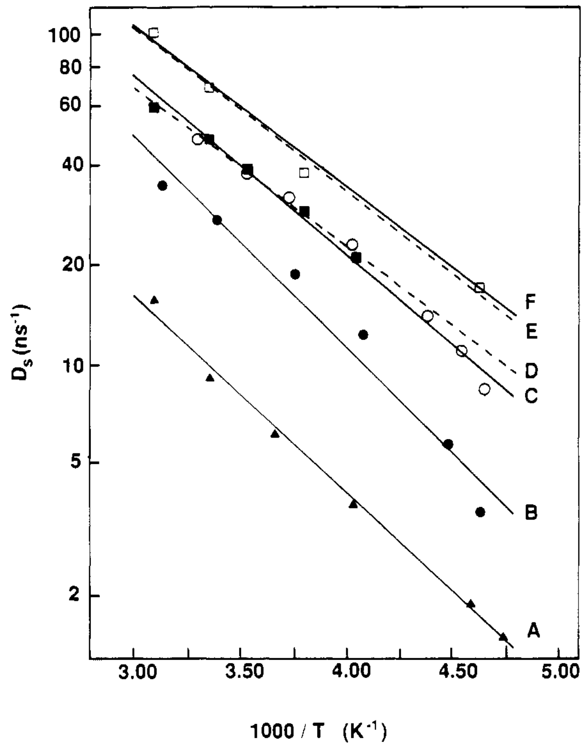
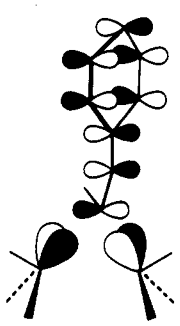


Figure 1. Temperature dependence of the phenyl spinning diffusion constant, D_s: (A) $Cp_2Co_3(\mu\text{-}CO)(CO)_3(\mu_3\text{-}CPh)$, filled triangles; (B) $Co_2(CO)_6(\mu\text{-}PhC{\equiv}CH)$, filled circles; (C) $Co_2NiCp(CO)_6(\mu_3\text{-}CPh)$, open circles; (D) $FeCo_2(CO)_9(\mu_3\text{-}PPh)$, filled squares; (E) $Co_3(CO)_9(\mu_3\text{-}CPh)$, open squares; (F) free benzene in $CDCl_3$, solid line.

While the exact origin of the barrier to phenyl rotation is unknown at this time, we are certain that it cannot be attributed to unfavorable steric interactions inherent in the molecular polyhedron (vide infra). The existence of an electronic barrier in **6** appears reasonable and is in line with the observed trends in clusters **3**–**5**. The observed barrier implies conformational bias between the polyhedral core and the π orbitals of the phenyl moiety. The basis for such an electronic preference is seen when the extended Hückel calculations by Hoffmann et al.[20] are considered. Overlap of the a_2 HOMO of $Co_2(CO)_6(\mu\text{-}PhC{\equiv}CH)$ and one of the phenyl's e_{2u} π^* orbitals would give rise to the favored phenyl orientation shown in the following diagram. Here the phenyl ring coincides with the symmetry plane that bisects the Co–Co bond.



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