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Carbon-13 Magnetic Resonance Spectra of Diamagnetic Cyano Complexes

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Fourier transform ^{13}C NMR spectra are reported for 19 diamagnetic cyano complexes in D_2O solution. Data are included for $M(CN)_6^{n-}$ complexes of nd^6 electron configuration where M = Fe(II), Ru(II), Os(II), Co(III), Rh(III), Ir(III), Pd(IV), or Pt(IV); square-planar $M(CN)_4^{n-}$ complexes of nd^8 configuration where M = Ni(II), Pd(II), Pt(II), or Au(III); tetrahedral $M(CN)_4^{n-}$ complexes of nd^{10} configuration where M = Cu(I), Zn(II), Cd(II), or Hg(II); and linear $M(CN)_2^{n-}$ complexes of nd^{10} configuration where M = Ag(I), Au(I), or Hg(II). Except for $Fe(CN)_6^{4-}$, the ^{13}C resonance in all the cyano complexes is found at higher field than uncomplexed CN^-, and the range of chemical shifts spans 92.5 ppm. Chemical-shift differences are discussed in terms of changes in σ and π bonding of CN^- to the metal ion. Metal–^{13}C spin coupling was observed for $Co(CN)_6^{3-}$ (126.0 Hz), $Rh(CN)_6^{3-}$ (33.6 Hz), $Pt(CN)_6^{2-}$ (808 Hz), and $Pt(CN)_4^{2-}$ (1034 Hz). Relaxation times T_1 and T_2 are reported for enriched (45% ^{13}C) samples of $Fe(CN)_6^{4-}$, $M(CN)_4^{n-}$ (where M = Ni(II), Pd(II), Pt(II), Au(III), Zn(II), Cd(II), or Hg(II)), $M(CN)_2^-$ (where M = Ag(I) or Au(I)), and $Co(CN)_6^{3-}$ (60% ^{13}C). In addition T_1 values for these complexes were measured at 10 °C temperature intervals between 30 and 70 °C. The mechanism of relaxation of the ^{13}C nucleus in the cyano complexes is discussed with the data in most cases consistent with scalar coupling to ^{14}N.

Introduction

As Fourier transform instrumentation has become widespread, the use of ^{13}C magnetic resonance as a spectroscopic tool for the investigation of metal complexes with carbon-containing ligands has become extensive.[2] Ligands with carbon directly bonded to the metal have attracted the greatest interest since large chemical shifts are often observed, and if the metal has a nuclear spin, spin coupling is also often measurable. Among the simplest such ligands are CO and CN^-. Although carbonyl complexes have been extensively and widely studied, comparatively little has been reported for cyano complexes. Hirota et al.[3] reported chemical shifts for a number of cyano complexes, and several Fe(II), Co(III), and Pt(IV) octahedral cyano complexes have been investigated.[4-9] The lack of more extensive investigation of diamagnetic cyano complexes seems surprising in view of the abundance of easily synthesized examples in several different molecular geometries. Further, many octahedral or square-planar cyano complexes of the late transition-metal ions and tetrahedral or linear complexes of the coinage or zinc family metal ions are very stable and resistant to hydrolysis in the absence of acid.[10] Thus a systematic investigation of ^{13}C NMR of these cyano complexes offers the interesting prospects of examining the ^{13}C resonance in several well-defined structural and electronic environments. Consequently, prompted in part by our interest in the electronic and structural features of cyano complexes generally and in part by our wish to further the understanding of the factors which affect ^{13}C resonance in metal complexes, we report here ^{13}C NMR spectra for 19 high-symmetry cyano complexes. Our study includes octahedral $M(CN)_6^{n-}$ complexes of nd^6 electronic configuration, square-planar $M(CN)_4^{n-}$ complexes of nd^8, and tetrahedral $M(CN)_4^{n-}$ and linear $M(CN)_2^{n-}$ complexes of nd^{10}. In addition, selected examples of each geometry were synthesized using $K^{13}CN$ (90% ^{13}C). The isotopically enriched complexes allowed the measurement of relaxation times for the ^{13}C nucleus. Metal–^{13}C spin coupling was observed for Pt in $Pt(CN)_6^{2-}$ and $Pt(CN)_4^{2-}$, Rh in $Rh(CN)_6^{3-}$, and Co in $Co(CN)_6^{3-}$, and coupling constants were determined in each case.

Experimental Section

Preparation of Compounds. The complexes studied here are all known complexes,[10] and most were prepared by standard methods. The compounds $K_4[Os(CN)_6]$[11] and $K_3[Rh(CN)_6]$[12] were prepared by fusion of $(NH_4)_2[OsCl_6]$[13] and $RhCl_3$, respectively, with KCN; the resulting mixtures were extracted with water, and the products were crystallized and recrystallized from water. Solution syntheses were employed for $K_3[Co(CN)_6]$,[14] $K_2[Pd(CN)_6]$,[15] $K_2[Pt(CN)_6]$,[16] $K_2[Ni(CN)_4]$,[17] $K_2[Pd(CN)_4]$,[18] $K_2[Pt(CN)_4]$,[19] $K[Au(CN)_4]$,[20] $K[Ag(CN)_2]$,[21] $K[Au(CN)_2]$,[22] $K_3[Cu(CN)_4]$,[23] and $K_2[M(CN)_4]$ (M = Zn, Cd, or Hg).[10] $K_4[Fe(CN)_6]$ was reagent grade, $K_4[Ru(CN)_6]$ was purchased from Alfa Inorganics (Danvers, MA), and $K_3[Ir(CN)_6]$ was purchased from D. F. Goldsmith (Evanston, IL).

Isotopically enriched complexes were prepared with $K^{13}CN$ (90% ^{13}C; Merck Sharp and Dohme, Canada). Small quantities of $M(CN)_2$ (M = Ni,[17] Pd,[18] Pt,[19] Zn,[10] or Hg), $Cd(OH)_2$, MCN (M = Ag or Au[24]), or *trans*-$[Au(CN)_2Br_2]^-$[20] were treated with stoichiometric amounts of $K^{13}CN$ in neutral, aqueous solution to produce $M(CN)_4^{n-}$ or $M(CN)_2^{n-}$ complexes containing 45% ^{13}CN. A sample of $K_4[Fe(CN)_6]$, 45% enriched with ^{13}C, was prepared by adding a concentrated aqueous solution of $FeCl_2{\cdot}4H_2O$ to a boiling aqueous solution of 1:1 KCN and $K^{13}CN$. The product was precipitated with ethanol and purified by dissolving in water and reprecipitating with ethanol. Isotopically enriched $K_3[Co(CN)_6]$ (60% ^{13}C) was prepared by dissolving $Co(CN)_2$ in aqueous $K^{13}CN$ solution.[14] The solution was concentrated, and the product crystallized as the solution was cooled. Because of concern for paramagnetic impurities, the sample was recrystallized from water four times.

Solutions for NMR spectra of the complexes with natural-abundance ^{13}C were nearly saturated (0.5–1.0 M) D_2O solutions; the

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Table I. Chemical Shifts and Line Widths for Diamagnetic Cyano Complexes in D_2O

complex	δ^{a}	$\Delta\nu_{1/2}$, Hz^{b}
Octahedral Hexacyano Complexes		
$Fe(CN)_6^{4-}$	177.2	3.2
$Ru(CN)_6^{4-}$	162.3	3.5
$Os(CN)_6^{4-}$	142.5	2.8
$Co(CN)_6^{3-}$	140.1^{c}	16
$Rh(CN)_6^{3-}$	131.9^{d}	5.2
$Ir(CN)_6^{3-}$	110.9	26
$Pd(CN)_6^{2-}$	104.2	2.0
$Pt(CN)_6^{2-}$	84.7^{e}	17
Square-Planar Tetracyano Complexes		
$Ni(CN)_4^{2-}$	136.6	2.5
$Pd(CN)_4^{2-}$	131.9	2.0
$Pt(CN)_4^{2-}$	125.7^{f}	2.2
$Au(CN)_4^{-}$	105.2	5.2
Tetrahedral Tetracyano Complexes		
$Cu(CN)_4^{3-}$	161.6	6.5
$Zn(CN)_4^{2-}$	147.0	5.5
$Cd(CN)_4^{2-}$	149.8	7.0
$Hg(CN)_4^{2-}$	153.2	4.0
Linear Dicyano Complexes		
$Ag(CN)_2^{-}$	150.0	3.0
$Au(CN)_2^{-}$	154.2	6.0
$Hg(CN)_2$	144.6	g

[a] To low field of Me_4Si; ±0.2 ppm. [b] Width at half-height ±5%. [c] Eight-line pattern, $^{1}J_{C-Co} = 126.0 \pm 0.8$ Hz. [d] Doublet, $^{1}J_{C-Rh} = 33.6$ Hz. [e] Three-line pattern (^{195}Pt, 33.7%), $^{1}J_{C-Pt} = 808$ Hz. [f] Three-line pattern, $^{1}J_{C-Pt} = 1034$ Hz. [g] Line width is temperature dependent: $\Delta\nu_{1/2} = 62$ Hz (30 °C), 15 Hz (70 °C).

D_2O also served as a source of lock signal for acquiring the ^{13}C spectra. Solutions of the ^{13}C-enriched complexes in D_2O for relaxation time measurements were purged free of O_2 with high-purity N_2.

NMR Spectra. All NMR spectra were obtained on a JEOL PFT-100 spectrometer equipped with the PG-100 computer controlled-pulse programmer. Carbon-13 spectra were obtained at 25.03 MHz with a 10 μs pulse (90° = 20 μs); internal deuterium served as a lock signal. Sample solutions were run either in 10-mm tubes or in small inserts in these tubes which were surrounded by D_2O. The temperature was the probe temperature (26 ± 1 °C) unless otherwise noted. Benzene was used as an external reference, and all chemical shifts are reported with respect to Me_4Si ($\delta(C_6H_6)$ 128.5).

Spin–lattice relaxation times (T_1) were determined by the standard 180°–τ–90° pulse sequence. Plots of ln $[I_\infty - I_\tau]$ vs. τ were linear in all cases investigated. Spin–spin relaxation times (T_2) were determined by the 90°–τ–180° pulse sequence, and plots of ln I_τ vs. τ were linear. Where possible, T_1 measurements were made at 10 °C intervals over the temperature range 30–70 °C. Repeated determinations were in good agreement.

Results

Chemical Shifts and Coupling Constants. Chemical shifts relative to Me_4Si and line widths of the ^{13}C resonance in the cyano complexes investigated are presented in Table I. The resonance line for the uncomplexed CN^- ligand in D_2O was observed at 166.2 ppm vs. Me_4Si with $\Delta\nu_{1/2} = 5.0$ Hz. Where the data overlap, there is good agreement between the results given in Table I and chemical shifts reported by Hirota et al.[3] Measured shifts agree to within 0.8 ppm in every case (within 0.1–0.3 ppm in most cases) except for $Fe(CN)_6^{4-}$, where δ was reported as 178.8 ppm (relative to Me_4Si)[3] or 1.6 ppm higher than observed here. The origin of the discrepancy in this case is not known but may be due to solvent and/or concentration effects.

Spin coupling beween ^{13}C and ^{195}Pt ($S = ^{1}/_{2}$, 33.7%) in $Pt(CN)_4^{2-}$ ($^{1}J = 1034$ Hz) and $Pt(CN)_6^{2-}$ ($^{1}J = 808$ Hz) was reported earlier by us[25] but was not observed by the previous workers for $Pt(CN)_4^{2-}$.[3] They did report coupling to ^{59}Co ($S = ^{7}/_{2}$, 100%) in $Co(CN)_6^{3-}$ giving an eight-line pattern with $^{1}J = 126$ Hz,[3] which agrees favorably with our results (footnote c, Table I). Coupling was also observed here for ^{103}Rh ($S = ^{1}/_{2}$, 100%) in $Rh(CN)_6^{3-}$; a well-resolved doublet gave $^{1}J = 33.6$ Hz.

Table II. Relaxation Times of ^{13}C in Isotopically Enriched Cyano Complexes

complex^{a}	T_1, s	T_2, ms
$Fe(CN)_6^{4-}$	7.5	110
$Co(CN)_6^{3-}$	>30	
$Ni(CN)_4^{2-}$	85	420
$Pd(CN)_4^{2-}$	88	210
$Pt(CN)_4^{2-}$	89	370
$Au(CN)_4^{-}$	71	640
$Zn(CN)_4^{2-}$	75	120
$Cd(CN)_4^{2-}$	65	190
$Hg(CN)_4^{2-}$	56	190
$Ag(CN)_2^{-}$	62	640
$Au(CN)_2^{-}$	33	

[a] Enriched 45% with ^{13}C, except $Co(CN)_6^{3-}$ which was enriched to 60%; 30 °C; 0.5 M (D_2O) purged free of O_2.

Cyanide-Exchange Reactions. In the absence of added CN^-, there was no evidence for ligand-exchange reactions or hydrolysis complicating the ^{13}C NMR spectra of the complexes investigated, except in the case of $Hg(CN)_2$. In this case an unusually broad line was observed at room temperature which decreased in width as the temperature was raised. This behavior may be explained by the presence of an exchange reaction which is accelerated toward the fast exchange limit as the temperature is raised.

In the presence of added CN^-, three reactions were examined which illustrate three different types of behavior. First, for 0.5 M $Ir(CN)_6^{3-}$, the ^{13}C spectrum was unaffected by 0.5 M added CN^-. Both the chemical shift and the line width for the complex were the same as in the absence of added CN^-, indicating that CN^- exchange is very slow (slow exchange limit). Second, for 0.6 M $Au(CN)_2^-$, the addition of 0.5 M CN^- gave a single, sharp line whose shift was the weighted average of the shifts of $Au(CN)_2^-$ and free CN^-. This behavior is consistent with very fast CN^- exchange (fast exchange limit). Finally for $Pt(CN)_4^{2-}$ in the presence of added CN^-, both the resonances for $Pt(CN)_4^{2-}$ and CN^- were broadened, indicating an intermediate exchange rate. The line widths were dependent upon the concentration of $Pt(CN)_4^{2-}$ and CN^- and the temperature. From quantitative measurements of line widths of the central peak of the $Pt(CN)_4^{2-}$ triplet, a rate constant of 30 M^{-1} s^{-1} at 30 °C was estimated for the exchange reaction. A more extensive study of CN^- exchange by ^{13}C NMR is in progress and will be reported in the future.

Relaxation Measurements. Spin–lattice (T_1) and spin–spin (T_2) relaxation times for ^{13}C in several isotopically enriched complexes are given in Table II. The value of T_1 for $Co(CN)_6^{3-}$ and T_1 and T_2 for $Fe(CN)_6^{4-}$ are uncertain because of the possibility of the presence of traces (<1%) of paramagnetic Co(II) or Fe(III) complexes resulting from synthesis. Paramagnetic substances can markedly alter relaxation times. In fact, the addition ca. 4 mol % $Cr(CN)_6^{3-}$ to shorten the relaxation time of ^{13}C in $Co(CN)_6^{3-}$ has been used to facilitate the accumulation of the spectrum by allowing shorter pulse intervals and thereby reducing the time required to obtain good signal to noise ratios.[7] In the present case, T_1 increased as $K_3[Co(CN)_6]$ was successively recrystallized. The value of 30 s obtained after four recrystallizations must be regarded as only a lower limit for T_1. The T_1 for $Fe(CN)_6^{4-}$ was the shortest of all the complexes investigated and likewise may signal trace paramagnetic impurities.

The temperature dependence of T_1 was also investigated for the complexes of Table II, except for $Co(CN)_6^{3-}$ and $Au(CN)_2^-$ where the signal to noise ratio was unfavorable.

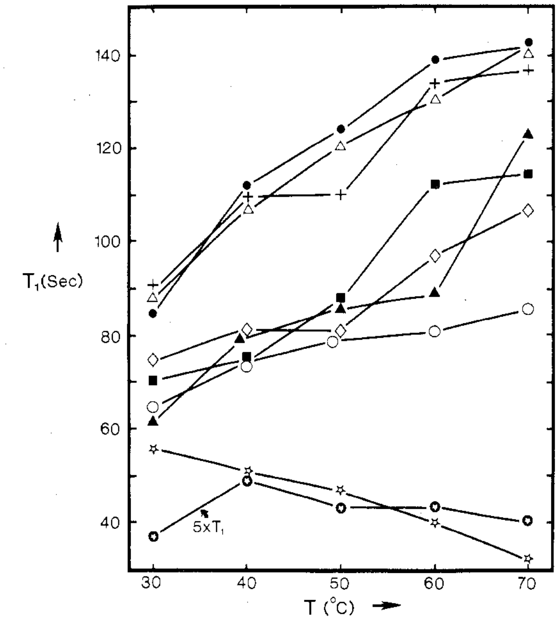

Figure 1. Variation of T_1 with temperature. Data obtained at 10 °C intervals for each complex are connected by straight lines for the sake of clarity: ●, $Ni(CN)_4^{2-}$; △, $Pt(CN)_4^{2-}$; +, $Pd(CN)_4^{2-}$; ◇, $Zn(CN)_4^{2-}$; ■, $Au(CN)_4^-$; ○, $Cd(CN)_4^{2-}$; ▲, $Ag(CN)_2^-$; ☆, $Hg(CN)_4^{2-}$; circled star, $Fe(CN)_6^{4-}$ ($5T_1$).

The results are summarized schematically in Figure 1. In each case, except for $Fe(CN)_6^{4-}$ and $Hg(CN)_4^{2-}$, T_1 increased with increasing temperature between 30 and 70 °C. For $Fe(CN)_6^{4-}$, T_1 increased from 30 to 40 °C but decreased at higher temperatures, while for $Hg(CN)_4^{2-}$, T_1 decreased over the whole range investigated.

Discussion

Carbon-13 Chemical Shifts. The data in Table I show three definite trends, which were first noted in the more limited data of Hirota et al.[3] First, a substantial shift to higher field is observed for the ^{13}C resonance of isoelectronic complexes of all geometries as the metal oxidation state is increased. Second, a shift to higher field down a periodic family is observed for the complexes with incompletely filled *n*d levels (octahedral nd^6 > square-planar nd^8). Third, a shift (though smaller) to lower field down a family is observed for the complexes with filled *n*d levels (tetrahedral $nd^{10} \approx$ linear nd^{10}). It is also of interest to note that the ^{13}C resonance of all the cyano complexes investigated, except $Fe(CN)_6^{4-}$, lies at higher field than the uncomplexed CN^- ligand. These results can be compared with typical chemical shifts for carbonyl complexes. Trends similar to the first two are observed, but virtually all ^{13}C chemical shifts of carbonyl complexes are to lower field than the uncomplexed CO ligand.[2] For example, ^{13}C shifts for octahedral nd^6 $M(CO)_6$ complexes have been reported as 226, 212, 202, and 192 ppm for M = V(1–), Cr(0), Mo(0), and W(0), respectively, while the resonance for CO is found at 181.3 ppm.[26–29]

Unfortunately theoretical interpretation of ^{13}C chemical shifts for σ-bonded carbon ligands in metal complexes has not been completely satisfactory. In fact considerable pessimism as to the value of qualitative explanations based on current shielding models has been expressed recently, summarized aptly by Evans and Norton.[29] Most explanations offered for ^{13}C chemical shifts for carbonyl complexes, for example, have been based on changes in the so-called "paramagnetic" term of the screening tensor, σ_p[2,30] (however, changes in the "diamagnetic" term, σ_d, may also be important[31]). However, the magnitude of σ_p depends upon three interrelated factors which are not often easily separated: (1) the carbon electron density and the radial extension of the 2p orbitals, (2) energies of electronic states of the molecule, and (3) π bond order between carbon and adjacent atoms. Recent MO calculations[32] for several arene carbonyl complexes of the type $(C_6H_6)M(CO)_3$ showed that the product of all three of these factors must be considered together in determining the ^{13}C chemical shifts of CO, and pessimism was again expressed about qualitative comparisons based on only a single factor. This pessimism is of course applicable to the cyano complexes investigated here. In spite of the pessimism regarding theoretical rationale and recognizing the complications surrounding qualitative arguments, a few further comments may nevertheless be cautiously advanced from our results. Our purpose here is to draw attention to the changes in σ and π bonding factors which affect the observed ^{13}C chemical shifts.

In many carbonyl complexes a downfield shift of ^{13}C resonance accompanied by a decrease in ν_{CO} stretching frequency has been interpreted as indicative of π back-bonding increase.[2,26,27] Recently though, it has been argued that inductive effects through the metal–carbon σ bond are also important in both carbonyl complexes and for the σ carbon of metal acetylide complexes.[33] As the electron-withdrawing power of the metal was increased, the ^{13}C resonance shifted to higher field. This high-field shift was explained as due to increased polarization of the multiple bond in which a shift of π electron density toward the carbon is caused by the inductive withdrawal of electron density through the metal–carbon σ bond.[33] A similar effect is observed for nitriles of the type X–CN.[34] As the electronegativity of X increases, the ^{13}C resonance of the nitrile carbon is observed to shift to higher field. Yonemoto has suggested this effect is a general feature of $X{-}C{\equiv}Y$ systems,[34] of which metal carbonyl, acetylide, and cyano complexes are examples. Thus for carbonyl complexes, the observed changes in ^{13}C chemical shift from complex to complex are likely the result of the combined effects of changes in σ donation (an increase causing a high-field shift) and π acceptance (an increase causing a low-field shift). The low-field shift of CO generally observed on complexation probably reflects the greater importance of the π-acceptor properties of the ligand than its σ-donor properties.

In contrast to the CO ligand, the anionic CN^- ligand is a better σ donor and a poorer π acceptor. Differences in σ bonding therefore will likely dominate ^{13}C chemical shifts, and the high-field shifts which are generally observed on complexation of CN^- would be consistent with this notion. In the case of $Fe(CN)_6^{4-}$, the only complex investigated with a lower field ^{13}C chemical shift than that of uncomplexed CN^-, π back-bonding is undoubtedly significant. For example, ν_{CN} for $Fe(CN)_6^{4-}$ is observed at lower frequency (2041 cm^{-1}) than free CN^- (2080 cm^{-1}),[35] consistent with population of the π^* CN orbital and reduction of the C–N bond order. All the other complexes investigated have ν_{CN} at higher frequency (in the range 2100–2200 cm^{-1}) than free CN^-. For example, ν_{CN} for $K_3Co(CN)_6$ and $K_2Pt(CN)_6$ are found at 2129 and 2189 cm^{-1}, respectively.[36] It is interesting to note, however, that changes in both σ and π bonding operate together to provide a high-field shift of the ^{13}C resonance in isoelectronic cyano complexes. As the metal oxidation state increases, π back-bonding will decrease due to the contraction of the filled metal *n*d orbitals, but at the same time σ donation will increase. Both effects will increase the shielding of the ^{13}C nucleus, but the σ donation of the anionic CN^- ligand will likely dominate.

The trends observed in the ^{13}C chemical shifts down a periodic family most certainly result from a combination of bonding factors, and explanations based on a single one are not likely to be useful or correct. However, it is interesting that complexes with partly filled *n*d levels shift upfield as *n* increases while those with filled levels shift downfield by a small amount. Further, the upfield shift is larger for the nd^6 complexes than for nd^8. Qualitatively this might be visualized as a consequence of the penetration of the CN^- ligand into the partly filled nd shell, which would be greater for nd^6 (six ligands sharing two empty nd orbitals) than nd^8 (four ligands sharing one empty nd orbital). As n increases from 3 to 5, the expansion of the filled d orbitals around the CN^- ligands is expected to increase and thus screen the ^{13}C nucleus. In contrast, the CN^- ligands probably do not penetrate the filled nd^{10} shell to any significant extent,[37] and the expansion of the nearly spherical shell as n increases would not serve to shield the ^{13}C nucleus. The small downfield shift observed for the nd^{10} complexes may result from small differences between much larger, compensating changes in diamagnetic and paramagnetic contributions to the shielding. The small differences may also be present for the partly filled nd shell complexes but are overshadowed by the larger differences ascribed to orbital penetration.

Carbon-13 Relaxation Mechanism. The relaxation mechanisms that are available to nonquadrupolar nuclei such as ^{13}C include dipole–dipole, scalar coupling, chemical-shift anisotropy, and spin–rotation. While it is frequently difficult to positively identify the dominant relaxation mechanism for a particular nucleus, the data presented in this study greatly restrict the choices.

Figure 1 shows the variation of the spin–lattice relaxation time (T_1) with temperature. With the exception of $Fe(CN)_6^{4-}$ (which is thought to be contaminated by a paramagnetic impurity because of its short T_1) and $Hg(CN)_4^{2-}$, the T_1 values for the enriched complexes studied increase with increasing temperature. Such evidence precludes spin–rotation interactions as the dominant relaxation mode because the effectiveness of the mechanism is directly dependent on τ_c, the molecular reorientation time, and the frequency of molecular collisions. Both of these parameters increase with increasing temperature and therefore cause a reduction in the spin–lattice relaxation time. It is the only mechanism that causes a decrease in T_1 with increasing temperature, the opposite of the experimental results obtained for the cyanide complexes. Spin–rotation is often favored for nuclei, such as ^{13}C with a large chemical shift range, that are located in a symmetrical environment. Although the complexes studied here possess a high degree of symmetry, it is the metal ion rather than the cyanide ligand which is at the center of symmetry. For example, it has been shown that spin–rotation is the dominant relaxation mechanism for the platinum nucleus in D_{4h} Pt(II) complexes and O_h Pt(IV) complexes.[25]

Chemical-shift anisotropy (CSA) will, in general, be an important relaxation mechanism at very high magnetic fields. At magnetic field strengths comparable to those used in this study, CSA makes a significant contribution to relaxation only when other mechanisms are very inefficient. This is a relatively rare occurrence. It has also been shown that in the extreme narrowing limit, which occurs with nonviscous solutions such as those used in this study, the ratio $T_2/T_1 = 6/7$.[38] This is significantly larger than the ratios of 10^{-2}–10^{-3} which are observed for ^{13}C in the cyanide complexes in this study.

In most organic compounds, carbon-13 nuclei, like protons, are predominantly relaxed by dipole–dipole interactions. In the presence of directly bonded, spin $^1/_2$ nuclei, intramolecular dipole–dipole interaction should be the dominant relaxation mechanism. The relaxation times reported in Table II show a relatively small variation in magnitude as the directly bound metal ion is changed. This is best illustrated by the square-planar cyanide complexes of Pt(II), Pd(II), and Ni(II). Nickel has no appreciable precentage of any spin nucleus, palladium contains 22.2% of ^{105}Pd with $I = {}^5/_2$, and platinum contains 33.7% of ^{195}Pt with $I = {}^1/_2$. Yet relaxation times for these complexes are the same within experimental error. Certainly, if intramolecular dipole–dipole interactions were important, they should occur in $Pt(CN)_4^{2-}$ producing a significantly different, presumably shorter, relaxation time than those of $Ni(CN)_4^{2-}$ and $Pd(CN)_4^{2-}$. In addition, T_1 is the same for the central peak in the $Pt(CN)_4^{2-}$ multiplet (noncoupled peak) as well as the satellite peaks (coupled peaks). There are only relatively small changes in the T_1's of ^{13}C in cyanide complexes of different molecular geometries (excluding $Fe(CN)_6^{4-}$). The small variations that do exist may well reflect the difference in contribution from intermolecular dipole–dipole interactions due to geometry effects.

It is the absence of change in T_1 of ^{13}C with changes in the directly bound metal nuclei and molecular geometry that suggests the nucleus is primarily relaxed by the fluctuating local magnetic field produced by the rapidly relaxing quadrupolar nucleus ^{14}N. This is referred to as scalar relaxation of the second kind. This mechanism is dependent upon some spin–spin coupling between the two nuclei and a reasonable relaxation rate, usually between 10–100 ms, for the quadrupolar nucleus.[39] This mechanism plays a dominant role in the relaxation of protons by ^{14}N and ^{11}B and therefore could also be important in the relaxation of ^{13}C by directly bonded ^{14}N. In general, there is also an appreciable difference in the T_1 and T_2 values when this mechanism is dominant. T_2 is usually significantly shorter, as observed in the ^{13}C relaxation of cyanide complexes, and can cause line broadening which is observed in the case of ^{1}H directly bonded to ^{14}N. The ratio of the relaxation times is given by

$$T_1/T_2 = {}^1\!/_3 A^2 S(S+1)\tau_s T_1 + 1$$

where A is the spin–spin coupling constant in radians per second, S is the spin of the nucleus causing relaxation, and τ_s is the correlation time of the relaxing nucleus which is usually equal to its T_1. With $\tau_s = 10$ ms and $S = 1$ for ^{14}N, one obtains ratios of T_1/T_2 in the range 10^2–10^3 assuming coupling constants in the range 10–100 Hz. This certainly seems to be a plausible explanation for the observed differences in T_1 and T_2. Although ^{13}C–^{14}N dipole–dipole relaxation is possible, the conditions employed in these experiments are generally those of the extreme narrowing limit in which $T_1 = T_2$. The somewhat shorter relaxation time for $Co(CN)_6^{3-}$ may be explained by additional scalar coupling of the second kind with ^{59}Co whose frequency is close to that of ^{13}C. This is supported by the fact that the heights and widths of the eight-line multiplet in the ^{13}C spectrum are unequal.

The evidence presented indicates that scalar coupling is likely the dominant relaxation mechanism for ^{13}C in most high-symmetry cyanide complexes. The small changes in T_1 observed when substituting different metal ions in the same symmetry complex indicate that intramolecular dipole–dipole interactions are not a major factor in the relaxation process. The origin of the decrease in T_1 with increasing temperature for $Hg(CN)_4^{2-}$ is not known. The decrease may be a result of a rapid exchange reaction between very low concentrations of free CN^- and $Hg(CN)_4^{2-}$. If the relaxation of the free CN^- under the conditions of the exchange were rapid, an acceleration of the exchange rate with temperature could lead to the observed results.

Registry No. $Fe(CN)_6^{4-}$, 13408-63-4; $Ru(CN)_6^{4-}$, 21029-33-4; $Os(CN)_6^{4-}$, 19356-45-7; $Co(CN)_6^{3-}$, 14897-04-2; $Rh(CN)_6^{3-}$, 19356-46-8; $Ir(CN)_6^{3-}$, 19356-47-9; $Pd(CN)_6^{2-}$, 20740-37-8; $Pt(CN)_6^{2-}$, 41517-45-7; $Ni(CN)_4^{2-}$, 48042-08-6; $Pd(CN)_4^{2-}$, 15004-87-2; $Pt(CN)_4^{2-}$, 15004-88-3; $Au(CN)_4^-$, 22806-79-7; $Cu(CN)_4^{3-}$, 19441-11-3; $Zn(CN)_4^{2-}$, 19440-55-2; $Cd(CN)_4^{2-}$, 16041-14-8; $Hg(CN)_4^{2-}$, 19426-03-0; $Ag(CN)_2^-$, 15391-88-5; $Au(CN)_2^-$, 14950-87-9; $Hg(CN)_2$, 592-04-1.

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Comparison of the Photocatalytic Behavior of Phosphinated Polymer-Anchored Iron Carbonyl Species and Homogeneous Phosphine Substituted Iron Carbonyl Species: Alkene Isomerization and Reaction with Trialkylsilanes

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A styrene–1% divinylbenzene resin whose phenyl rings have been derivatized with PPh_2 groups serves as an "anchor" for $Fe(CO)_n$ ($n = 3, 4$) groups; the anchor is the Fe–P bond. The photocatalytic activity of suspensions of the polymer-anchored $Fe(CO)_n$ has been compared to that of homogeneous solutions of $Fe(CO)_n(PPh_3)_{5-n}$ ($n = 3$–5). 1-Pentene isomerization and reaction with $HSiEt_3$ can be affected with each system. Observed quantum yields for 1-pentene isomerization exceed unity for each catalyst precursor, and the initial *trans*- to *cis*-2-pentene ratio depends on the catalyst precursor, implicating the retention of the triarylphosphine groups in the actual catalytically active species. Irradiation of $Fe(CO)_n(PPh_3)_{5-n}$ ($n = 4$) results in loss of CO, not PPh_3, suggesting a photoinert anchor to the $Fe(CO)_n$ groups in the polymer systems. These experiments establish the viability of photogenerating catalysts anchored to polymer supports without destruction of the anchor bond in the photogeneration procedure.

Recent studies have shown that photogenerated coordinatively unsaturated intermediates are capable of serving as catalysts for a variety of reactions involving olefins.[1-10] We have reasoned that it may be possible to generate metal-centered catalysts which are extensively coordinatively unsaturated by irradiation of polymer-anchored, but fully coordinatively saturated, organometallic complexes. The simple notion is that the polymer-anchored species may be "matrix isolated" in the sense that the photogenerated intermediates are incapable of reacting with one another to generate catalytically inactive aggregates. It is well established, for example, that irradiation of mononuclear binary metal carbonyls in rigid matrices at low temperature results in extensive loss of CO, and in several instances all CO's can be dissociated from the metal to generate elemental metal.[10-21] Consequently, the generation of multiply coordinatively unsaturated species seems a reasonable possibility in the anchored systems. Importantly, such an approach may provide a way to study the reactions of such sites under conditions where sufficient thermal activation energy exists to study catalytic chemistry but at milder conditions than would be required for thermal generation of multiple coordinative unsaturation.

By now the study of polymer-anchored thermal catalysts is well-known,[22-37] but polymer-anchored systems exposed to light have received little detailed study. The aim of this report is to describe our results pertaining to the photocatalytic activity of $Fe(CO)_n$ ($n = 3, 4$) species anchored to a phosphinated styrene–divinylbenzene resin. An important component of the results concerns the parallel study of homogeneous "models" of the polymer-anchored systems. Owing to a number of previous photocatalytic studies,[9,10] there is

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