Copper Complexes with Free-Radical Ligands

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Abstract: We have synthesized and investigated copper complexes containing a series of different pyridylnitronyl nitroxide radicals as ligands. Complexes in which a single radical was bound to $Cu(HFAA)_2$ (1:1 complexes) were stable in solution and could be isolated as crystalline solids in some instances. Complexes with 2 mol of radical to 1 mol of $Cu(HFAA)_2$ (2:1 complexes) could be isolated as crystalline solids in some cases but these complexes dissociated to 1:1 complexes in solution. ESR studies of the 1:1 complexes showed that these molecules have ground singlet states. The energy difference between the singlet and triplet states was found to depend on the position of the pyridyl nitrogen which binds to the copper atom. The complex formed with the ortho pyridyl radical is diamagnetic and has a relatively large singlet-triplet energy splitting. The triplet states of complexes formed from the meta and para radicals are thermally accessible and we were able to estimate exchange energies through studies of the temperature dependence of the area of the ESR signals. Dipolar splittings were observed from these complexes and were used to determine average electron-electron separations in the triplet state. The ground singlet state of the complexes can be accounted for by assuming charge transfer from the copper to the radical to yield Cu(III) complexes.

Introduction

If one constructs transition metal complexes in which both the ligands and the metal have unpaired electron spins, one is able to investigate the interaction of spins in the $2p\pi$ orbitals of the ligands with the d electrons of the metal. If a single radical is coordinated with a transition metal having one unpaired electron spin, the energy levels are split into singlet and triplet states with an energy separation of $2J$. If there is appreciable overlap of the orbitals containing the spins, one predicts large exchange and dipolar interactions.[1] When the exchange energy is large compared to the g value difference of the parent radical and metal ($J \gg \Delta g$) the ESR spectrum from a solution of the complex will be centered at a position between the lines from the parent species.[2] This signal may show hyperfine structure from both the metal atom and from nuclei in the radical ligand but the dipolar interaction between the electron spins normally becomes large when J becomes appreciable and the lines are broadened by incomplete rotational averaging of the dipolar interaction.[3] When the exchange energy becomes of the order of kT one begins to preferentially populate the lower of the singlet or triplet energy levels and the magnetic susceptibility deviates from a Curie law temperature dependence. The equation for the temperature dependence of the magnetic susceptibility (χ_m) for systems of this type is given by[4]

$$\chi_m = \frac{2g^2\beta^2N}{3kT}\left[\frac{1}{1 + \frac{1}{3}\exp\frac{-2J}{kT}}\right] \qquad (1)$$

Measurements of the temperature dependence of the magnetic susceptibility allows one to determine both the sign and magnitude of the exchange energy in some instances.

ESR investigations of complexes of this type allow one to obtain information about both the exchange energy and the electron-electron dipolar interaction in some cases. If one observes a signal at an intermediate position between the spectral lines from the metal and the radical one is able to place a lower limit on the magnitude of the exchange energy. The area of this signal is proportional to the magnetic susceptibility and measurement of the temperature dependence of the area of the ESR signal can be used along with eq 1 to determine the sign and magnitude of the exchange energy in cases in which $J \sim kT$. If the complex is frozen in a rigid glass at a temperature at which there is an appreciable population of the triplet state one is able to measure the magnitude of the dipolar constants (D and E).[5] If one uses the point dipole approximation one can obtain an estimation of the separation of the electron spins (r) from the magnitude of D.[6]

$$D = \frac{3}{2}\frac{\mu}{r^3} \qquad (2)$$

ESR and magnetic susceptibility measurements have been carried out on di-*tert*-butyl nitroxide (DBNO) complexes with CoX_2[7] (X = Cl, Br, I), with palladium halides,[8] with $Cu(HFAA)_2$ (HFAA = hexafluoroacetylacetonate), and with $Cu(TFAA)_2$ (TFAA = trifluoroacetylacetonate).[9] The Co complex has a single unpaired electron and the magnetic susceptibility follows a Curie-Weiss law indicating that two of the cobalt's electrons have paired with electrons from two complexed DBNO radicals. The Pd complexes have the structure $[PdXDBNO]_2$ and are diamagnetic. The ESR spectra from mixtures of DBNO and $Cu(HFAA)_2$ and $Cu(TFAA)_2$ are reported to be broadened with a loss of hyperfine structure. Magnetic susceptibility measurements with the $Cu(HFAA)_2$·DBNO complex indicate that it is a ground state singlet with a triplet state about 645 cm^{-1} above the singlet state. The nitroxide group of the DBNO molecule is coordinated directly with the d orbitals of the metals in these complexes and one expects the strong exchange interaction which is observed in each case.

Metal complexes of 2,2,5,5-tetramethyl-3-imidazoline-1-oxyl-4-carboxylic acid have also been reported.[2] The metal is coordinated to the carboxylic group and one of the nitrogens in the imidazoline ring in these complexes and is held away from the nitroxide group. Two radicals are bound to a copper atom and the three-electron system is described by a quartet and two doublet states. The exchange energy for this copper complex was evaluated to be -66 cm^{-1} or less. One might expect a smaller exchange interaction in this type or molecule as the copper atom and nitroxide groups are separated and overlap between the orbitals containing the unpaired electron spins should be smaller.

We have synthesized and investigated the magnetic properties of a series of $Cu(HFAA)_2$ complexes with pyridylnitronyl nitroxide radicals (Figure 1). Complexes in which a single radical is coordinated to the copper atom (1:1 complexes) were stable in solution and were investigated in each case. Solid complexes with two radicals coordinated to the copper atom (2:1 complexes) could be isolated from mixtures of $Cu(HFAA)_2$ with either the meta or para radicals. Both proton[10] and carbon[11] hyperfine coupling constants have been reported for these radicals. These measurements show that

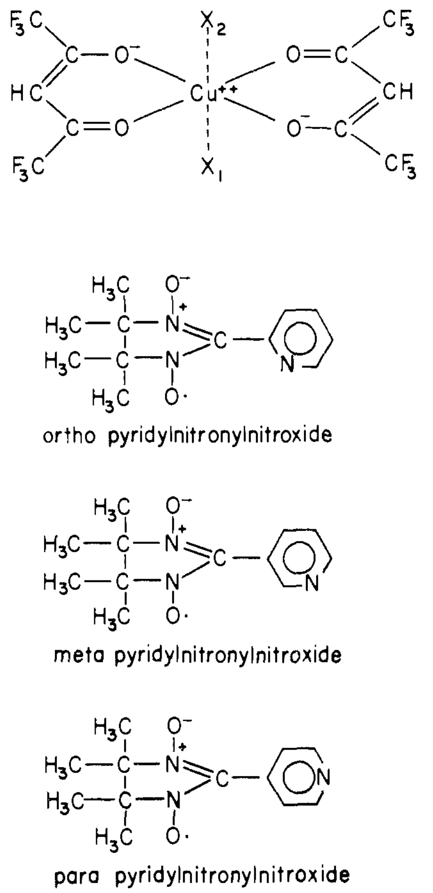

Figure 1. Structure of complexes. In the 1:1 complexs X_1 is one of the pyridylnitronyl nitroxide radicals while X_2 is solvent. In the 2:1 complexes X_1 and X_2 are radicals.

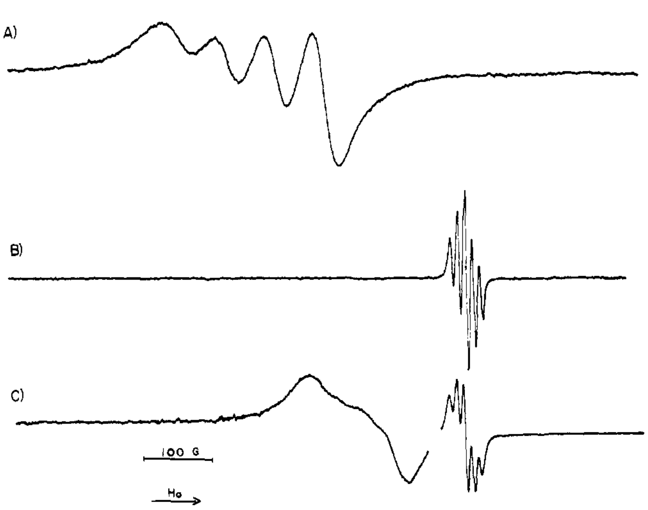

Figure 2. ESR spectra. (A) Spectrum of $Cu(HFAA)_2$ in $CHCl_3$. (B) Spectrum of the meta pyridylnitronyl nitroxide radical. (C) Spectrum of the 1:1 complex of the meta pyridylnitronyl nitroxide radical and $Cu(HFAA)_2$.

Table I. Analytical Data and Magnetic Susceptibilities

Compd	% C	% H	Mp, °C	μ_B
	1:1 Complexes			
Theoretical	37.12	2.55		2.828
Ortho complex	36.72	2.35	66	0
Para complex	34.17	1.94	160-162	2.677
	2:1 Complexes			
Theoretical	43.16	3.62		3.870
Meta complex	42.86	3.64	184	3.186
Para complex	43.32	3.36	190	2.995

most of the spin density in these radicals is localized on the nitroxide groups of the nitronyl nitroxide ring. The radicals are coordinated to the d_{z^2} orbital of the copper atom by the pyridyl nitrogen atom. The separation of the nitronyl nitroxide ring from the copper atom varies with the position of the nitrogen atom in the pyridyl ring and one expects changes in the magnitude of the exchange interaction with the structure of the complex. All of the 1:1 complexes were found to have ground singlet states. The triplet states of the meta and para complexes were thermally accessible and we were able to estimate the singlet-triplet separation through measurements of the temperature dependence of the area of the ESR signal. Dipolar splittings from samples frozen in rigid glasses were also observed and we were able to determine average electron-electron separations in the triplet state.

Experimental Section

A. Synthesis. We were able to obtain pure crystalline 1:1 complexes with the ortho and para radicals but were unable to isolate the 1:1 complex of the meta radical. Mixtures of various concentrations of the meta radical with $Cu(HFAA)_2$ were found to always crystallize as 2:1 complexes. Crystalline 2:1 complexes were obtained from the meta and para radicals but could not be prepared with the ortho radical.

All of the complexes were prepared by a similar procedure. Appropriate molar quantities of the radical and $Cu(HFAA)_2$ were dissolved in chloroform and the solvent was evaporated. All of the complexes except the 1:1 ortho complex were then recrystallized from mixtures of chloroform and benzene. The ortho complex was recrystallized from a mixture of benzene and cyclohexane. Analytical data for the complexes are given in Table I.

B. Magnetic Susceptibility. The magnetic susceptibility of the solid complexes was determined at 297 K with the Faraday method. Values for the magnetic moments are listed in Table I. The diamagnetic correction to the magnetic susceptibility was estimated from Pascal's constants and subtracted from the experimental molar susceptibility along with the temperature-independent paramagnetic term for copper.[4] The moments which were measured are smaller than those predicted for a pure triplet state in the 1:1 complexes or a pure quartet state in the 2:1 complexes indicating pairing of the electrons from the copper atom and the radicals.

C. ESR and Optical Spectra. The ESR spectra were recorded with a JEOL 3BSX X-band ESR spectrometer with 100-kHz field modulation. Solution spectra were taken with chloroform as the solvent while 2-methyltetrahydrofuran was used as a glass for spectra taken at low temperature. Optical spectra were taken with a Cary 14 spectrophotometer.

Results and Discussion

The ESR spectra of solutions of the 1:1 complexes of $Cu(HFAA)_2$ with the meta and para pyridylnitronyl nitroxide radicals consisted of a single broad line at nearly an average position between the spectrum from $Cu(HFAA)_2$ and that from the radical (Figure 2). A weak signal from the radical was also observed indicating a small amount of dissociation of the complex. The solution spectra of 2:1 complexes of these radicals were identical except for a much larger signal from dissociated radical. The 2:1 complexes apparently dissociate into 1:1 complexes plus unbound radical when they are dissolved in chloroform. An ESR spectrum was not observed from the 1:1 ortho pyridylnitronyl nitroxide complex even when the sample was heated to 80 °C in xylene where the complex started to decompose. When γ-picoline was added to solutions of the ortho, meta, or para complexes one immediately observes an ESR spectrum which is a superposition of the spectrum from the nitronyl nitroxide radical and the spectrum from $Cu(HFAA)_2(\gamma\text{-picoline})$. The γ-picoline apparently displaces

Table II. ESR Data

Compd	g, solution $CHCl_3$	g, solid	$1/T_2$, G (297 K)	D, G	r, Å	$2J$, cm^{-1}
Nitronyl nitroxide radicals	2.0068					
$Cu(HFAA)_2$, solid		2.1198				
$Cu(HFAA)_2$ solution	2.1566					
Cu(HFAA), solution[a]	2.1306					
1:1 ortho complex						<-1000
1:1 meta complex, solution	2.0664		106	192	5.25	-299 ± 10
2:1 meta complex, solid		$g_\parallel = 2.0479$ $g_\perp = 2.1115$				
1:1 para complex, solution	2.0691		130	576	3.64	-310 ± 50
1:1 para complex, solid		2.0934	~120			>-80
2:1 para complex, solid		2.0568	90			

[a] Done in pyridine.

the nitronyl nitroxide radical from the copper and the ESR spectra of the individual species are observed.

It is possible for the nitronyl nitroxide radicals to coordinate to the copper through the nitroxide groups rather than through the nitrogen in the pyridine ring. In order to determine the position of coordination we attempted to make complexes of the phenylnitronyl nitroxide radical[12] with $Cu(HFAA)_2$. We were unable to obtain crystalline complexes of this radical with $Cu(HFAA)_2$. The ESR spectrum of mixtures of this radical with $Cu(HFAA)_2$ was a superposition of the lines from $Cu(HFAA)_2$ and the radical indicating that this radical does not readily coordinate with the copper complex. These results show that coordination through the nitroxide group is much weaker than that through the pyridyl nitrogen atom in molecules of this type. In the case of the 1:1 complex of the ortho nitronyl nitroxide radical the nitroxide group is held close to the copper atom which is coordinated to the pyridyl nitrogen and it is possible for this group to interact more strongly with the metal.

The position of the ESR signal from the 1:1 complexes of the meta and para radicals shows that the exchange energy is greater than the g value difference of $Cu(HFAA)_2$ and the radical ($J \gg \Delta g$). The g values of the complexes and the line width of the signals are listed in Table II along with the g values of the starting radicals and $Cu(HFAA)_2$. The width of the signals from the complexes probably arises from incomplete rotational averaging of the dipolar interaction between the two unpaired spins in the triplet state of the complex. Values of the dipolar constant D were determined from ESR spectra taken of samples frozen in 2-methyltetrahydrofuran glasses. The complexes have near axial symmetry and the value of E was too small to measure. The dipolar constants are listed in Table II along with average electron–electron separations calculated using the point dipole approximation. The dipolar constant of the para 1:1 complex is larger than that of the meta complex indicating a smaller electron–electron separation in the para complex. The larger line width observed for the signal from the para complex in solution can be accounted for by the larger dipolar interaction.

The temperature dependence of the magnetic susceptibility of the samples was determined by monitoring changes in the area of the ESR signals with temperature. Experiments were carried out with chloroform solutions of the meta and para 1:1 complexes, with the solid para 1:1 complex, and with solid samples of the meta and para 2:1 complexes. The ESR signal from solutions of the complexes broadened as the temperature was lowered. The signal from the 1:1 complex of the para radical became extremely broad at temperatures below about −40 °C and it was difficult to accurately measure the area of the signal as it overlapped with the sharp lines from residual uncomplexed radical in the sample. The problem in measuring the area of this signal produces some error in our estimate of the exchange energy for this radical. The area of the signals from both complexes initially increased as the temperature was lowered, passed through a maximum, and then decreased. A plot of the area of the signal from the meta 1:1 complex vs. temperature is shown in Figure 3. The temperature dependence of the areas of the signals was fitted with eq 1 to obtain values of the exchange energies. A theoretical fit is shown in Figure 3 and values for the exchange energies are listed in Table II.

The ESR spectra of polycrystalline samples of 1:1 and 2:1 complexes of the para nitronyl nitroxide radical consisted of a single broad line. The spectrum of a polycrystalline sample of the 2:1 complex of the meta nitronyl nitroxide radical showed two lines characteristic of an axially symmetric molecule. The signals from all of the solid samples were between the signals from the isolated radicals and that from $Cu(HFAA)_2$ indicating that $J > \Delta g$. The g values are listed in Table II. The g values of the 2:1 complexes were smaller than those from 1:1 complexes. This behavior is predicted in the limit of large exchange energies as one must average twice the g value of the radical with that of $Cu(HFAA)_2$ in the 2:1 complexes.

The area of the ESR signals of polycrystalline samples of the 1:1 para complex and the 2:1 meta complex varied linearly with the inverse of temperature down to the lowest temperature accessible in our experiments (−150 °C). The area of the signal from the para 2:1 complex varied linearly with the inverse of temperature over most of the region investigated but showed some curvature at the lowest temperatures studied. Apparently the exchange energies for these complexes depend on the environment of the molecules. In solution the 1:1 complexes are surrounded by solvent molecules and intermolecular interactions are small so one observes behavior characteristic of isolated complexes. In the solid state the copper atoms of the 1:1 complexes may interact with neighboring copper atoms and perturb the exchange interaction between copper and the radical. Measurements of magnetic susceptibilities over an extended temperature range are necessary to determine the sign and magnitude of the exchange energy in the solid polycrystalline complexes.

The UV-visible spectra of $Cu(HFAA)_2$, the individual radicals, and the complexes were taken and compared. The spectra of the meta and para 1:1 complexes are nearly a superposition of the spectra of $Cu(HFAA)_2$ and that of the radicals. The d electron transitions of $Cu(HFAA)_2$ are overlapped to form a single broad line which is centered at 580 nm. This line overlaps with transitions from the radicals in the spectra of the complexes. As a consequence it was impossible to monitor changes in the position of the d electron transition when the radical complexes with the copper. The spectrum of the ortho nitronyl nitroxide 1:1 complex showed one new transition at 438 nm in addition to the lines from $Cu(HFAA)_2$

Table III. Optical Transitions, Wavelength (nm), and Extinction Coefficients

Compd									
Cu(HFAA)$_2$	240.6		310.6	327.9 (s)[a]			580.0		
	9811		19 405	10 267			41		
Ortho radical	251.8	267.3	285.0	352.9	367.9		574.3		
	7750	8274	7394	9173	16 099		496		
Meta radical		262.4	290.0 (s)	352.3	368.2		583.3	620	690
		10 296	6170	9147	17 082		464	464	160
Para radical		262.2	278.8	352.9	368.2		551.1	594.1	644.5
		10 315	9847	8993	20 590		214	287	220
1:1 ortho complex		282.5	293.8	352.3	368.5	438.2	578.3		
		21 228	23 180	14 843	25 823	1812	686		
1:1 meta complex	295.0	307.3	328.2	353.2	368.8		592.2	624.8	
	22 013	22 034	15 128	17 245	29 800		456	450	
1:1 para complex	262.2	284.7	307.9 (s)	353.6	368.5		550 (s)	600	640
	27 071	28 863	24 483	16 103	35 372		162	290	266

[a] s = shoulder.

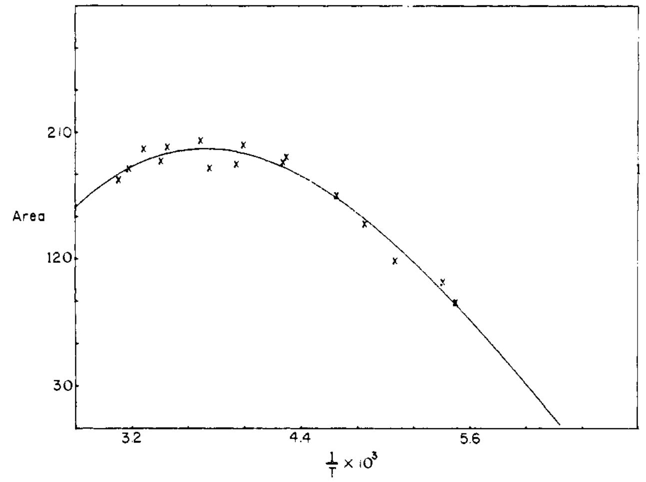

Figure 3. A plot of the area (arbitrary units) of the ESR signal from the 1:1 complex of the meta pyridylnitronyl nitroxide radical and Cu(HFAA)$_2$ vs. the reciprocal of temperature. The solid line is the theoretical curve calculated with eq 1.

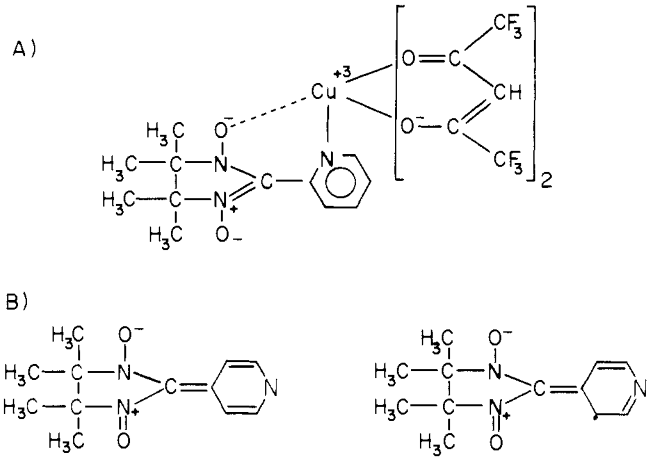

Figure 4. (A) Structure of the 1:1 complex of the ortho pyridylnitronyl nitroxide radical with charge transfer from copper to the radical. (B) Resonance structures placing unpaired spin density at the ortho and para positions of the aromatic ring.

and the radical. Transitions at about this wavelength have been reported for Cu(III) complexes.[13] Table III list the positions of transitions and extinction coefficients.

The ground singlet state of the 1:1 complexes may be accounted for by transfer of an electron from the copper to the radical to yield Cu(III) complexes. The nitronyl nitroxide radicals are strong oxidizing agents and when coordinated with Cu(HFAA)$_2$ the unpaired d electron of the copper may be transferred to the nitroxide group of the radical (Figure 4A) In the ortho complex the nitroxide group is held close to the copper atom and one expects a strong interaction between the metal and the nitroxide group. The optical transition at 438 nm which is observed from this complex supports the postulate of charge transfer from the metal to the nitroxide group to form a diamagnetic Cu(III) complex. The nitroxide groups are held at a greater distance from the copper in the meta and para 1:1 complexes and the singlet-triplet separation is smaller in these compounds than that of the ortho complex. The ground singlet state of the meta and para complexes may be accounted for by charge transfer from the copper to the radical but the charge transfer interaction is weaker because of the greater separation between the copper and the nitroxide group.

The dipolar splittings observed from the triplet states of the para and meta 1:1 complexes allowed us to calculate the average separation of the unpaired spins. The spins are found to have more than an angstrom greater separation in the 1:1 meta complex (5.25 Å) than in the para complex (3.64 Å). If one assumes that the spins are localized in the nitronyl nitroxide rings of the radicals and on the copper atom in the triplet state one cannot explain the difference in the spin separation by the relative geometry of the nitronyl nitroxide with respect to the copper atom. The spin in the radical can be delocalized into the aromatic ring via the resonance structures shown in Figure 4B. These structures place unpaired spin at the ortho and para carbon atoms but not at the meta carbon atom. The smaller electron-electron separation which is observed from the para complex may be due to a partial redistribution of the spin into the aromatic ring through resonance structures of this type.

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A Variable Temperature Carbon-13 Nuclear Magnetic Resonance Investigation of Intramolecular Rearrangement in $(CO)_4CoEX_3$ Complexes[1]

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Abstract: The temperature-dependent ^{13}C NMR spectra for 12 compounds of the form $(CO)_4CoEX_3$ (where E = C, Si, Ge, Sn, or Pb and X = F, Cl, CH_3, C_4H_9, $CH_2C_6H_5$, or C_6H_5) in $CFCl_2H$ solution have been recorded. At higher temperatures a single ^{13}C carbonyl resonance is observed for all molecules, indicating a time averaging of the axial and radial carbonyl signals due to an intramolecular exchange process. At lower temperatures the exchange process is observed to slow; coalescence temperatures range from less than −160 °C when $EX_3 = SnCl_3$ to −10 °C when $EX_3 = CF_3$. Complete line shape fitting of the spectra permits determination of the activation parameters for the exchange for most of the compounds studied. The results indicate that the free energy barriers to intramolecular rearrangement, which range from about 4.5 to 11.8 kcal/mol, are determined mainly by the steric requirements of the EX_3 group. The barrier increases with increasing steric requirement of the EX_3 group, as measured by the van der Waals contact angle with adjacent CO groups. Enthalpies of activation are in the range 6-7 kcal/mol for trihalogeno groups, 8.3-9.3 kcal/mol for $E(C_6H_5)_3$ groups, and 7-8 kcal/mol for trialkyltin groups. The experimental observations are discussed in the light of possible mechanisms for the intramolecular exchange.

Intramolecular rearrangements at five-coordinate centers have been of long-standing interest. Among the transition elements the most clearly defined five-coordinate species are organometallic compounds. Most commonly these compounds exist as singlet ground state molecules with an 18-electron configuration in the valence orbitals of the central metal atom. In such systems the configuration about the metal is an idealized trigonal bipyramid, of D_{3h} symmetry.

The barriers to rearrangements in such organometallic compounds are generally low. Iron pentacarbonyl has been extensively studied.[3-6] The free-energy barrier to intramolecular rearrangement is almost certainly less than 5 kcal mol^{-1}. Similarly, the intramolecular rearrangements in $Fe(PF_3)_5$, $Ru(PF_3)_5$, and $Os(PF_3)_5$ have been observed to be rapid on the NMR time scale at the lowest obtainable temperature, −160 °C.[7] Other compounds of the form ML_5, such as $M[P(OR)_3]_5{}^n$ with M = Fe, Co, or Ni and $n = 0, +1$, or $+2$, respectively,[8,9] have been studied. Free energies of activation for rearrangement in these systems are on the order of 10 kcal mol^{-1}, and there is little variation in $\Delta G^{\ddagger}$ with M. Steric interactions probably contribute importantly to the barrier to rearrangement, as evidenced by the fact that the barrier is higher for these compounds than for $Fe(CO)_5$ or $Fe(PF_3)_5$, and by the observation of a higher barrier for $Fe[(P(OCH_2CH_3)_3]_5$ than for $Fe[P(OCH_3)_3]_5$.

A group of compounds of the form $XML_4{}^n$, in which X = H, has been studied by Meakin, Jesson, and co-workers.[7,10] In the series in which M = Fe, Ru, Co, Ir, Os, or Rh, and L = PF_3,[7] the molecules are stereochemically nonrigid on the ^{31}P NMR time scale, but the intramolecular rearrangements can, in general, be observed to slow at low temperatures. Similarly, the intramolecular exchange in $HNi[P(C_2H_5)_3]_4{}^+$ has been stopped on the NMR time scale;[10] $\Delta G^{\ddagger}$ is estimated to be 4.6 kcal mol^{-1} at 126 K.

Compounds of the form $XM(CO)_4$ have not been systematically examined. Low-temperature ^{13}C NMR spectra of $C_5H_5NFe(CO)_4$,[11] $PF_3Fe(CO)_4$,[5] $R_3PFe(CO)_4$,[12,13] and (olefin)$Fe(CO)_4$[14,15] have been reported. Of these, stopped exchange has been observed only for the olefin complexes. The olefinic group occupies a radial position in the trigonal bipyramid and intramolecular rearrangement is impeded by the necessity for the olefin group to rotate during rearrangement. None of the other systems shows evidence of slow exchange in the NMR spectra at the lowest temperature studied. Finally, in $CF_3Co(CO)_3PF_3$ the exchange between cis and trans isomeric forms, as observed in the ^{19}F NMR spectra, is slow at −70 °C.[16,17]

We recently reported preliminary data on the intramolecular rearrangements in $X_3SnCO(CO)_4$ compounds.[18] We report here on a more extensive investigation of $X_3ECo(CO)_4$ compounds, in which E = Sn, Ge, Si, or C, and X = Cl, C_6H_5, alkyl, or F, using ^{13}C NMR spectra. With the exception of the $SnCl_3$ compound, intramolecular exchange between axial and radial CO groups has been observed in the slow exchange region at low temperatures.

Experimental Section

Compound Preparation. Dicobalt octacarbonyl was obtained from Pressure Chemical Co. Before use in preparing compounds, the $Co_2(CO)_8$ was enriched to approximately 15% in ^{13}CO. Samples (0.5-1.0 g) of $Co_2(CO)_8$ in hexane were stirred under an appropriate volume of 30% enriched ^{13}CO for periods of 4-8 h at ambient temperature.[19] All operations were performed under a nitrogen atmosphere or in absence of any other gas than CO. The $(CO)_4CoEX_3$ compounds were prepared following previously reported procedures ($EX_3 = CF_3$,[20] $SiCl_3$,[21] $GeCl_3$,[22] $SnCl_3$,[23] $GePh_3$,[22] $SnPh_3$,[22] $PbPh_3$,[22] $Sn(CH_3)_3$,[22], $Sn(n\text{-}C_4H_9)_3$,[24] and SiF_3[25]; Ph = C_6H_5). The compounds in which $EX_3 = SiPh_3$ and $Sn(CH_2Ph)_3$ were prepared according to the method of Patmore and Graham.[22] All compounds were identified and their purities checked using infrared spectroscopy. For several compounds elemental analyses were also obtained.

^{13}C NMR Procedures. NMR samples were prepared by dissolving 0.1-0.3 g of the compound (depending on the solubility at low tem-