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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-

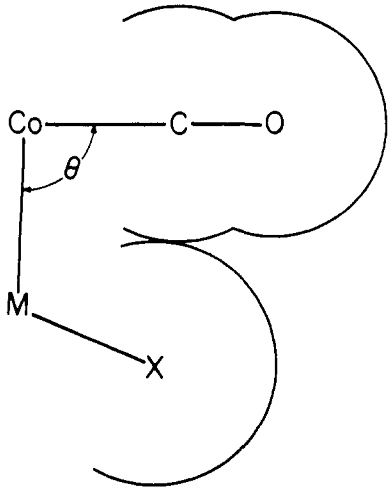


Figure 1. Illustration of van der Waals contact angle θ between CO and EX_3 groups.

perature) in 0.5 mL of CD_2Cl_2 and filtering into a 12-mm NMR tube. The CD_2Cl_2 served as an internal deuterium lock source. The solutions were degassed and approximately 2.5 mL of $CFCl_2H$ (Freon 21) vacuum transferred to the tube. The tubes were then sealed under vacuum. Most of the samples survived for several weeks when stored at −78 °C in the dark; all samples were stable for reasonable periods of time in room light at room temperature.

^{13}C NMR spectra were recorded on a Varian XL-100/Digilab FT NMR spectrometer, operating at 25.2 MHz. Proton decoupling was not employed. The upfield resonance of $CFCl_2H$ was used as a secondary standard; the conversion to Me_4Si was taken as 94.2 ppm. All downfield shifts are defined as positive. In general, about 2 h of data collection was required at each temperature. In some instances, as much as 12 h collection time was used.

Temperature Measurement. Temperature measurements were calibrated to as low as −127 °C. Temperatures were measured with a copper-constantan thermocouple placed in a 12-mm tube filled with a volume of solvent equal to that contained in the sample tubes, and with the thermocouple positioned at the level of the instrument coils. A thermal gradient of approximately 4 °C existed from the surface of the solvent to the bottom of the tube. At the position of the instrument coils the temperature was found to be an average of the extreme values. The sample temperature was controlled using a Varian variable temperature controller. The temperature was recorded before and after each data collection. No changes in temperature were detected over periods as long as 12 h. A reasonable bound to the uncertainty in the temperature determination is ±1 °C.

Data Analysis. The ^{13}C NMR spectra were simulated with a two-site exchange program developed in these laboratories. For a general two-site exchange problem, with the assumption that the baseline is linear, possible variables for a theoretical fit include p_{axial}, the fractional population of the downfield site of exchange; T_2(axial) and T_2(radial), the transverse relaxation times of the two sites of exchange; ν_{axial} and ν_{radial}, the chemical shifts of the two sites; and τ_{av}, the average time between exchanges for the two sites ($\tau_{av} = \tau_{ax}\tau_{rad}/(\tau_{ax} + \tau_{rad})$).

The two-site computer simulation program was designed for interactive use. All parameters associated with the exchange process could be optimized either with the aid of a graphics terminal display of the theoretical line shape overlaid on the data, or by nonlinear regression procedures which minimize the sum of squares of deviations between calculated and observed lines. Up to nine Lorentzian-shape peaks may be added to help simulate any additional, nonexchanging absorptions in the data region. For the spectra examined in this study, p_{axial} was set to 0.25. The chemical shifts, ν_A and ν_B, were determined from low-temperature spectra representing stopped exchange. There was no evidence in any of the spectra that the weighted average of these two shifts varied with temperature. The transverse relaxation times, T_2, were very similar for the axial and equatorial ^{13}C signals at low temperature, and were constrained to be equal. The precise values of T_2(axial) and T_2(radial) are difficult to determine in the exchange region because the ^{13}C NMR absorptions are broadened through interaction with the quadrupolar cobalt nucleus.[18] When possible, values of T_2(axial) and T_2(radial) in the exchange region were estimated by interpolating from the values observed in the fast and slow exchange limits.

Table I. Bond Distances (Å) in $(CO)_4CoEX_3$ Trigonal Bipyramid Structures

	EX_3			
	SiF_3[26]	$SiCl_3$[27]	SiH_3[29]	GeH_3[28]
Co-E	2.23	2.25	2.38	2.42
$Co-C_{axial}$	1.80	1.80	1.80	1.80
$Co-C_{radial}$	1.78	1.77	1.80	1.80
$C-O_{axial}$	1.13	1.14	1.14	1.13
$C-O_{radial}$	1.12	1.15	1.14	1.13
Bond angle				
$E-Co-C_{radial}$	85.4°	85.2°	81.7°	83.8°

This leaves only the exchange parameter τ_{av} as a variable parameter in the simulation of the exchange spectra. Generally, spectra were collected at 3-5 °C intervals through the exchange region, thus providing 5-12 values for τ_{av} as a function of temperature. Values for the activation parameters associated with the process were determined using the Arrhenius equation.

Steric Effects. The estimation of steric requirements for the EX_3 groups consisted in determining the angle between the Co-E and Co-CO vectors at which van der Waals contact occurs between the CO group and the EX_3 group, as illustrated in Figure 1. This angle was determined with the aid of a simple computer program. The calculations employed the bond distances from the structures of $Co(CO)_4SiF_3$,[26] $Co(CO)_4SiCl_3$,[27] $Co(CO)_4GeH_3$,[28] and $Co(CO)_4SiH_3$[29] (listed in Table I) as well as published values for covalent radii[30] (C = 0.77, Si = 1.18, Ge = 1.22, Sn = 1.40, Co = 1.26 Å), van der Waals radii[30-33] (C = 1.65-1.70, F = 1.50-1.60, Cl = 1.70-1.90, O = 1.50, H = 1.30-1.45 Å) and other experimental structures. From the structural data, the Co-CO and CoC-O distances were fixed at 1.80 and 1.15 Å, respectively. The $Co-SiX_3$ distance (X = halogen) was chosen as 2.25 Å on the basis of crystal structure information. The selected $Co-GeX_3$ and $Co-SnX_3$ distances of 2.29 and 2.47 Å, respectively, follow from the trends in covalent radii of group 4A atoms. This same change in Co-Si and Co-Ge bond distances is observed in the crystal structures of the SiH_3 and GeH_3 complexes. Also, because of the change in bond length between the halide and hydride structures, the $Co-Sn(CH_3)_3$ distance was chosen as 2.60 Å. The $Co-CF_3$ distance was set at 2.02 Å, a value close to the sum of covalent radii. The following distances were also chosen on the basis of structural data for these or similar compounds: Si-F = 1.52, Si-Cl = 2.00, C-F = 1.35, Ge-Cl = 2.10, Sn-Cl = 2.31, Sn-C = 2.18, C-H = 1.09 Å. When X is a multiatom group such as CH_3, which has relatively high symmetry, it is possible to estimate the contact angle assuming that the X group freely rotates. However, when X is phenyl it is difficult to make a meaningful estimate of the contact angle, since the van der Waals radius of the phenyl group might vary considerably, depending on the aspect which is presented to the CO group making contact. For this reason we have not attempted to make estimates of the contact angle for the EPh_3 groups. Proceeding as described, the estimated van der Waals contact angles θ (using the full range of reasonable van der Waals radii) are CF_3, 111-117°; SiF_3, 102-107°; $SiCl_3$, 104-112°; $GeCl_3$, 101-109°; $SnCl_3$, 93-101°; $Sn(CH_3)_3$, 100-106°. With the assumption of linear carbonyl groups, contact always occurred first with the carbonyl carbon rather than the oxygen. Other choices for internuclear distances and radii might be employed without seriously changing the results. For instance, essentially the same trend in contact angles is obtained if accepted values of covalent radii are used throughout for estimating internuclear distances. However, the present model seems most reasonable in terms of the structural data presently available.

Results

The temperature dependence of the ^{13}C NMR spectra in the carbonyl region for $(CO)_4CoSn(CH_2Ph)_3$ is displayed in Figure 2. This figure illustrates several features common to the ^{13}C NMR spectra of the $(CO)_4CoEX_3$ species. At low temperatures a pair of lines with an intensity ratio of 1:3, assigned

Table II. ^{13}C Chemical Shifts (ppm) of Carbonyl Carbons in (CO)$_4$CoEX$_3$ Compounds

	Av chemical shift[a,b]	Axial chemical shift[b]	Radial CO chemical shift[b]	Δ(axial − radial), ppm
EX$_3$				
CF$_3$	193.6	199.2	191.7	7.5
SiF$_3$	193.4	199.6	191.4	8.2
SiCl$_3$	193.8	199.3	192.0	7.3
GeCl$_3$	191.6	197.4	189.7	7.7
SnCl$_3$	191.1			
Si(C$_6$H$_5$)$_3$	199.1	203.6	197.6	6.0
Ge(C$_6$H$_5$)$_3$	199.3	204.3	197.7	6.6
Sn(C$_6$H$_5$)$_3$	199.0	204.9	197.1	7.8
Pb(C$_6$H$_5$)$_3$	199.8	206.4	197.6	8.8
Sn(CH$_2$C$_6$H$_5$)$_3$	198.8	205.3	196.6	8.7
Sn(*n*-C$_4$H$_9$)$_3$	200.6	206.2	198.8	7.4
Sn(CH$_3$)$_3$	200.4	205.8	198.6	7.2

[a] Fast exchange value. [b] All shifts are ±0.1 ppm downfield from Me$_4$Si with CCl$_2$FH as secondary standard (−94.2 ppm).

Table III. ^{13}CO Coupling Constants to ^{13}C of CO Groups in (CO)$_4$CoEX$_3$

EX$_3$[a]	^2J(E-C) (axial)	^2J(E-C) (radial)	^2J(E-C) (fast exchange)
Sn(C$_6$H$_5$)$_3$-(^{117,119}Sn)	95	100	105
Sn(CH$_2$C$_6$H$_5$)$_3$		99	105
Sn(CH$_3$)$_3$	68	72	
Sn(*n*-C$_4$H$_9$)$_3$		84	
SnCl$_3$			94
Pb(C$_6$H$_5$)$_3$-(^{207}Pb)		148	150
SiCl$_3$(^{29}Si)	106	106	
	^3J(F-C) (axial)	^3J(F-C) (radial)	
CF$_3$	14.4	10.4	

[a] Separate ^{117}Sn and ^{119}Sn coupling was not observed.

to the axial and three radial carbonyls, respectively, is observed. The axial carbonyl resonance invariably occurs 6-9 ppm downfield from that for the radial carbonyl. As temperature increases, the lines first collapse, and then a single line, positioned at the weighted average of the axial and radial carbonyl resonances, emerges. At still higher temperatures the line is broadened through scalar coupling with the cobalt nucleus;[34] at room temperature the ^{13}C signal is very difficult to observe. However, at temperatures lower than −70 °C scalar coupling does not pose a problem. The effect of lower temperature on the relaxation behavior of ^{59}Co and ^{13}C has been noted previously.[18,35] It was not possible to observe separate resonances for the axial and radial carbonyls of Cl$_3$SnCo(CO)$_4$. However, at the lowest temperatures reached, −160 °C, the ^{13}C signal exhibits a much broadened line, which suggests that the system is near the coalescence temperature. Table II lists the ^{13}C chemical shifts observed for all compounds studied.

Several of the EX$_3$ ligands contain nuclei which may undergo scalar coupling with ^{13}C. These scalar interactions were not always observed in the ^{13}C NMR spectra because of the large line widths of the signals, and the presence of intramolecular exchange. The coupling constants which were observed are listed in Table III. In some instances scalar coupling was also observed at higher temperature, in the fast exchange region. The existence of scalar coupling in the fast exchange region verifies that the exchange is indeed intramolecular. However, there is little doubt of this in any case since several of the compounds are known to undergo substitution at room temperature at a rate that is slow on the NMR time scale.[36]

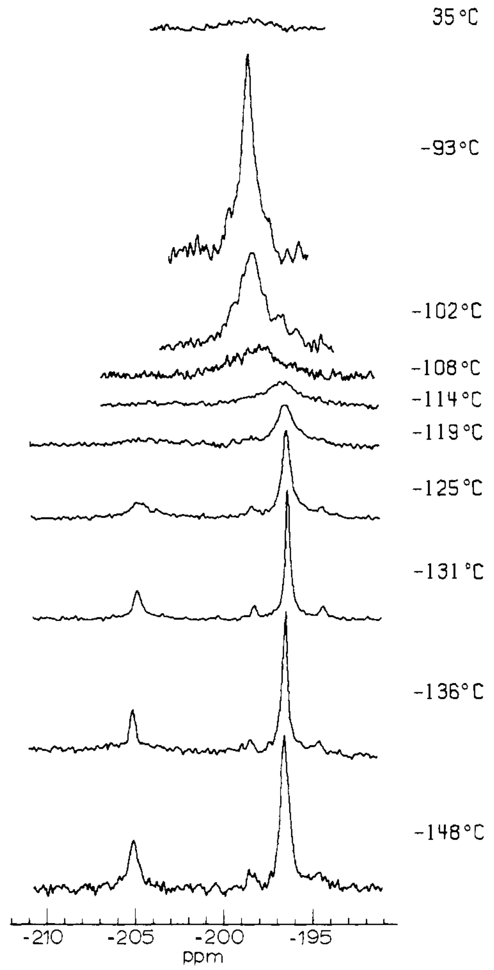


Figure 2. ^{13}C NMR spectra of (CO)$_4$CoSn(CH$_2$C$_6$H$_5$)$_3$ in the carbonyl region at various temperatures.

The coupling of the ^{13}C carbonyls to the ^{19}F of CF$_3$ is displayed in Figure 3. The axial and radial CO resonances both form quartets through equivalent coupling to the three ^{19}F atoms. The axial CO resonance of (CO)$_4$CoSiF$_3$ is broadened relative to the radial CO signal, presumably also through coupling to ^{19}F, but separate peaks of the quartet were not discernible.

Computer Simulations. The simulated temperature dependence of the ^{13}CO NMR of (CO)$_4$CoSn(CH$_2$PH)$_3$ is shown superimposed on the observed spectra in Figure 4. At temperatures below coalescence the determination of τ_{av} was greatly aided by the sensitivity of the relative intensity of the two resonances to this value. In the fast exchange region the line width of the single resonance is dependent on τ_{av}, T_2(axial), and T_2(radial). Because of the coupling to the quadrupolar cobalt nucleus and the variation in field homogeneity at very low temperatures, less weight must be attached to fittings that are dependent only on line width. A typical Arrhenius plot obtained from the line shape fits over a range of temperatures is shown in Figure 5. Coalescence temperatures and activation parameters for all compounds for which data were obtainable are listed in Table IV.

Certain of the complexes provided special problems for analysis. Separate axial and radial ^{13}CO resonances could not be obtained for (CO)$_4$CoSnCl$_3$, and a line shape simulation was not attempted. The ^{13}C resonances of (CO)$_4$CoCF$_3$ are

Table IV. Coalescence Temperatures and Activation Parameters for Axial-Radial Exchange in $(CO)_4CoEX_3$

EX_3	Coalescence temp, °C[a]	$\Delta G^{\ddagger}$,[b] kcal/mol	$\Delta H^{\ddagger}$,[b,c] kcal/mol	$\Delta S^{\ddagger}$,[b,c] cal/mol K	$\Delta G^{\ddagger}$[d] est
CF_3	−10 (6)				11.8
SiF_3	−114 (2)	6.9	6.0 (0.4)	−5.9 (2.6)	6.9
$SiCl_3$	−85 (3)	8.3	6.9 (0.5)	−7.3 (2.8)	8.3
$GeCl_3$	−133 (3)	6.1	6.9 (0.5)	6.1 (3.3)	6.1
$SnCl_3$	<−160				<5
$Si(C_6H_5)_3$	−61 (4)	9.5	9.0 (0.8)	−2.5 (4.0)	9.5
$Ge(C_6H_5)_3$	−75 (3)	8.8	9.0 (0.7)	0.9 (3.6)	8.8
$Sn(C_6H_5)_3$	−109 (1)	7.2	8.3 (0.2)	6.5 (1.1)	7.2
$Pb(C_6H_5)_3$	−121 (2)	6.6	9.3 (0.8)	17.9 (5.3)	6.6
$Sn(CH_2C_6H_5)_3$	−111 (1)	7.0	8.0 (0.5)	5.8 (3.4)	7.1
$Sn(n\text{-}C_4H_9)_3$	−112 (1)	7.1	8.1 (1.3)	6.4 (8.5)	7.1
$Sn(CH_3)_3$	−118 (2)	6.8	7.0 (0.6)	1.1 (4.1)	6.8

[a] Estimated maximum uncertainty in parentheses. [b] Based on Arrhenius plots. [c] Uncertainties at 90% confidence limit in parentheses. [d] Estimated from eq 1.

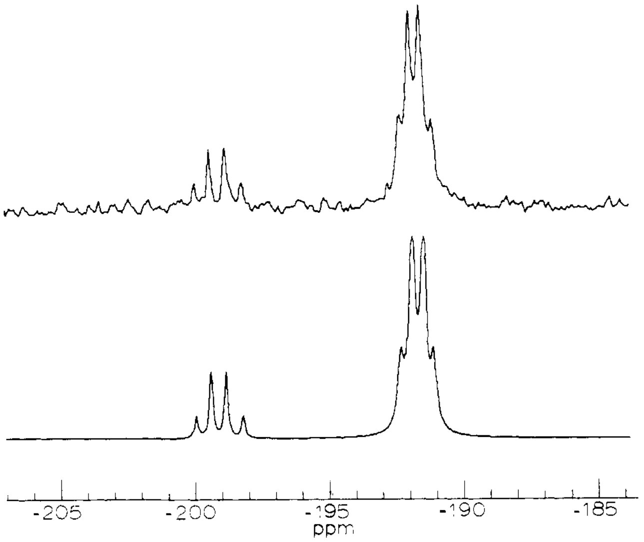


Figure 3. ^{13}C NMR spectrum of $(CO)_4CoCF_3$ in the carbonyl region, at −110 °C. Chemical shifts are measured downfield from Me_4Si. The lower spectrum is computer simulated, using the chemical shift and coupling constant parameters of Tables II and III.

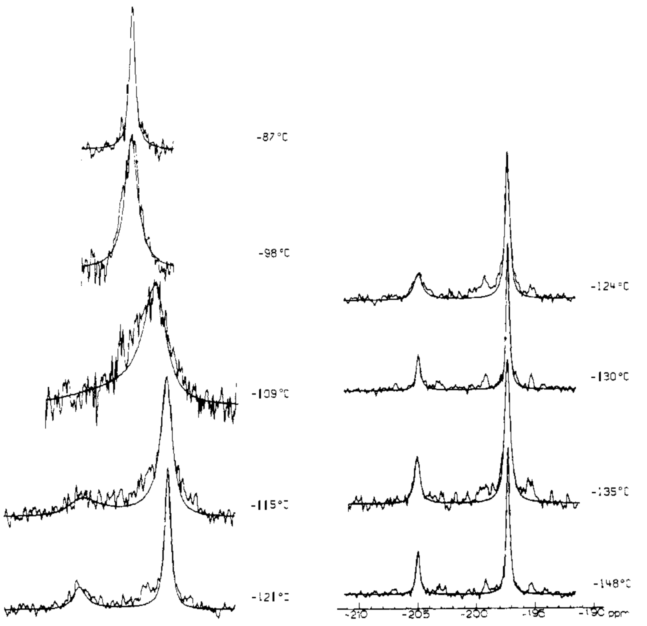


Figure 4. Computer simulation of the ^{13}C NMR spectra of $(CO)_4$-$CoSn(CH_2C_6H_5)_3$ at various temperatures. The theoretical line shape is overlaid on the experimental data.

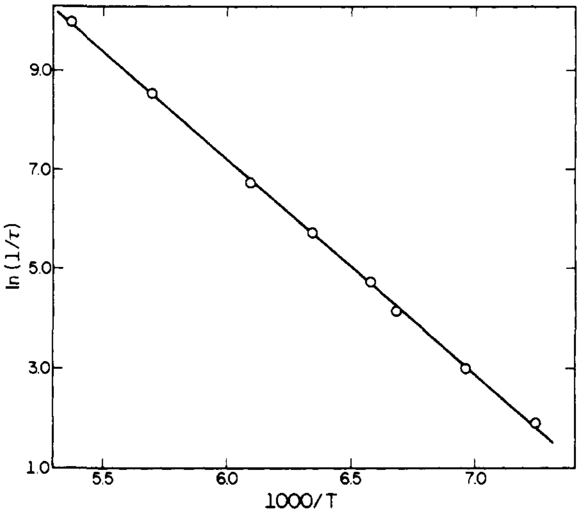


Figure 5. Ln $(1/\tau_{av})$ vs. $1/T$ for $(CO)_4CoSn(CH_2C_6H_5)_3$.

split into quartets, and are significantly broadened at the relatively high temperature at which coalescence occurs. The spectra obtained in this temperature region were not of adequate quality to warrant simulation. The coalescence temperature, T_c, was estimated from the spectra and $\Delta G^{\ddagger}$ at coalescence temperature was estimated from the chemical shift separation:

$$k = \pi\sqrt{2}\Delta\delta = \frac{kT_c}{h}\exp(-\Delta G^{\ddagger}_{est}/RT_c)$$

$$\Delta G^{\ddagger}_{est} = -RT_c\left[\ln\left(\frac{\Delta\delta(\text{Hz})}{T_c}\right) - 22.27\right] \qquad (1)$$

where T_c is the coalescence temperature and $\Delta\delta$ is the chemical shift separation of the axial and radial carbonyls.

Discussion

^{13}CO Chemical Shifts. Correlation of ^{13}CO chemical shifts with other physical properties, such as carbonyl stretching frequencies,[38-40] is occasionally possible. Selected spectroscopic data for $(CO)_4CoEX_3$ complexes are presented in Table V. The CO stretching parameters calculated from the IR data fall essentially into two sets, as do the CO chemical shifts. In one set the X group in EX_3 is halogen; in the other it is aryl or alkyl. The range of either variable within each set is rather small, and no correlations in the variations are especially evident.

In $(CO)_4CoEX_3$ compounds the axial ^{13}CO resonance invariably occurs downfield from the radial ^{13}CO resonance. This is in contrast to the results obtained from six-coordinate

Table V. Selected Physical Data for $(CO)_4CoEX_3$ Complexes

EX_3	$A_1,^2$ cm^{-1}	$A_1,^1$ cm^{-1}	E, cm^{-1}	Ref	F_{radial}[a]	F_{axial}[a]	^{59}Co e^2Qq/h, MHz	Ref
CF_3	2129	2063	2051	This work	17.43	17.19		
SiF_3	2128	2073	2049	41	17.40	17.35		
$SiCl_3$	2125	2071	2049	41	17.32	17.38	131	42
$GeCl_3$	2122	2069	2050	22	17.37	17.29	162	42
$SnCl_3$	2120	2068	2048	22	17.34	17.27	163	42
$Si(C_6H_5)_3$	2093	2032	2004	This work	16.71	16.67	101	42
$Ge(C_6H_5)_3$	2091	2030	2006	22	16.72	16.64	110	43
$Sn(C_6H_5)_3$	2087	2027	1999	22	16.62	16.59	104	42
$Pb(C_6H_5)_3$	2081	2022	1997	22	16.56	16.51	111	42
$Sn(CH_2C_6H_5)_3$	2080	2022	1983	This work	16.41	16.51	100	18
$Sn(n\text{-}C_4H_9)_3$	2072	2015	1984	This work	16.37	16.40		
$Sn(CH_3)_3$	2082	2020	1988	22	16.47	16.48	97	44

[a] Force constants, calculated as described in ref 41, are in mdyn Å^{-1}.

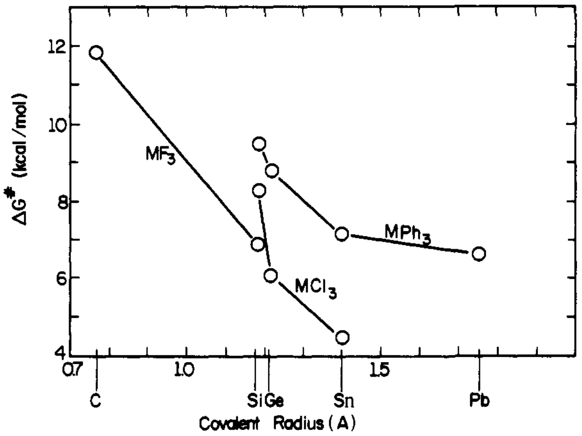


Figure 6. Free energy barrier to intramolecular exchange vs. covalent radius of E in $(CO)_4CoEX_3$ compounds.

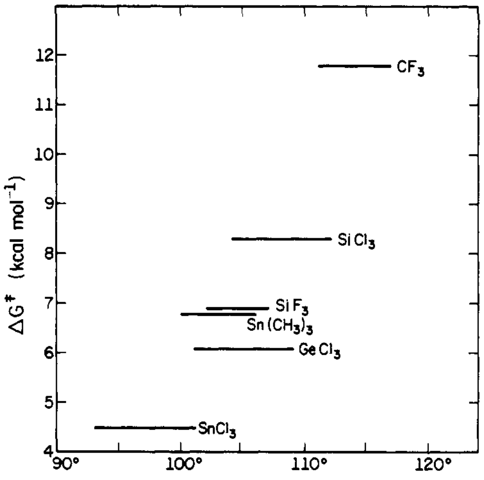


Figure 7. Variations in $\Delta G^{\ddagger}$ for intramolecular exchange with calculated van der Waals contact angle θ in $(CO)_4CoEX_3$ compounds.

metal carbonyls of the form $(CO)_5MEX_3$, in which the trans carbonyl signal is generally upfield from that for the cis.[37]

For a given X group, the axial-radial shift difference in $(CO)_4CoEX_3$ increases in the order E = C < Si < Ge < Sn < Pb. This trend in chemical shift separations strongly suggests that the shift separation in the $SnCl_3$ compound is substantial. Hence, our inability to observe separate signals for this compound at low temperatures is the result of especially facile exchange, and not due to an accidental degeneracy of the axial and radial ^{13}CO resonances.

Electronic and Steric Effects of EX_3 Group on Exchange Kinetics. The results of the NMR exchange studies, embodied in the data listed in Table IV, provide interesting insights into the nature of the intramolecular process. Consider first the variations in $\Delta G^{\ddagger}$. The EX_3 groups studied represent a range in $\Delta G^{\ddagger}$ from less than 5 kcal mol^{-1} to nearly 12 kcal mol^{-1}. Comparison of the values for $\Delta G^{\ddagger}$ with spectroscopic parameters such as those listed in Table V does not reveal meaningful correlations. For example, the variation in spectroscopic properties in the series of triphenyl derivatives is relatively slight, whereas there is a substantial variation in $\Delta G^{\ddagger}$. Thus, there appears to be no correlation between relative free energy barriers to intramolecular rearrangement and variations in ground state electronic properties of the $(CO)_4CoEX_3$ compounds.

Comparison of the $\Delta G^{\ddagger}$ values with the relative steric requirements of the EX_3 groups does reveal interesting correlations. Figure 6 shows a graph of the $\Delta G^{\ddagger}$ values for all groups studied as a function of the covalent radius of E in EX_3, in which the points for related compounds are connected by lines. This figure shows that, for a given type of X group, the barrier to rearrangement increases with decreasing covalent radius of the central atom, E. This in turn suggests that the barrier increases with increasing steric requirement of the EX_3 group as a whole. The steric requirements of some of the EX_3 groups can be expressed in terms of the van der Waals contact angles, θ, calculated as described in the Experimental Section. A larger value for θ connotes a larger steric requirement. (Although we might have chosen instead to calculate the cone angles of the EX_3 groups as described by Tolman,[45-47] contact angles seem a preferable measure of steric requirement in the particular environment of interest here. However, the trends we observe using the contact angles would doubtless parallel those obtained using cone angles.)

Figure 7 shows the variation in $\Delta G^{\ddagger}$ vs. the calculated values of θ for all the EX_3 groups in which X = halogen. In addition, the datum for $Sn(CH_3)_3$ is shown. It is quite clear from this figure that $\Delta G^{\ddagger}$ increases markedly with increasing contact angle θ. Although the contact angles cannot be readily estimated for the EPh_3 groups, the trend in $\Delta G^{\ddagger}$ values within this series roughly parallels that for the halogen derivatives.

The extent to which electronic factors, such as the relative electron-releasing or electron-withdrawing characteristics of EX_3, or the extent to which EX_3 is capable of acting as a π acceptor ligand, influence the barrier to rearrangement is also of interest. At first glance it might seem that the more electron-withdrawing groups possess lower barriers *because* they are electron withdrawing. Thus, the low barrier for $SnCl_3$

might be ascribed to its ability to act as a π acid, and thus to its similarity to CO.[18] There is, however, no real basis in the data for such a conclusion. While the precise steric requirement of the phenyl groups is difficult to estimate, there is no doubt that they are large, bulky groups, for which the contact angle θ would be large.[48] Thus, the relatively high values of $\Delta G^{\ddagger}$ for the EPh_3 series can be ascribed to steric factors. It is noteworthy that $\Delta G^{\ddagger}$ values for $Sn(CH_3)_3$ and the other two trialkyltin groups are in line with those of the trihalogeno groups on the basis of steric effects alone, as illustrated in Figure 7. We conclude that variations in steric requirement are the *major* factor in determining the relative free energies of activation for the intramolecular rearrangement. From this it follows that *the transition state in the rearrangement involves a more crowded environment about EX_3 than the ground state.*

We may now ask how the steric contribution to $\Delta G^{\ddagger}$ for rearrangement is manifested in the enthalpies and entropies of activation. Unfortunately, the existence of scalar coupling between ^{13}C and ^{59}Co, which leads to scalar relaxation,[34] complicates the interpretation of the activation parameter data. Although all the cases for which $\Delta H^{\ddagger}$ values are listed in Table IV gave good Arrhenius graphs, the possibility exists that line shapes in the fast exchange region are affected by the scalar relaxation. In general, the line broadening effects should be most severe in those cases in which the coalescence temperature is relatively high, and in which e^2Qq/h for cobalt is relatively low. This means that in the series of EPh_3 compounds, the line broadening in the region above coalescence should be most severe for $SiPh_3$, and least important for $PbPh_3$. The effect of line broadening in the region above coalescence would be to yield a smaller apparent value for $\Delta H^{\ddagger}$. Correspondingly, $\Delta S^{\ddagger}$ would be more negative than the correct value.

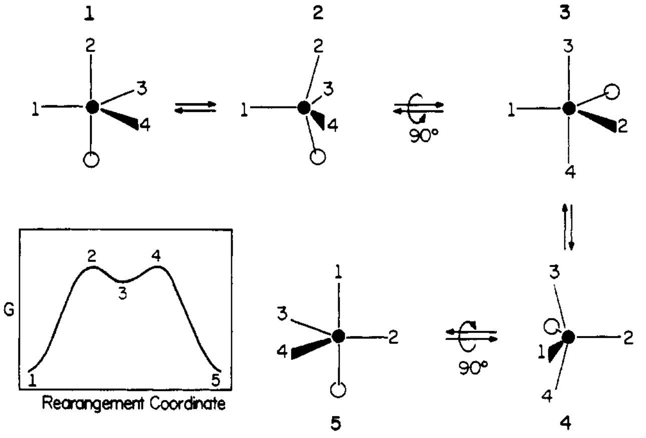
There is unfortunately no simple way to correct for the ^{13}C line broadening due to scalar relaxation, because the ^{13}C–^{59}Co coupling constants are not known, nor is T_1 for ^{59}Co. However, even crude estimates of these quantities suggest that in many of the compounds studied the line broadening effects cannot be very large. It thus appears at least likely that the variations in $\Delta H^{\ddagger}$ are not far different from those shown in Table IV. This suggests that a large part of the variation in $\Delta G^{\ddagger}$ in each series of related molecules is due to variations in $\Delta S^{\ddagger}$. If the steric repulsions that develop in the approach to the transition state could be relieved by particular orientations of the EX_3 groups,[50] then the increasing steric requirements of the EX_3 groups would be reflected in more negative values of $\Delta S^{\ddagger}$, as observed.

It is reasonable to expect that in the absence of special steric effects, $\Delta S^{\ddagger}$ values for the exchange should be near zero. With the exception of the $Pb(C_6H_5)_3$ derivative, this is found to be the case. The origin of the rather large value of $\Delta S^{\ddagger}$ for the lead compound is not clear. However, it should be kept in mind that the uncertainty in this quantity is rather large.

Although there does not appear to be much variation in $\Delta H^{\ddagger}$ within a given series of related EX_3 groups, this quantity does seem to vary significantly from one set to another. The $\Delta H^{\ddagger}$ values for the trihalogeno set appear to be lower than for the trialkyltin set, and these in turn are slightly lower than for the triaryl compounds. This trend, particularly the lower values for the trihalogeno compounds, may be a reflection of an electronic contribution to the barrier for rearrangement; the enthalpy of activation is lower for the more electron-withdrawing EX_3 groups. However, the entire range of $\Delta H^{\ddagger}$ values is at most about 3 kcal/mol.

Mechanism of Intramolecular Rearrangement. Permutational analysis reveals that the NMR experiment as carried out in this work is not capable of distinguishing between several different pathways for the intramolecular exchange.[51,52] In this work we have approached the question of exchange mechanism from a more classical or phenomenological perspective. By discovering the manner in which alterations in electronic and steric properties of the EX_3 group affect the exchange kinetics we might hope to deduce some features of the pathway by which exchange occurs. The experimental results show that free-energy barriers to rearrangement increase with increasing steric requirement of the EX_3 group, and that the electron-releasing or -withdrawing properties of the EX_3 group have only a small effect on enthalpies of activation. It remains to test plausible alternative pathways for exchange in terms of these observations.

Scheme I

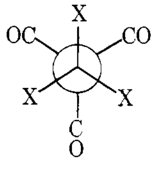


We consider three idealized reaction pathways for intramolecular exchange: (a) a Berry pseudorotation (BPR),[53] (b) a turnstile rotation (TR),[54] (c) an umbrella process (U). Defining the nature of the reaction processes in terms of such idealized pathways is limited by the lower symmetry of the L_4MY system as compared with L_5M. The EX_3 group may impose distortions in intermediates of relatively low symmetry. Nevertheless, by proceeding as though the geometries were those expected for an L_5M system, some insights into the differences in reaction pathways may be gained.

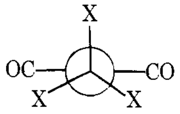
Intramolecular exchange of axial and radial CO groups via the BPR, Scheme I, requires formation of an intermediate or transition state, **3**, in which EX_3 occupies a radial position. In the limiting case in which the heteroligand Y in L_4MY is L, the transition state for intramolecular exchange is the square-based pyramidal structure **2**. When Y differs from L, the energy of **3** relative to the ground state structure depends on the degree of site preference of Y for the axial as opposed to the radial position of the trigonal bipyramid (tbp). When the site preference becomes large, **3** can become the transition state in the overall process of two successive BPRs that leads to axial–radial exchange of the L_4 set.

There is both experimental and theoretical basis for the idea that relatively good π acceptor or weak σ donor ligands are relatively more stable in the radial positions of the tbp.[55] The BPR mechanism predicts that there should be variation in $\Delta H^{\ddagger}$ for intramolecular exchange among the $(CO)_4MEX_3$ compounds, depending on the relative propensities of the EX_3 groups for siting in the radial position. Thus, for example, $\Delta H^{\ddagger}$ should be smaller when X is halogen than when X is alkyl or aryl. This is supported by the data in Table IV, although the range in $\Delta H^{\ddagger}$ values is small.

The steric requirements for the tbp structures with EX_3 in the axial and radial positions are also different. When EX_3 is axial it encounters three CO groups at nominal 90° angles, whereas when EX_3 is radial it encounters only two CO groups at nominal 90° angles. However, because of the different symmetries of these species, the steric requirements are not simply related to the number of carbonyl groups making contact. For instance, van der Waals contact of an axial SiF_3 group that is in a staggered conformation with respect to the three radial carbonyls occurs at a minimum angle of 88°. The minimum contact angle of a radial SiF_3 group with two collinear carbonyls is 98°. These conformations correspond to the Newman-type projections a and b, respectively. Thus the steric requirement of EX_3 in the radial site is greater than for EX_3 in the axial site. This effect is enhanced by the tendency of the E-Co-CO angles to be less than 90°, as indicated in Table I. In ML_5 compounds an increased barrier to intramolecular exchange, presumed to proceed via BPR, has been associated with increased steric requirement of L.[9,56] The BPR process suggests an important role for the steric properties of EX_3 in the exchange process in the compounds of interest here. Our conclusions here are in generally good agreement with the results of recent LCAO-MO-SCF ab initio calculations of the barrier to intramolecular rearrangement in $CH_3Co(CO)_4$.[57]

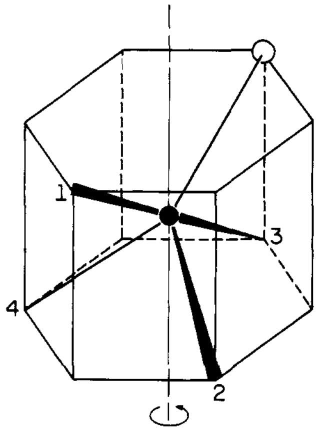


a



b

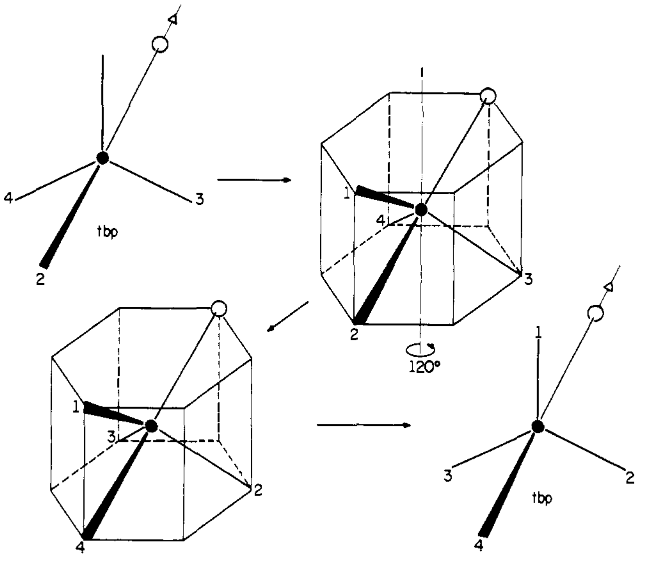
The TR process, outlined in approximate form in Scheme II, is rather more complex to visualize than the BPR. We have shown a particular TR pathway, not the only one that might be visualized.[54] The TR process also appears to account for the observed dependence of the barrier on steric properties of EX_3. The rotational motion of the pair set with respect to the trio set involves along the way an eclipsed configuration, **6**, which may be taken to represent the transition state for the exchange. This configuration is similar to the tbp configuration with EX_3 radial that occurs in the BPR process. In fact it has previously been indicated[58] that the TR pathway may be viewed as a form of the BPR pathway for ML_5 species, in which vibrational excitation is present. An increased steric requirement of the EX_3 group should lead to increased free-energy barrier. A rotational motion of EX_3 would be required to carry it past the eclipsing CO group in the rotation, shown in Scheme II, thus accounting for the more negative values of $\Delta S^{\ddagger}$ for larger EX_3 groups.



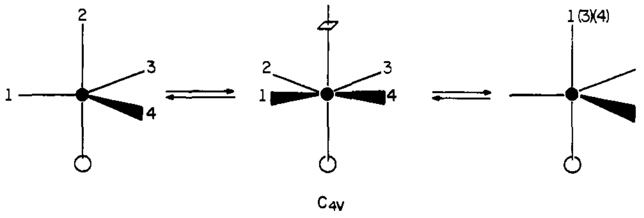
6

It is a characteristic of the TR pathway that it is not necessary to formulate a tbp intermediate in which the Y group of L_4MY occupies an unfavorable siting, as is the case in the BPR process. However, it is difficult to see how much can be made of this point, since the formation of such an intermediate or transition state is merely replaced in the TR process by formation of a structure such as **6**. The rules by which the energy of **6** depends on the electronic characteristics of the Y group are not known; they could be just as disadvantageous for certain types of Y groups as radial siting in a tbp structure. An additional uncertainty in the formulation of the TR process for L_4MY compounds is whether to locate the Y group in the pair or trio set.

Scheme II



Scheme III



The U process, shown in Scheme III, involves a pairwise twisting of the four CO groups in $(CO)_4MEX_3$ to form an intermediate of idealized C_{4v} symmetry. Depending on the nature of EX_3 the C_{4v} species could be the transition state in the exchange process. In the U process, the EX_3 groups must assume an axial position in a square-based pyramidal (sq-bp) structure. The energy of such a structure relative to the ground state structure can be expected to vary with the electronic characteristics of EX_3. The relative preferences for siting in sq-bp structures are uncertain; a tentative view is that relatively poor π acceptor and/or weaker σ donor ligands are preferably in a basal position in the sq-bp structure.[55,59] Thus, we might expect that the least stable sq-bp structures with axial ligands would be the EPh_3 or perhaps the SnR_3 groups.

The U process does not appear to lead to a substantial steric role for the EX_3 group. The sq-bp intermediate has a *lower* steric requirement for the apical ligand than the tbp ground state. To the extent that the sp-bp structure resembles the transition state, the steric characteristics of EX_3 in the U process would seem to be small. We conclude that the U process is not in very good accord with the observed systematics of the exchange process.

On the basis of only two available comparisons,[12,13] it appears that intramolecular exchange is slower in $(CO)_4CoEX_3$ compounds than in the isoelectronic $(CO)_4FeMX_3$. No evidence of slowed exchange is seen in the ^{13}C NMR spectrum of $(CO)_4FePPh_3$ at −110 °C,[12] whereas the coalescence temperature for $(CO)_4CoSiPh_3$ occurs at about −60 °C. It has been observed that in d^8 complexes in general, the barriers to intramolecular rearrangement are higher in Co than in the analogous Fe compounds.[9b] Analysis of this characteristic difference in terms of the mechanism for rearrangement reveals that both steric and electronic factors are contributing. The PPh_3 ligand should be a comparatively stronger π acceptor toward Fe than the $SiPh_3$ group is toward Co. Thus, the lower barrier in the Fe compound might be ascribed to the fact that siting of PPh_3 in the radial position of a tbp is less unfavorable than for $SiPh_3$. In addition, the P–Fe–Co_{radial} bond angles in $(CO)_4FePPh_3$ are greater than 90°,[60] whereas in all the cobalt compounds studied,[26-29] this angle is *less* than 90°. Thus the steric factors are less important for the iron complexes. The equilibrium geometries are apparently affected by variations in relative σ and π bonding characteristics of ligands and the effective charge on the metal. Minimum energy geometries along the reaction coordinate could be similarly affected by bonding variations.

In summary, we have shown that the barrier to intramolecular axial-radial exchange of CO groups in $(CO)_4CoEX_3$ compounds is sharply dependent on the nature of the EX_3 group. The free-energy barrier to the exchange increases with increasing steric requirement of the EX_3 group. Most of this increase appears to arise in an increasingly negative $\Delta S^{\ddagger}$. For EX_3 groups with substantially differing electron-releasing abilities $\Delta H^{\ddagger}$ is 2–3 kcal/mol lower for the trihalogeno ligands than for EPh_3 or SnR_3 ligands.

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References and Notes

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