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Nuclear Magnetic Resonance Study of Structural Dynamics in μ-Carbonyl-bis-μ-stannylene-diiron Hexacarbonyl Clusters

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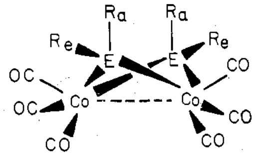
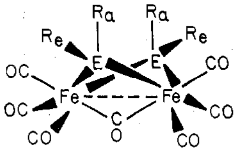
The compound $[\mu\text{-}(C_6H_5)(CH_3)Sn]_2Fe_2(CO)_7$ was synthesized to differentiate bridge deformation from iron–tin bond cleavage in R group interchange processes of stereochemically nonrigid $[\mu\text{-}R_2Sn]_2Fe_2(CO)_7$ complexes. It is found from proton NMR studies that both processes can occur, the former with $\Delta G^\ddagger = 11.8 \pm 0.6$ kcal/mol (298 K) and the latter with $\Delta G^\ddagger = 19.2 \pm 0.9$ kcal/mol (298 K). The bridge deformation in the related, more soluble molecule $[(n\text{-}C_4H_9)_2Sn]_2Fe_2(CO)_7$ occurs with simultaneous, stereospecific interchange of bridge and terminal carbonyl ligands, as monitored by ^{13}C NMR spectra. The complex $[(C_6H_5)(CH_3)SnFe(CO)_4]_2$ exists in two isomeric forms which interconvert in solution with $\Delta G^\ddagger = 25.5 \pm 0.7$ kcal/mol (298 K). The iron–tin bond cleavages are proposed to yield $R_2Sn{\rightarrow}Fe$ stannylene intermediates.

The process which interchanges axial (R_a) and equatorial (R_e) groups at a rate fast on the proton NMR time scale in $(R_2E)_2Co_2(CO)_6$ (A) and $(R_2E)_2Fe_2(CO)_7$ (B) cluster compounds has been discussed in terms of two distinct mechanistic patterns. One possible process is a "flapping" or deformation of the R_2E bridges, in which passage through a planar Co_2E_2 or Fe_2E_2 intermediate or transition state would serve to permute R_e and R_a moieties.[3,5] The other possible process would involve scission of Co_2–E and Fe_2–E bridges, to form $R_2E{\rightarrow}Co$ and $R_2E{\rightarrow}Fe$ species.[3-5] These are analogous to carbene complexes,[6,18] and rotation about the E→Co and E→Fe bonds, followed by closure of the bridge, would provide a pathway for R_e–R_a interconversion. Though the flapping process might seem plausible for molecules of type A, the observation that R_e–R_a interchange takes place at nearly the same rate in type B complexes[5] appears contradictory, since the presence of a fixed, bridging carbonyl would surely present some obstruction to "flapping". Our interest in bond-breaking reactions of group 4 metal–transition metal complexes[7,8] and in the nature of silylene, germylene, and stannylene analogues of carbene complexes,[8] has prompted our investigation of the above problem. Our goal has been to map out the relative energetic requirements of the two processes discussed above for a type B molecule, which on the surface presents the greatest potential contradiction in terms of mechanistic information.



A

E = Ge, Sn
R = CH_3



B

E = Si, Ge, Sn
R = CH_3, n-C_4H_9, C_6H_5

Experimental Section

The synthesis and handling of all compounds were carried out in an atmosphere of prepurified nitrogen or argon. Solvents were thoroughly dried in a manner appropriate to each and distilled under nitrogen immediately prior to use (except where otherwise noted). Elemental analyses were performed by either Ms. H. Beck (Northwestern University Analytical Services Laboratory) or Schwarzkopf Microanalytical Laboratory (Woodside, N.Y.).

Phenylmethyltin Dichloride. Triphenylmethyltin[9] (10.46 g, 28.6 mmol) was placed in a 300-ml three-necked flask and dissolved in 100 ml of ether. Approximately 12.7 ml (ca. 57.2 mmol) of a saturated solution (4.5 M at room temperature) of HCl in ether was syringed into a dropping funnel attached to the flask and was diluted with 25 ml of ether. This solution was added dropwise with stirring to the $(C_6H_5)_3SnCH_3$ solution over a period of 2 h, and the reaction mixture then allowed to stir overnight. Next, the ether and benzene were removed in vacuo, yielding at this point a white solid which was "wet" with a yellow, nonvolatile oil. Purification was accomplished by "sublimation" of the solid–liquid mixture at 10^{-3} Torr and 35 °C onto a water-cooled cold finger. This afforded 5.48 g (68%) of colorless crystals of phenylmethyltin dichloride, mp 46–47.5 °C. Anal. Calcd for $C_7H_8SnCl_2$: C, 29.78; H, 2.86. Found: C, 29.24; H, 3.01. ^{1}H NMR ($CDCl_3$): multiplet centered at δ 7.5 (5 H); singlet at δ 1.23 (3 H), $J_{{}^{117,119}Sn\text{-}CH_3} = 68$ Hz.

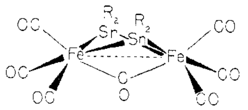
Bis-μ-phenylmethylstannylene-diiron Octacarbonyl, $[(C_6H_5)(CH_3)SnFe(CO)_4]_2$. To a slurry of 7.39 g (21.4 mmol) of $Na_2Fe(CO)_4{\cdot}1.5(\text{dioxane})$[10] in 100 ml of benzene at room temperature was added 5.48 g (19.45 mmol) of $(C_6H_5)(CH_3)SnCl_2$. The mixture was allowed to stir for 5 days, after which time the solvent (and released dioxane) were removed in vacuo. The resultant yellow-orange powder was recrystallized twice from 4:1 hexane–pentane in the following manner. A saturated solution was prepared in the mixed solvent. The solution was filtered and then slowly cooled to −78 °C and allowed to digest at that temperature for 2 days, after which time the supernatant was removed via syringe and the yellow solid was washed with three 10-ml portions of pentane, precooled to −78 °C. The product was dried overnight under high vacuum; yield 3.27 g (44%). Anal. Calcd for $C_{22}H_{16}Sn_2Fe_2O_8$: C, 34.89, H, 2.13. Found: C, 35.13, H, 2.19. Ir(C_6H_{12}): ν(CO) 2052 (m), 2001 (vs) cm^{-1}.

μ-Carbonyl-bis-μ-phenylmethylstannylene-diiron Hexacarbonyl, $[(C_6H_5)(CH_3)Sn]_2Fe_2(CO)_7$. Under nitrogen, 4.32 g (5.70 mmol) of $[(C_6H_5)(CH_3)SnFe(CO)_4]_2$ was placed in an inert-atmosphere photolysis apparatus consisting of a Pyrex vessel with a quartz insert. Methylcyclohexane (MCH) was added to the $[(C_6H_5)(CH_3)Sn\text{-}Fe(CO)_4]_2$ and the mixture was stirred until the compound dissolved. The solution was then irradiated for 10 h at 0 °C using a 450-W high-pressure mercury vapor lamp, during which time the color of the solution changed from a pale yellow to a dark orange and a considerable amount of solid collected on the inside surfaces of the apparatus. Next, the MCH was removed in vacuo, and the entire apparatus was taken into a glovebag where the dark orange solid was collected. The product was then rinsed several times with pentane, and a saturated solution was prepared in dry, deoxygenated CH_2Cl_2. This solution was carefully layered with pentane and then placed in a freezer at −35 °C where it remained until the two layers completely diffused together (ca. 2 days); during this time microcrystals formed. The temperature was then slowly lowered to −78 °C using a dry ice–methanol bath, and the crystals were allowed to stand overnight at −78 °C. Next, the supernatant was removed via syringe and the solid rinsed with two 5-ml portions of pentane (precooled to −78 °C). After the material was dried under high vacuum, the recrystallization procedure was repeated. The compound isolated this way was in the form of a dark orange microcrystalline solid. The compound is only slightly air sensitive as a solid but somewhat more so in solution. It is sparingly soluble in nonpolar solvents, dissolving in chlorinated hydrocarbons more readily. Due to loss in transfer and purification attempts, the yield (0.85 g, 20%) was somewhat low. Anal. Calcd for $C_{21}H_{16}Sn_2Fe_2O_7$: C, 34.58; H, 2.21; mol wt 729. Found: C, 34.31; H, 1.75; mol wt (mass spectrometric), parent ion centered at 729. Ir (CH_2Cl_2): ν(CO) 2049 (m), 2021 (vs), 1992 (s), 1973 (s), 1820 (s) cm^{-1}.

μ-Carbonyl-bis-μ-di-*n*-butylstannylene-diiron Hexacarbonyl, $[(n\text{-}C_4H_9)_2Sn]_2Fe_2(CO)_7$. A 6.21-g (7.74-mmol) portion of $[(n\text{-}C_4H_9)_2SnFe(CO)_4]_2$[8c] was placed in the photolysis apparatus (vide supra), dissolved in MCH, and irradiated at 0 °C for 1.5 h, during which time the solution changed from a pale yellow to a very dark yellow-brown. The solution was then transferred under N_2 to a three-neck flask and the solvent removed in vacuo to yield a dark yellow-brown oil. The product was then dissolved in an equal volume of pentane, slowly cooled to −70 °C (at which temperature the remaining traces of starting material crystallized out), and the supernatant was removed via syringe and reserved. The pentane was evaporated from the supernatant under high vacuum, yielding 5.36 g (89%) of a very dark yellow-brown air-sensitive oil as product. The compound is extremely soluble in common organic solvents. Anal. Calcd for $C_{23}H_{36}Sn_2Fe_2O_7$: C, 35.71; H, 4.69; mol wt 774. Found: C, 35.42; H, 4.71; mol wt (mass spectrometric), parent ion centered at 774. Ir (MCH): ν(CO) 2044 (s), 2015 (s), 1987 (vs), 1965 (vs), 1921 (vw), 1835 (s) cm^{-1}.

Instrumental Measurements. Infrared spectra were obtained using either a Beckman IR-9 or a Perkin-Elmer Model 267 spectrophotometer and were calibrated with polystyrene film.

Mass spectra were obtained by Dr. L. A. Raphaelian of the Northwestern University Analytical Services Laboratory using a CEC 21-104 mass spectrometer at ionizing voltages of both 10 and 70 eV. Samples were prepared quickly in air and introduced by the direct-inlet method.



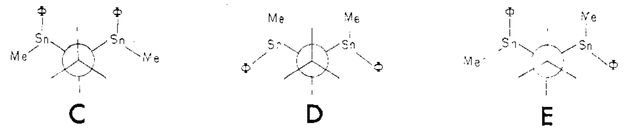


Figure 1. Newman projections of the geometrical isomers of $[(C_6H_5)(CH_3)Sn]_2Fe_2(CO)_7$.

Routine NMR spectra were recorded on either a Varian T-60 (60 MHz) or a Hitachi Perkin-Elmer R20-B (60 MHz) spectrometer. The variable-temperature proton spectra were recorded on a Bruker HFX-90 (90 MHz) spectrometer and were calibrated using a Hewlett-Packard 5216A frequency counter by measuring the frequency separation from the locking signal. Continuous-wave signal averaging was accomplished using a Fabri-Tek Instruments, Inc., 1074 computer. The various temperatures were obtained and maintained by use of a calibrated Bruker B-ST 100/700 temperature control unit and are considered accurate to within ±2 °C. For the 270-MHz spectra, a Bruker HFX-270 spectrometer with a superconducting magnet was utilized. Temperatures were controlled with the same type of unit as in the 90-MHz proton work.

Carbon-13 NMR spectra were obtained by the pulse Fourier transform technique[28] using the same Bruker HFX-90 spectrometer operating at 22.63 MHz. Data acquisition and processing was accomplished with a Fabri-Tek Instruments, Inc., 1074 computer, a Krohn-Hite Model 3200 low-pass filter, and a hard-wired pulse programmer.[11] Typical pulse widths were 20–25 μs, with 0.8–1.2-s delay between pulses. Proton decoupling was accomplished with a Bruker B-SV 2 broad-band power amplifier. A small amount of hexafluorobenzene was added to each sample to provide a signal for the ^{19}F lock. Samples were prepared in nitrogen-filled serum-capped 10-mm NMR tubes. Each spectrum is the result of between 1024 and 3072 pulses. A small amount of $Cr(acac)_3$ was added to each sample to reduce the longitudinal relaxation times (T_1's),[12] but care was taken not to exceed a 1:100 $Cr(acac)_3$:CO mole ratio in order to avoid possible artificial line broadening.[13]

Kinetic Analyses. Line shape analysis was performed with a local version of the program EXCNMR, originally written by G. M. Whitesides and extensively modified by Dr. M. R. Walczak of this laboratory. The program utilizes the formalism of Kubo and Sack.[14]

For the ^{13}C NMR computer simulation, it was assumed that the relative signs of the tin–carbon coupling constants were the same. This procedure yielded a satisfactory fit.

Kinetic analysis of $[(C_6H_5)(CH_3)Sn]_2Fe_2(CO)_7$ proton spectra required several nonroutine procedures. Since the resonances were close together, normally small changes in chemical shift with temperature interfered with the simulation procedure. This was remedied by graphing chemical shift vs. temperature in the regions just below and just above slow exchange and extrapolating these curves to regions of higher temperature (the plots were found to be approximately linear), using the corrected chemical shifts for line shape simulation. At temperatures below ca. 235 K, it was found that there was a small amount of viscosity broadening. This was taken into account by measuring the line width of the major methyl peak in this temperature region, which is not involved in exchange at these temperatures (spectra were recorded down to 160 K in 1:1 CF_2Cl_2–$CHCl_2F$, and no broadening of the peak was observed), and using the ratio (line width at that temperature):(line width at slow exchange) as an appropriate correction factor. A final complication involved a small temperature dependence of the isomer C–isomer E equilibrium constant. This could be taken into account by minor changes in relative populations.

The kinetic study of the isomerization of $[(C_6H_5)(CH_3)Sn\text{-}Fe(CO)_4]_2$ was carried out in the following manner. The ^{1}H NMR spectrum in toluene-d_8 was found to consist of two multiplets at δ 8.00 and 7.36 (5 H) and two singlets at δ 1.37 and 1.34 (3 H, $J_{^{117,119}Sn-CH_3}$ = 41.6 Hz). The two singlets each represent the methyl resonance of one of the two possible isomers. Samples in sealed NMR tubes were heated in a constant-temperature bath in the dark; they were periodically removed and immersed in cold water immediately, and spectra were recorded and integrated. By monitoring the relative intensity of the two peaks the relative concentrations could be found. Treatment of the data was then by standard methods.[15]

Results

Experiment Design and Synthesis. To resolve the question of whether flapping or bridge scission was taking place in type B molecules, a complex with unsymmetrical substitution at

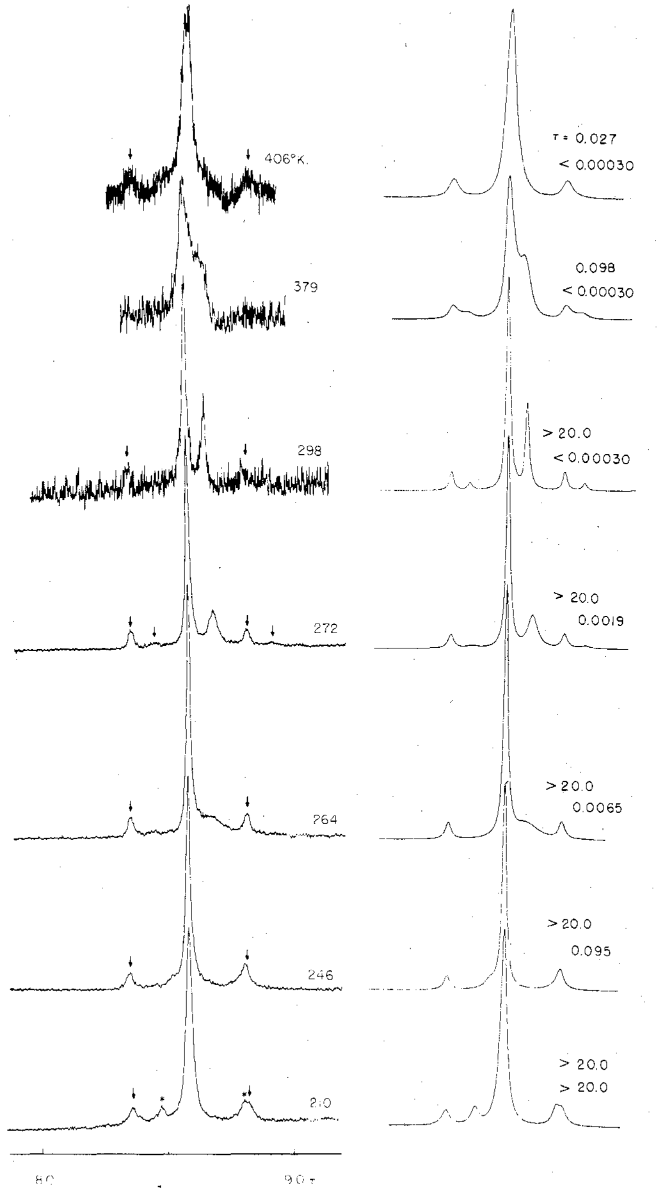
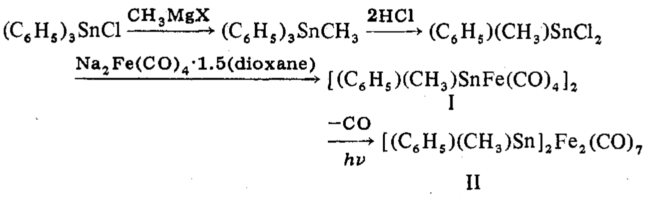


Figure 2. Left: Variable-temperature 90-MHz ^{1}H NMR spectra of compound II, $[(C_6H_5)(CH_3)Sn]_2Fe_2(CO)_7$, in the methyl region as a solution in CH_2Cl_2 (210–272 K) and in toluene-d_8 (298–406 K). Spectra are the results of 4–8 CW time-averaged scans. Arrows denote ^{117,119}Sn satellites; asterisks, the methyl resonances of isomer E in the slow-exchange limit. Right: Computer-generated spectra for the mean preexchange lifetimes (τ, in s) for isomerization of C (top) and ring deformation in E (bottom).

the tin (i.e., $R_a \neq R_e$ on a particular tin) was synthesized. The target molecule was that in which $R_2Sn = (CH_3)(C_6H_5)Sn$. Here three geometrical isomers are possible (Figure 1) based upon structures of similar molecules.[16,17] The flapping process would, if the bridge carbonyl is ignored for the moment, interconvert isomers C and D, as well as the magnetically nonequivalent methyls and phenyls of isomer E. As defined, flapping alone will not provide a pathway for C–E or D–E interchange, nor, of course, would it seem plausible without some complementary mobility of the bridging carbonyl. On the other hand, rapid interconversion of C, D, and E at a rate comparable to R_a–R_e interchange in symmetrical systems would provide strong support for Fe–Sn–Fe bridge rupture. For R sufficiently bulky, $R_2Sn \rightarrow M$ complexes have been isolated,[18] though the stability of such species for more normal substituents has been questioned.[8,19]

Scheme I



$$(C_6H_5)_3SnCl \xrightarrow{CH_3MgX} (C_6H_5)_3SnCH_3 \xrightarrow{2HCl} (C_6H_5)(CH_3)SnCl_2 \xrightarrow{Na_2Fe(CO)_4\cdot 1.5(\text{dioxane})} \underset{\text{I}}{[(C_6H_5)(CH_3)SnFe(CO)_4]_2} \xrightarrow[h\nu]{-CO} \underset{\text{II}}{[(C_6H_5)(CH_3)Sn]_2Fe_2(CO)_7}$$

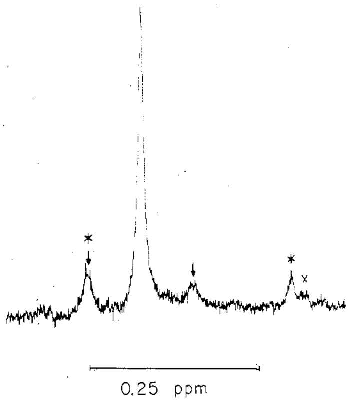


Figure 3. ^{1}H NMR spectrum (270 MHz) of compound II at 225 K. Arrows denote ^{117,119}Sn satellites, asterisks denote the methyl resonances of isomer E, and × denotes a trace impurity. Note that, as opposed to the 90-MHz spectra, the upfield methyl resonance of isomer E is no longer overlapped by the high-field tin satellite. However, the downfield methyl resonance of E is now coincident with the downfield tin satellite.

The method employed to introduce an unsymmetrically substituted diorganotin moiety into the bridge in a system B compound is presented in Scheme I. Details are given in the Experimental Section. The first step is a standard Grignard reaction; the second involves cleavage of two phenyl groups from $(C_6H_5)_3SnCH_3$ with HCl. Hydrogen chloride was chosen since it has been established that HCl will preferentially cleave a phenyl group from a tin rather than an alkyl group[20] and since the by-product, benzene, was more conveniently removed than would be the phenyl halide resulting from halogen cleavage. The third step involves reaction of the dichlorotin compound with iron tetracarbonyl dianion, a well-established route to these octacarbonyl complexes.[8c] It was found in this case that the reaction proceeded more cleanly in benzene than in the usual solvent, THF.[8c] The final step involves the photolytic decarbonylation of the octacarbonyl to yield the heptacarbonyl complex. This photolytic step also worked well for decarbonylation of $[(n\text{-}C_4H_9)_2SnFe(CO)_4]_2$ to the corresponding heptacarbonyl, $[(n\text{-}C_4H_9)_2Sn]_2Fe_2(CO)_7$ (III). Thermal decarbonylation (refluxing in toluene) resulted in low yields of the desired product and extensive decomposition to a metallic mirror.

Proton NMR Studies. Variable-temperature 90-MHz ^{1}H NMR spectra of II are shown in Figure 2. The low solubility necessitated the use of CW time averaging at all temperatures and in all solvents. At low temperature the spectrum of II exhibits three methyl resonances in an intensity ratio of 10.6:1.0:1.0. The relative populations were quantitatively verified by integration, computer simulation (relative populations considered accurate to ±4%), and a study at 270 MHz. The latter shows (Figure 3), among other things, the high-field methyl resonance displaced from the high-field ^{117,119}Sn satellite which had overlapped it in the 90-MHz spectrum. Such an experiment also shifts the low-field methyl resonance to the position of the low-field Sn satellite. The methyl pattern observed is ascribed to an equilibrium mixture of isomer E plus either C or D; E plus C is most reasonable based on results for the related $[(C_6H_5)(CH_3)Z]_2Fe_2(CO)_6$ (Z = P, As)

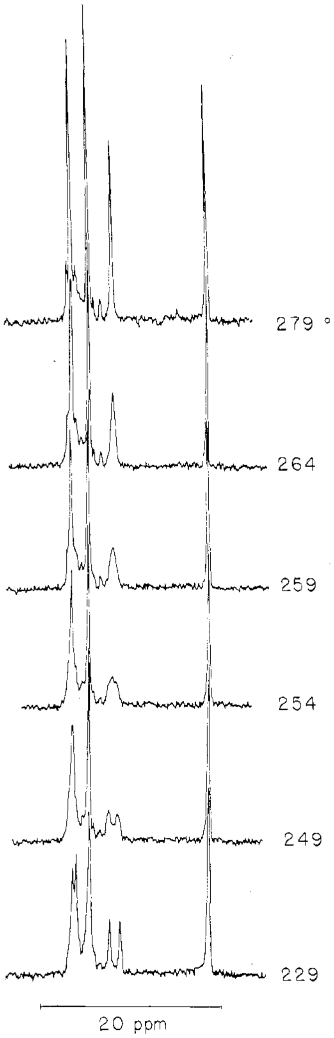


Figure 4. Proton-decoupled variable-temperature ^{13}C NMR spectra of compound III in the *n*-butyl region. Assignment of resonances (left to right): β carbons, γ carbons, α carbons, δ carbons.

Table I. ^{13}C NMR Coupling Shifts and Coupling Constants for $[(n\text{-}C_4H_9)_2Sn]_2Fe_2(CO)_7$

Resonance	*T*, K	Chem shift, ppm[a]	$J_{^{117,119}Sn-^{13}C}$, Hz
CO_t	229	206.0	66.3
CO_t	229	208.9	56.6[b] 29.2[b]
CO_b	229	252.1	61.6
Butyl[c]	229	22.3 } α carbons 23.8 } α carbons	
		28.0 } β carbons 28.5 } β carbons	
		26.3	
		12.1	
Butyl[c]	279	28.3 β carbons	24.0

[a] Relative to TMS = 0. [b] The 4C peak has two sets of tin satellites (see ref 23). [c] Proton decoupled.

compounds.[3b,21] Apparently, one isomer (probably D) is either absent or present in such a small amount as to be undetectable. As the temperature is raised (Figure 2), the resonances assigned to E collapse, coalesce, and grow in as a single sharp line at room temperature, while the resonance assigned to C remains unchanged. Line shape analysis (vide infra) (Figure 2) yields a free energy of activation ($\Delta G^{\ddagger}$)[14] of 11.8 ± 0.6 kcal/mol at 298 K. At very high temperatures isomer E begins to exchange with isomer C. Line shape analysis for this process yields a $\Delta G^{\ddagger}_{298}$ of 19.2 ± 0.6 kcal/mol. The observation of $^{117,119}Sn-CH_3$ coupling at high temperature (Figure 2) is assurance that the $Sn-CH_3$ bonds remain intact.

Carbon NMR Studies. A deformation or flapping process as a means for R_a-R_e interchange in type B complexes would seem to require temporary displacement of the bridging carbonyl and then subsequent repositioning. With this in mind and with the hope of further elucidating the rearrangement pathway, the compound $[(n\text{-}C_4H_9)_2Sn]_2Fe_2(CO)_7$ (III) was synthesized (see Experimental Section) to provide a more soluble analogue of II for ^{13}C NMR study.

The proton-decoupled ^{13}C NMR spectra (22.6 MHz) of III in the *n*-butyl region are shown in Figure 4. At 229 K, two sharp resonances are assigned to the α-carbon atoms at 23.8 and 22.3 ppm vs. TMS. As the temperature is raised, the signals are seen to collapse, coalesce, and finally re-form as one sharp peak at 279 K. Similar changes can be detected for the β-carbon resonances (28.0 and 28.5 ppm). These results indicate R group interchange is also occurring in this system as expected. The free energy of activation at spectral coalescence (251 K) is estimated to be 12.5 ± 0.5 kcal/mol and is essentially identical with that found by ^{1}H NMR for compound II (11.8 ± 0.6 kcal/mol at 298 K). This assures that mechanistic results can be transferred from III to II.

Variable-temperature ^{13}C NMR spectra of III in the CO region are presented in Figure 5. At slow exchange, three major resonances are seen in an intensity ratio of 2:4:1, occurring at 206.0, 208.9, and 252.1 ppm vs. TMS, respectively. The 2- and 4-carbon peaks are assigned to terminal carbonyls[22] while the single low-field signal is assigned to the bridging carbonyl.[22] Each of these resonances is flanked by ^{117,119}Sn satellites (Table I).[23] As the temperature of the sample is raised, the carbonyl resonances collapse and by room temperature have coalesced to a single broad peak. It should be noted that no exchange with the impurity $[(n\text{-}C_4H_9)_2SnFe(CO)_4]_2$ is observed (Figure 5). The line shape changes were also found to be independent of concentration over a fourfold range and were identical in toluene as the solvent.

Though the mechanistic implications of the ^{13}C NMR collapse pattern will be discussed in detail later, several features of the spectra are worth pointing out at this stage. First, the bridging carbonyl is observed to exchange rapidly with the terminal carbonyls, as a flapping process would require. Second, as the temperature is raised, the bridge peak and the 2-carbon peak are seen to broaden much more rapidly than the 4-carbon peak, even considering the difference in populations. This is quite obvious in the region of initial collapse; and even at 264 K, where the bridge and 2-carbon terminal peaks are almost completely collapsed, the 4-carbon peak is still quite sharp. Also, the rate at which the bridging carbonyl exchanges (leaves its site) can be estimated from line broadening using the modified Bloch equations[14,24] ($\Delta G^{\ddagger}_{251}$ = 12.0 ± 0.5 kcal/mol) or at a more sophisticated level (vide infra) by line shape analysis (Figure 5). In either case, the rate of exchange is, within experimental error, identical with the rate of α-carbon interchange in the *n*-butyl groups.

Kinetic and Mechanistic Analysis. Activation parameters derived from least-squares fitting of the line shape analysis rate data are set out in Table II. The nature of the Arrhenius log *A* values for the proton data suggests possible errors.[14] Considering the limited temperature range available, the narrow frequency separation of the exchanging sites, and potential line broadening incurred in the time averaging, this is not surprising. Thus, reference should be made to the far more accurate quantity, $\Delta G^{\ddagger}$. In addition, we have followed other authors[25] in listing activation parameters calculated assuming log *A* = 13. All of these data are set out in Table II.

Consideration of the rate data indicates that the dynamic requirements for the flapping (bridge deformation) mechanism

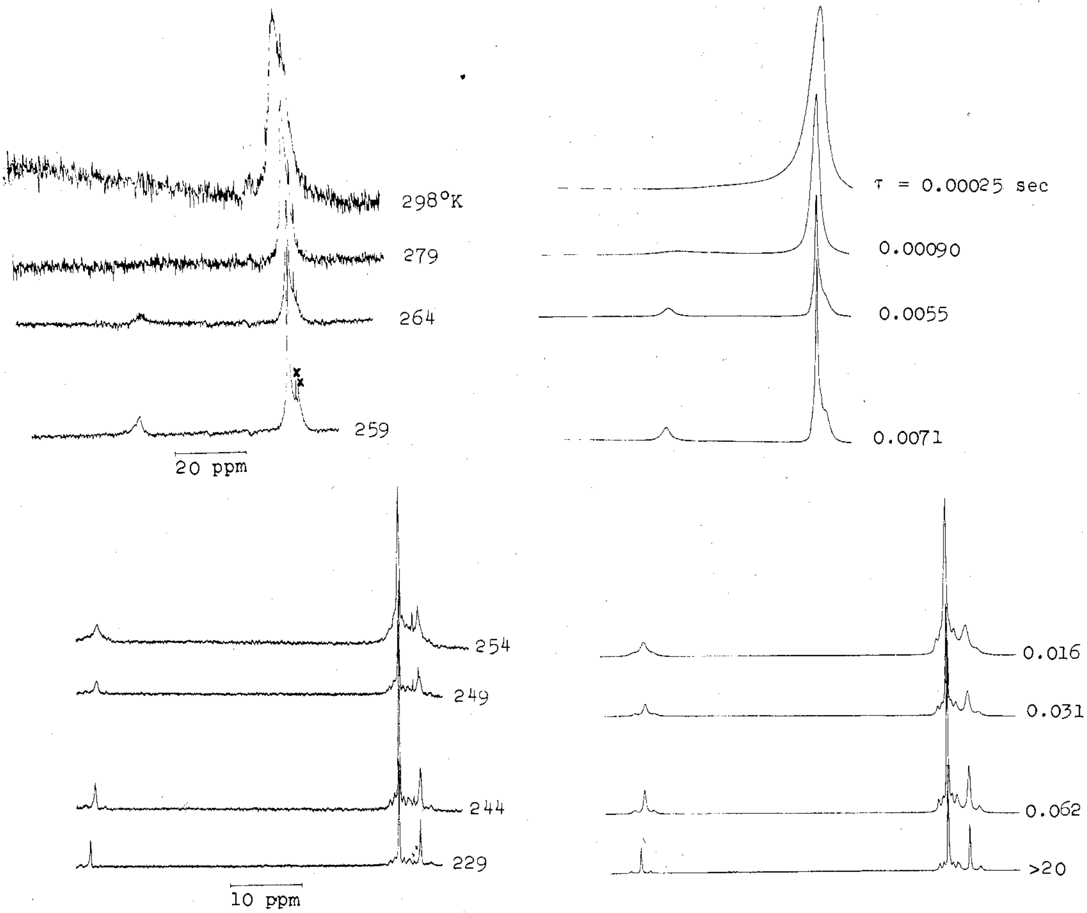


Figure 5. Variable-temperature ^{13}C NMR spectra of compound III in the carbonyl region (left) and computer simulation based upon mechanism A (right) (see text). Note the two different sweep widths and that two sharp resonances (marked by X in the slow-exchange spectrum and at 259 K) are due to traces of $[(n\text{-}C_4H_9)_2SnFe(CO)_4]_2$ present as an impurity (see text). The solvent is CH_2Cl_2.

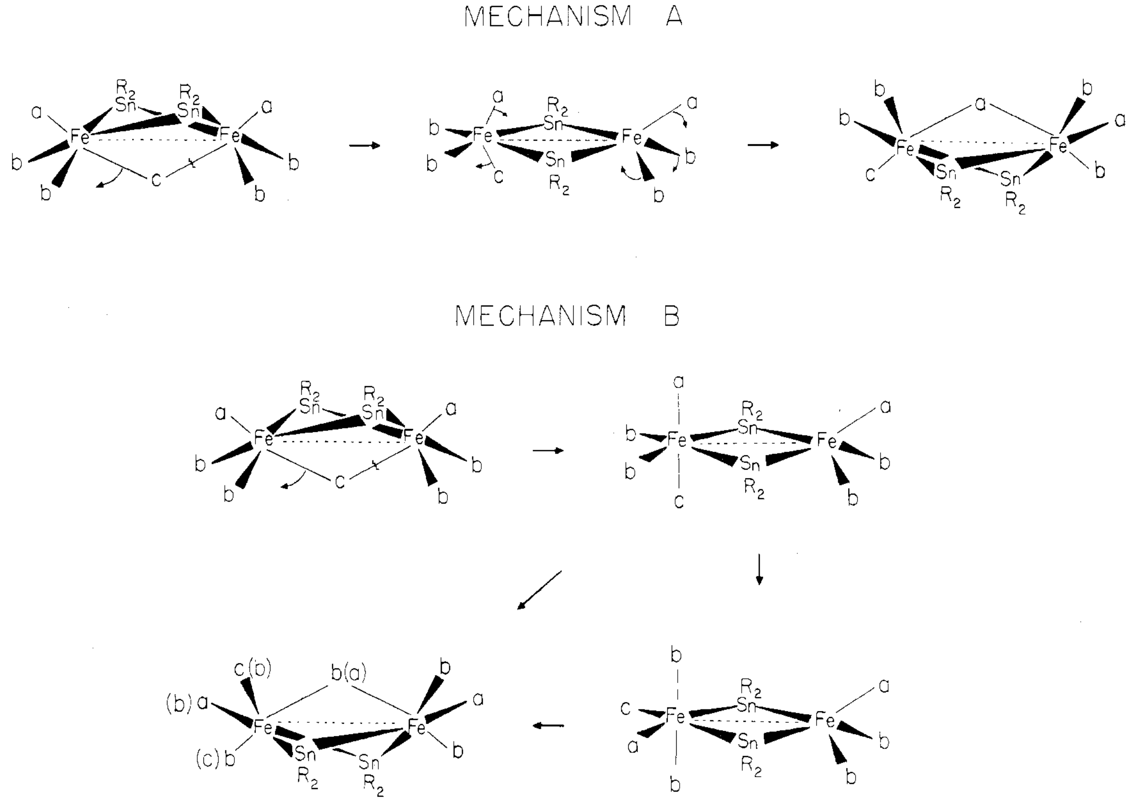
Table II. Activation Parameters

Compd	$\Delta G^{\ddagger}_{298}$, kcal/mol	$\Delta H^{\ddagger}_{298}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(mol deg)	E_a, kcal/mol	log A
I (isomerizn)	25.5 ± 0.7	18.0 ± 1.7	−25.3 ± 5.1	18.6 ± 1.7	7.4 ± 1.1
II (low-T process)	11.8 ± 0.6[a]	18.8 ± 1.5[a]	23.4 ± 5.8[a]	19.4 ± 1.5[a]	18.3 ± 1.3[a]
	12.3 ± 0.5[b]	12.3 ± 0.5[b]	0.0 ± 0.5[b]	12.9 ± 1.2[b]	13.0 ± 1.0[b]
II (high-T process)	19.2 ± 0.9[a]	13.8 ± 3.1[a]	−18.1 ± 7.9[a]	14.4 ± 3.1[a]	9.3 ± 1.3[a]
	20.2 ± 0.6[b]	20.2 ± 0.6[b]	0.0 ± 0.5[b]	20.8 ± 1.8[b]	13.0 ± 1.0[b]
III (from Bu resonances)	12.5 ± 0.5[c]				
III (from CO resonances)	12.4 ± 0.3	14.4 ± 0.7	6.8 ± 2.5	15.0 ± 0.7	14.7 ± 0.6
$[(CH_3)_2Ge]_2Co_2(CO)_6$	11.4 ± 0.5[d]	12.4 ± 0.5[d]	3.5 ± 1.2[d]	12.9 ± 0.5[d]	13.9 ± 0.5[d]
$[(CH_3)_2Sn]_2Co_2(CO)_6$	12.0 ± 0.5[d]	12.0 ± 0.5[d]	0.0 ± 1.3[d]	12.5 ± 0.5[d]	13.2 ± 0.5[d]
$[(CH_3)_2Si]_2Fe_2(CO)_7$	11.5 ± 0.5[e]				
$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3[Ge(CH_3)_2]$	21.1 ± 0.9[f]	19.7 ± 0.7[f]	−5.0 ± 2.0[f]	20.5 ± 0.7[f]	12.2 ± 1.0[f]

[a] See text. [b] Calculated assuming log A = 13.0 ± 1.0. [c] From coalescence at 251 K. [d] Axial–equatorial CH_3 exchange, from ref 3b. [e] Calculated using data for axial–equatorial CH_3 exchange in ref 5, from coalescence at 226.5 K. [f] For exchange between isomeric forms, from ref 32.

have been fulfilled. In compound II, methyls on isomer E interchange far more rapidly than interchange with isomer C ($\Delta\Delta G^{\ddagger} \approx 7$ kcal/mol). The stipulation that the bridging carbonyl be displaceable to accommodate flapping is also satisfied. Thus, the low-temperature NMR results are most compatible with bridge deformation. Only at higher temperatures is a spectral process consistent with bridge scission observed. It is next possible, from the data at hand, to inquire in detail as to which dynamic processes involving the carbonyl groups accompany flapping and give rise to the ^{13}C NMR spectral changes observed.

A rigorous group theoretical and combinatorial mathematical method is available for enumerating those permutations of nuclear spins which are "differentiable" by NMR,[26] i.e., those which should in theory give rise to different line shape collapse patterns. These permutations can then hopefully be identified with various reaction mechanisms. For the case of an $(R_2Sn)_2Fe_2(CO)_7$ compound in which the presence of Sn isotopes with spins is included (this lowers the symmetry) there are 1272 possible NMR-differentiable reactions for the carbonyl system alone. Rejecting those permutations which do not include the bridging carbonyl still leaves 1080 NMR-differentiable reactions to be considered. Though further inspection indicates that some of the remaining permutations can be rejected because they do not involve exchange of the appropriate spins, it also becomes apparent that the process of compiling, analyzing (by hand), and computing theoretical line shapes for such a large number of


MECHANISM A

MECHANISM B

Figure 6. Two possible mechanisms for the low-temperature dynamic process in $(R_2E)_2Fe_2(CO)_7$ complexes.

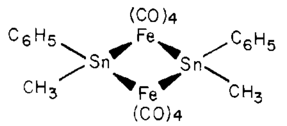
reactions is too laborious and time consuming an exercise to be justified.[37] Therefore we have taken the more pragmatic albeit subjective approach of testing processes which, based upon precedent and intuition, appear to be chemically most reasonable. These mechanisms will then be translated into site permutations and theoretical line shapes will be computed.

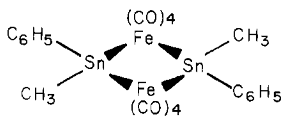
The first process to be considered (mechanism A in Figure 6) can be described as follows. First, the CO bridge opens, moving that carbonyl into a terminal position. In concert with or subsequent to this event, the Fe_2Sn_2 ring flattens and a type a carbonyl enters the bridge. To avoid a final configuration in which Fe–Sn bonds are eclipsed with respect to Fe–CO bonds on the uninvolved $Fe(CO)_3$ moiety, a twist of the latter group about the Fe–Fe vector by at least $2\pi/6$ is required. This rapid twisting is reasonable since there is evidence for such a process in the isoelectronic $(RS)_2Fe_2(CO)_6$ and $(R_2Z)_2Fe_2(CO)_6$ systems[3b]—apparently retraction of the bridging carbonyl frees the present system for $Fe(CO)_3$ rotation. Permutationally, this mechanism preferentially exchanges carbonyls a and c, and the twist on the other $Fe(CO)_3$ moiety provides the only pathway for involving type b sites in the exchange process. These preferences qualitatively explain the rapid collapse in the ^{13}C NMR spectra of the bridge and 2-carbon resonances, while the major terminal carbonyl resonance remains relatively sharp. Figure 5 displays computed spectra for the above mechanism.[29]

It was of interest next to test to what degree the a → c exchange was preferential. To accomplish this, a mechanism (mechanism B in Figure 6) was devised in which the breaking of the carbonyl bridge produced an intermediate $>Fe(CO)_4$ group which was allowed to pseudorotate prior to completion of the flapping process and reclosure of the bridge. Nonrigidity has been observed before in $>M(CO)_4$ systems.[27] The above processes, as in the previous case, would occur along with twisting of the $Fe(CO)_3$ group. Spectra computed for the case where the intermediate undergoes one $2\pi/4$ pseudorotation prior to bridge closure (i.e., exclusive b → c interchange) were in gross disagreement with experimental ^{13}C NMR spectra. Likewise, theoretical spectra for the case of random entry of any of the $>Fe(CO)_4$ ligands into the bridge position produced an unsatisfactory match; here a type b carbonyl is twice as likely to enter the bridge position as carbonyl a. Figure 7 shows computed spectra for the situation in which a and b carbonyls have an equal probability of becoming bridge carbonyls. Spectra were generated for rates which produced the closest correspondence to the experimental spectra. Even so, the agreement is considerably worse than for mechanism A, as shown.

Last, spectra were computed for a mechanism in which carbonyl groups are allowed to move randomly about the molecular skeleton. The results of these calculations are also presented in Figure 7. Again the agreement is poor, even when rates are varied for optimum fit.

Isomerization of $[(C_6H_5)(CH_3)SnFe(CO)_4]_2$. Reference to the molecular structures of $[R_2EFe(CO)_4]_2$ compounds[16] indicates that compound I should exist in the two geometrically isomeric forms





The product obtained upon initial crystallization (see Experimental Section) exhibits two methyl resonances, of unequal intensity in the ^1H NMR spectrum, which are assigned to the two isomers (see Experimental Section). In solution at room temperature, the relative intensities change until equilibrium is reached, with a half-life of several days. Careful recrystallization and rinsing with pentane results in high enrichment of one isomer. In order to obtain some quantitative idea of the minimum energy required to equilibrate these isomers (presumably via scission of one or both Fe–Sn bonds) a brief kinetic study was undertaken, by monitoring the relative

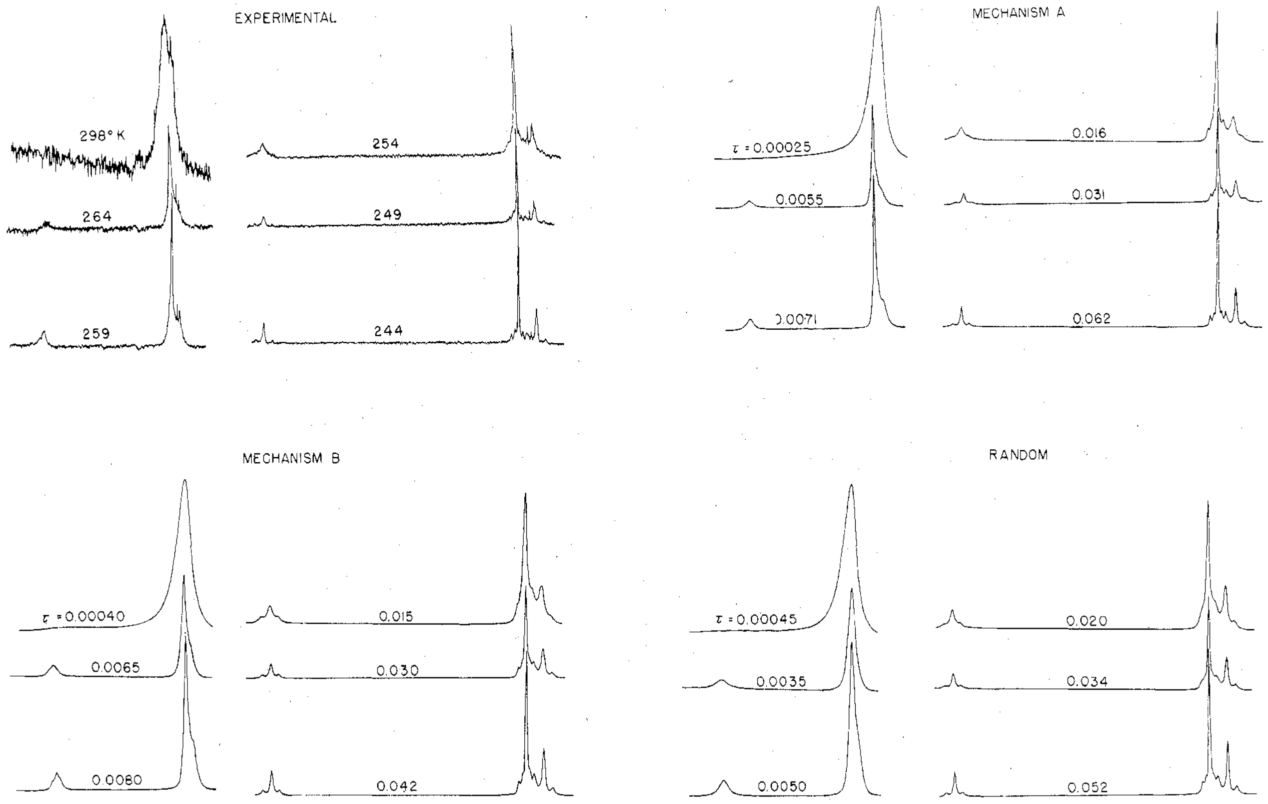
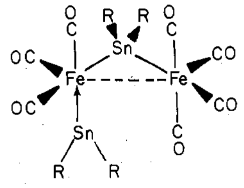


Figure 7. Experimental variable-temperature ^{13}C NMR spectra of compound III in the carbonyl region and computer-generated spectra based upon mechanism A, mechanism B, and random exchange (see text).

intensities of the methyl resonances in toluene-d_8 as a function of time. The isomerization obeys good first-order kinetics, and studies over a temperature range from 312 to 358 K resulted in the Arrhenius parameters shown in Table II. At 298 K, we estimate $\Delta G^{\ddagger} = 25.5 \pm 0.7$ kcal/mol.

Discussion

The purpose of the present investigation was to examine the relative energetic requirements of $SnFe_2$ bridge flapping (deformation) and Fe–Sn bridge rupture in $(R_2Sn)_2Fe_2(CO)_7$ cluster complexes. The evidence in favor of bridge deformation as the low activation energy process is persuasive. Methyl exchange within isomer E of $[(C_6H_5)(CH_3)Sn]_2Fe_2(CO)_7$ takes place far more readily ($\Delta G^{\ddagger} \approx 12$ kcal/mol) than isomerization to structure C ($\Delta G^{\ddagger} \approx 19$ kcal/mol). The alternative explanation to flapping is rupture of *both* Sn–Fe bonds to yield two $(C_6H_5)(CH_3)Sn{\rightarrow}Fe$ stannylene[18] units, which then must simultaneously rotate $2\pi/2$ about the Sn–Fe axes before reclosure of the bridges. That this should occur in isomer E, without the possibility of interchange with isomer D, which requires the above process to take place for only one $(C_6H_5)(CH_3)Sn<$ unit, seems unreasonable. Furthermore, movement of the bridge carbonyl out of its position, which would seem to be a requirement for flapping, takes place at the same rate as R_a–R_e interchange (Table II). In $(R_2E)_2Co(CO)_6$ complexes (E = Ge, Sn), R_a–R_e interchange also takes place. Our mechanistic results strengthen the original proposal[3a] that the exchange process is due to bridge flapping. The similarity between the cobalt and iron systems is evident in the nearly identical activation parameters for R_a–R_e interchange (Table II). Also the rates for both the $(R_2E)_2Fe_2(CO)_7$ and $(R_2E)_2Co_2(CO)_6$ systems exhibit a rather surprising insensitivity to the identity of E[30] (Table II). The high-temperature process E $\rightleftharpoons$ C in $[(C_6H_5)(CH_3)Sn]_2Fe_2(CO)_7$ requires an activation energy of ca. 19 kcal/mol. The most reasonable pathway for this process is, as already mentioned, scission of an Fe–Sn bond to yield a stannylene complex; this cleavage might well occur in concert with a carbonyl bridge scission such as in[31]



Rotation about the Sn→Fe bond, followed by bridge re-formation would effect E $\rightleftharpoons$ C isomer equilibration. Furthermore, the compound $(\eta\text{-}C_5H_5)_2Fe_2(CO)_3[\mu\text{-}(CH_3)_2Ge]$ exists in two isomeric forms which only interconvert rapidly above ca. 100 °C.[32] A reasonable description[32] of the isomerization requires the scission of the Ge–Fe bridge to yield a $(CH_3)_2Ge{\rightarrow}Fe$ complex; in this system the energetic requirements are similar to those in the present case: $\Delta G^{\ddagger} \approx 21$ kcal/mol.[32]

The complex $[(C_6H_5)(CH_3)SnFe(CO)_4]_2$ was also examined for high-temperature Fe–Sn bond-breaking processes.[34] Here isomerization requires a free energy of activation of ca. 26 kcal/mol. It is not certain whether this increase in $\Delta G^{\ddagger}$ reflects a necessity to break two Sn–Fe bonds or a decrease in ring strain compared to three-membered R_2EFe_2 cycles. The substantial bond dissociation energies (47–85 kcal/mol)[33] found in group 4 metal–transition metal complexes and the firm precendent[8,18] for stannylene complexes mitigates against the formation of diradicals as a major pathway in any of the above cleavages.

The ^{13}C NMR results presented here indicate that the carbonyl ligands readily accommodate the Fe_2Sn_2 deformation by a highly stereospecific rearrangement. This is portrayed in mechanism A, Figure 6, which features preferential interchange of type a and c CO groups. Although rapid exchange of bridge and terminal carbonyls between two metals spanned by a single CO bridge is not unknown,[35] it does not appear to be common.[36] Interestingly, the synchronous mechanism proposed for bridge–terminal CO interchange in other singly bridged systems[35b] is topologically similar to our mechanism A.

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Registry No. I, 56213-21-9; II, 58602-09-8; III, 56280-09-2; $(C_6H_5)(CH_3)SnCl_2$, 15649-26-0; $(C_6H_5)_3SnCH_3$, 1089-59-4; $[(n\text{-}C_4H_9)_2SnFe(CO)_4]_2$, 15613-38-4; $Na_2Fe(CO)_4$, 14878-31-0.

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(2) Fellow of the Alfred P. Sloan Foundation.

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