

Preliminary communication

FLUXIONAL PROCESSES IN $[\mu\text{-Sn}(\text{CH}_3)(\text{C}_6\text{H}_5)]_2\text{Fe}_2(\text{CO})_7$: THE IMPORTANCE OF Fe—Sn—Fe BRIDGE DEFORMATION VERSUS SCISSION

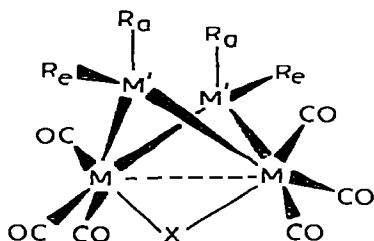
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Among the diverse structural rearrangements undergone by Group IV metal—transition metal complexes [1], the process which permutes axial and equatorial R groups at a rate fast on the PMR timescale in $(\text{R}_2\text{M}')_2\text{Co}_2(\text{CO})_6$ [2] (A) and $(\text{R}_2\text{M}')_2\text{Fe}_2(\text{CO})_7$ [3] (B) systems [4] ($\text{M}' = \text{Si}, \text{Ge}, \text{Sn}$) is one of the most fascinating and perplexing. For A both “flapping” (deformation) of

$\text{M} \begin{array}{c} \text{M}' \\ \diagup \quad \diagdown \\ \text{---} \end{array} \text{M}$ bridges [2] and metal—metal bond cleavage to $\text{R}_2\text{M}' \rightarrow \text{M} - \text{M}$ species [5]



(A) $\text{M} = \text{Co}$; $\text{X} = \text{nothing}$; $\text{M}' = \text{Ge}, \text{Sn}$; $\text{R} = \text{CH}_3$

(B) $\text{M} = \text{Fe}$; $\text{X} = \text{CO}$; $\text{M}' = \text{Si}, \text{Sn}$; $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$

are plausible pathways. The seemingly obstructive presence of the bridging carbonyl in B along with roughly comparable activation energetics for R group interchange in A and B could be construed as support for the bond-breaking mechanism operating in both systems. Our interest in transition metal complexes of divalent Group IV molecules and in scission reactions of metal—metal bonds [6], prompts us to report the results of a study which indicate that for system B [and by implication for A] *both* processes occur, but at considerably different rates.

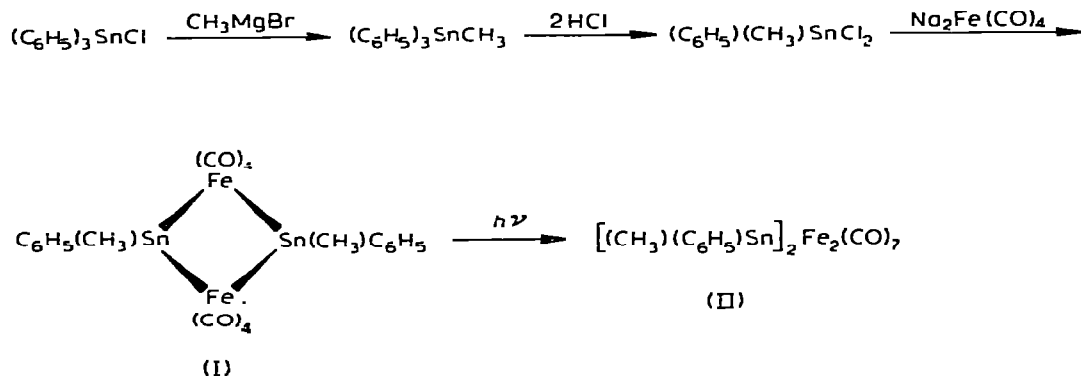
We have synthesized the complex $[(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Sn}]_2\text{Fe}_2(\text{CO})_7$ (II)* via the route outlined in Scheme 1. This compound can exist in three geometrical

* Anal. Found: C, 34.31; H, 1.75; mol. wt. (mass spectrometric), parent ion centered at 729.

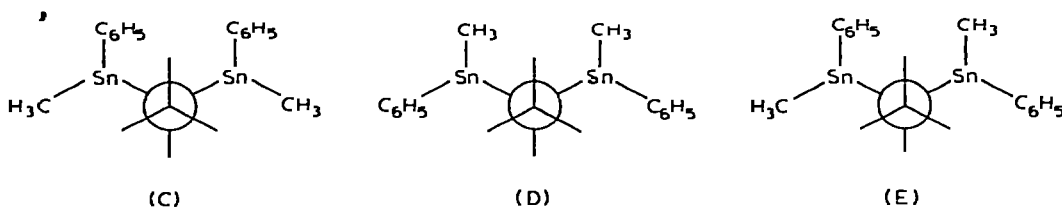
$\text{C}_{21}\text{H}_{16}\text{O}_7\text{Fe}_2\text{Sn}_2$ calcd.: C, 34.58; H, 2.21%; mol. wt., 729.

Infrared: $\nu(\text{CO})$, (CH_2Cl_2) : 2049m, 2021vs, 1992s, 1973s, 1820s cm^{-1} .

SCHEME 1



isomers (C, D, E). At low temperature, the PMR spectrum of II (Fig. 1) exhibits three methyl resonances in a ratio of 10.6/1.0/1.0; this conclusion was quantitatively verified by integration, computer simulation (relative populations considered accurate to $\pm 4\%$) and by studies at 270 MHz. We ascribe this pattern to an equilibrium mixture of E plus either C or D; E plus C is most reasonable based



upon results for the related system $[(\text{C}_6\text{H}_5)(\text{CH}_3)\text{As}]_2\text{Fe}_2(\text{CO})_6$ [7]. As the temperature is raised, the methyl resonances assigned to E collapse and coalesce to a single line. At coalescence (255 K), $\Delta G^\ddagger = 12.7 \pm 0.3$ kcal/mole. Only at considerably higher temperatures (Fig. 1) is exchange observed with isomer C. For this process preliminary lineshape analysis yields $\Delta G^\ddagger = 22.2 \pm 0.7$ kcal/mole (379 K).

Since a "flapping" mechanism for this system would seem to require complementary mobility of the bridging carbonyl, we have examined ^{13}C spectra of the more soluble $[(n\text{-C}_4\text{H}_9)_2\text{Sn}]_2\text{Fe}_2(\text{CO})_7^*$. At 240 K, three carbonyl resonances are observed at 206.0(2C), 208.9(4C), and 252.1(1C) ppm vs. TMS. As the temperature is raised, the resonances broaden, collapse, and finally coalesce. Initial lineshape analysis studies yield $\Delta G^\ddagger = 12.6 \pm 0.7$ kcal/mole (261 K). No exchange with added $[(n\text{-C}_4\text{H}_9)_2\text{SnFe(CO)}_4]_2$ [8] is detected**. The concurrent interchange of n-butyl groups can also be monitored by observing the proton-decoupled ^{13}C spectra of the α -carbon atoms (23.8 and 22.3 ppm at 246 K) as a function of temperature. From coalescence at 261 K, we estimate for exchange

*From photolysis of $[(n\text{-C}_4\text{H}_9)_2\text{SnFe(CO)}_4]_2$ [8]. Anal. Found: C, 35.95; H, 4.90; mol. wt. (mass spectrometric), parent ion centered at 774. $\text{C}_{73}\text{H}_{36}\text{O}_7\text{Fe}_2\text{Sn}_2$ calcd.: C, 35.71; H, 4.69%; mol. wt., 774. Infrared: $\nu(\text{CO})$ (methylcyclohexane): 2044s, 2015s, 1987vs, 1965vs, 1921vw, 1835s cm^{-1} .

**Interestingly, the ^{13}C NMR of this compound exhibits axial and equatorial ^{13}CO 's at 263 K which broaden and finally coalesce at ca. 320 K.

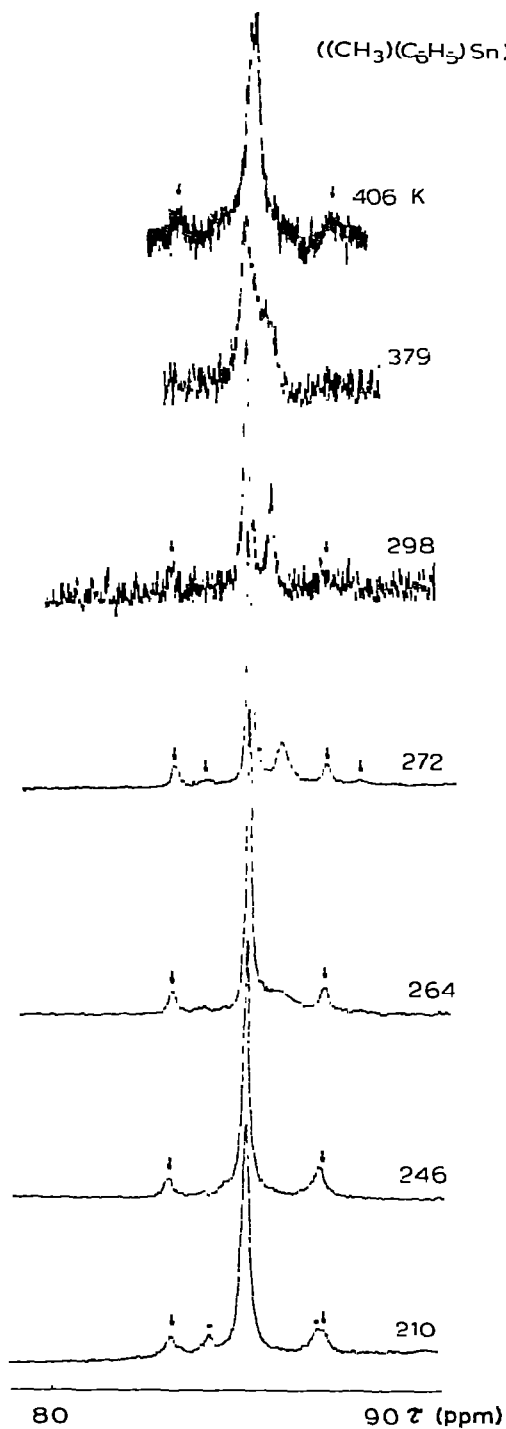


FIG. 1. Variable temperature 90 MHz PMR spectra of compound II in the methyl region, as a solution in CH_2Cl_2 (210-272 K) and in toluene- d_6 (298-406 K). Spectra are the result of 4-8 cw time-averaged scans. Arrows denote $^{117,119}\text{Sn}$ satellites, asterisks the methyl resonances of isomer E in the slow exchange limit.

$\Delta G^\ddagger = 13.0 \pm 0.5$ kcal/mole, which is comparable to II, and to ΔG^\ddagger for carbonyl interchange.

The results of these experiments strongly support the deformation mechanism as the low temperature pathway for tin substituent interchange in B. This is facilitated by or occurs in concert with rapid bridge-terminal interchange [9] of carbonyl ligands (a detailed kinetic analysis is in progress).

At higher temperatures, exchange processes best explained by cleavage of the metal-metal bonds are observed. Though stannylene (R_2Sn) transition metal complexes are known for R sufficiently bulky [10], this work suggests that considerable energy is required to populate such a configuration for the more usual tin substituents [6,11]. We also find compound I to exist as two isomers. The barrier for interconversion of these is $\Delta G^\ddagger = 26.6$ kcal/mole (312 K), and may reflect, in comparison to II, differences in ring strain and the ability of carbonyls to move into bridging positions.

Acknowledgments

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