must be involved at some stage. One reasonable pathway is[9]

$$(Me_3Si)_2O \xrightarrow{t\text{-BuLi}} LiCH_2SiMe_2OSiMe_3 \; -\!\circ\!\!\longrightarrow$$

$$Me_3SiCH_2SiMe_2OLi \xrightarrow{H_2O} Me_3SiCH_2SiMe_2OH$$

Reactions of *t*-butyllithium with other alkylsilyl compounds are under investigation.

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[9] This sequence would involve a 1,3-anionic rearrangement of silicon from carbon to oxygen. Such rearrangements are unknown but find precedent in the rapid anionic rearrangements of silicon–nitrogen compounds which have recently been described[10] and in the C → O rearrangements of organosilyl groups studied by Brook and his coworkers.[11]

[10] R. E. Bailey and R. West, *J. Am. Chem. Soc.*, **86**, 5369 (1964); R. West, M. Ishikawa, and S. Murai, *ibid.*, **90**, 727 (1968).

[11] A. G. Brook, *ibid.*, **80**, 1886 (1958); A. G. Brook, C. M. Warner, and M. E. McGriskin, *ibid.*, **81**, 981 (1959); A. G. Brook and B. Iachia, *ibid.*, **83**, 827 (1961).

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Some Aspects of the Molecular Dynamics of Methyl-Substituted Cyclopentadiene Compounds of Silicon and Tin

Sir:

The recent appearance of several examples of stereochemically nonrigid σ-cyclopentadienyl complexes[1-6] has resulted in apparently contradictory explanations of their behavior. We feel it important to restate the fundamental concepts involved and also report some of our preliminary work on this subject.

Muetterties[7] has already pointed out the importance of considering molecular dynamics in inorganic systems. With regard to stereochemically nonrigid ring systems, we wish to emphasize that (1) the so-called "static" or (low temperature) limiting structure need not refer to the molecules locked in a given configuration, (2) rearrangement continues to occur even though individual nonequivalent environments can be identified by some appropriate technique, and (3) nonequivalent environments can be observed only when the lifetime of the molecule in one configuration is long by comparison with the time scale of the measurement. Thus, stereochemically nonrigid cyclopentadienyl groups give rise to σ-bonded ir (10^{-13} sec) spectra but equivalent proton nmr (10^{-1} to 10^{-9} sec) signals. Moreover, these two observations place limits on the lifetime of the molecule in a given configuration. In several cases,[1,2] by going to lower temperatures, the intramolecular exchange could be slowed down sufficiently to observe the nmr spectra of the individual configurations.

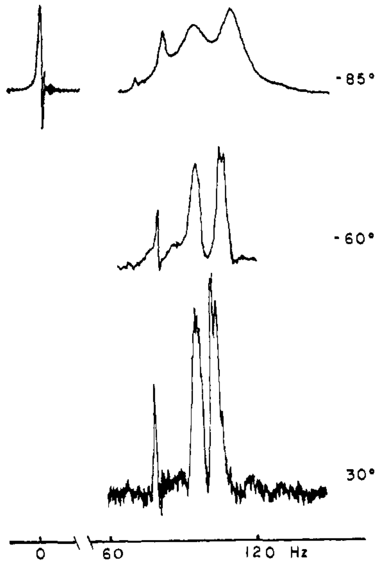

Figure 1. Proton nmr spectra of the ring protons of $(CH_3)_3Sn$-$C_5H_4CH_3$ showing broadening at temperatures below −60°. Note that the benzene resonance (as internal reference) remains sharp at this temperature. The peak at 80 Hz is due to the cyclopentadienyl resonance of $(CH_3)_3SnC_5H_5$. (Resonances are given in Hz upfield from benzene.)

The assertion by Fritz[2,4] (adopted by others[3]) that substitution of a methyl group onto the cyclopentadienyl ring causes the compound to assume a static configuration is neither verified by the following analysis nor by our experimental observations. The characteristic 2:2:3 pattern observed in the nmr for the methylcyclopentadienyl moiety in $Sn(C_5H_4CH_3)_4$, and heretofore assumed to be due to a static structure with the metal atom bonded to the unique carbon, is in fact *precisely* the pattern expected for a dynamic σ-methylcyclopentadiene group. To test this hypothesis, we have reinvestigated the temperature-dependent nmr spectrum of $Sn(C_5H_4CH_3)_4$ as well as other members of the general class of compounds $(CH_3)_nM(C_5H_5)_{4-n}$ and $(CH_3)_n$-$M(C_5H_4CH_3)_{4-n}$ where M = Si, Ge, Sn and $n = 0, 1, 2, 3$. On cooling $Sn(C_5H_4CH_3)_4$ to −80°, a noticeable broadening of the resonances was observed. With $(CH_3)_3SnC_5H_4CH_3$ we obtained at −85° the spectrum in Figure 1. Significant broadening of the ring proton resonances has occurred, clearly showing the expected dynamic behavior. Similarly, the cyclopentadienyl resonance in $(CH_3)_3SnC_5H_5$ showed broadening at this temperature.

We found it more convenient to study $(CH_3)_3SiC_5H_4$-CH_3 because, as expected, the entire range from "static" to dynamic behavior could be readily observed. The nmr spectra from −4 to +135° are given in Figure 2. From the changes in the τ 3 to 7 region it is clear that some rearrangement process is taking place although the complexity of the signals prevents a detailed analysis at present. At temperatures below +8°, the signal τ 8.0 due to the ring methyl group becomes an apparent triplet. Proton spin-decoupling measurements were carried out at −50°. Irradiation at 257 and 236 Hz downfield from the ring methyl resonance caused partial collapse of the signal at τ 8.0, but at no single frequency did irradiation produce a singlet for the ring methyl

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(1) M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Am. Chem. Soc.*, **88**, 4371 (1966).

(2) H. P. Fritz and C. G. Kreiter, *J. Organometal. Chem.* (Amsterdam), **4**, 313 (1965).

(3) R. Hüttel, U. Raffay, and H. Reinheimer, *Angew. Chem.*, **79**, 859 (1967).

(4) H. P. Fritz and K. E. Schwarzhans, *Chem. Ber.*, **97**, 1390 (1964).

(5) G. A. Shchembelov and Yu. A. Ustynyuk, *Dokl. Akad. Nauk SSSR*, **173**, 847 (1967).

(6) G. A. Shchembelov and Yu. A. Ustynyuk, *ibid.*, **173**, 1364 (1967).

(7) E. L. Muetterties, *Inorg. Chem.*, **4**, 769 (1965).

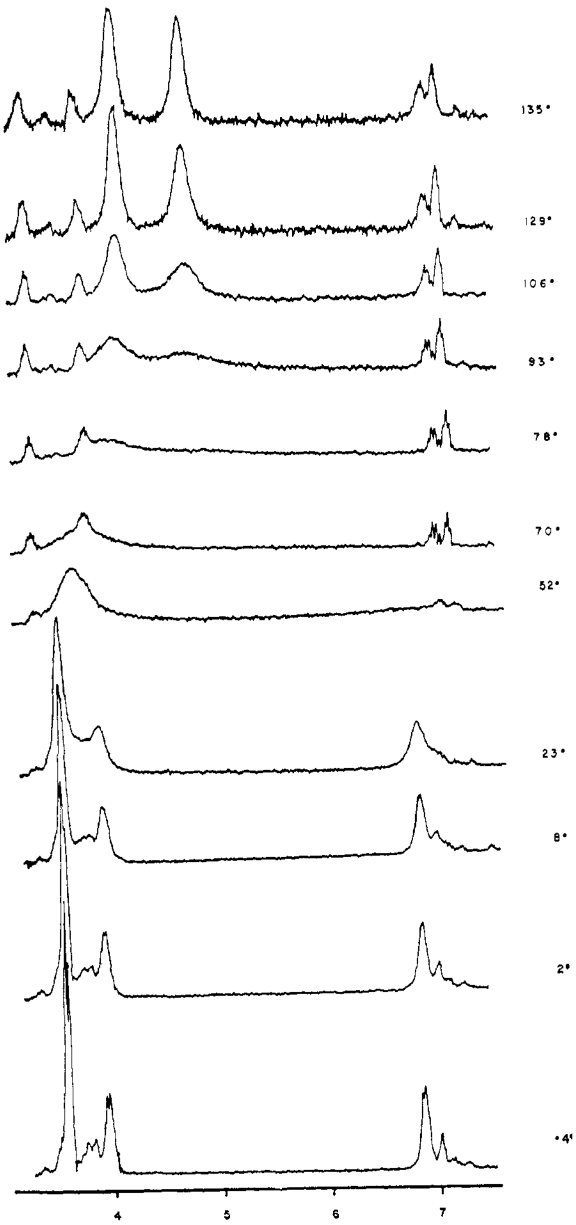
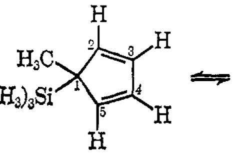


Figure 2. Proton nmr spectra of $(CH_3)_3SiC_5H_4CH_3$ in the region τ 3 to 7. The peaks at τ 3.3, 3.8, 7.1, and 7.2 appear irreversibly at temperatures above 0°. They are not present in a freshly distilled sample of $(CH_3)_3SiC_5H_4CH_3$. All other features of these spectra are completely reversible.

resonance. Thus the fine structure is due to coupling of the ring olefinic protons to the methyl group and not simply three separate methyl resonances from isomers I, II, and III. We ascribe the complex, low-temperature spectrum to the three isomers rearranging slowly on the nmr time scale. The simultaneous appearance of resonances at τ 6.9 and 7.0, assigned to the tertiary hydrogens H(5) and H(4) in structures II and III, respectively, lends support to our claims.[8]



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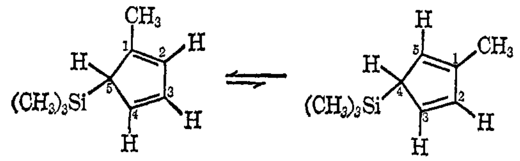

II

III

To further verify the assumption that methyl substitution on the cyclopentadienyl ring does not grossly affect the nonrigid behavior of these systems, we have prepared trimethyltinpentamethylcyclopentadiene, $(CH_3)_3SnC_5(CH_3)_5$, which shows two singlets in the nmr at τ 10.03 and 8.19 in the ratio 3:5.[9] [By comparison, hexamethylcyclopentadiene exhibits two peaks at τ 9.09 and 8.30 in the ratio 2:1.[10]] These are assigned to the trimethyltin unit and a σ-pentamethylcyclopentadienyl group undergoing rapid intramolecular rearrangement by direct analogy to the $(CH_3)_3SnC_5H_5$ system. The presence of Sn to ring methyl hydrogen coupling at the rapid exchange limit gives clear evidence that the predominant path for rearrangement is *intra*molecular and not *inter*molecular exchange, and rearrangement *via* hydride shift[5,6] is unlikely in these systems since it cannot account for the behavior of $(CH_3)_3SnC_5(CH_3)_5$ where no ring hydrogens are present. Although significant broadening of both the ring methyl and Sn-methyl resonances occur at −100°, complete collapse is not observed. Further studies are in progress on other members of the general class of group IVA compounds indicated above. A detailed report of their systematic behavior will be published soon.

[8] Either peak may be due to either isomer. We are not able at present to decide between the two alternative assignments.

[9] ^{117,119}Sn–H coupling = 50.0 and 48.0 Hz for the τ 10.03 peak. ^{117,119}Sn–H coupling (isotopes not resolved) average is 19.7 Hz for the τ 8.19 peak.

[10] L. de Vries, *J. Org. Chem.*, **25**, 1838 (1960).

[11] Alfred P. Sloan Foundation Fellow, 1967–1969.

[12] National Science Foundation, Predoctoral Fellow, 1966–1968.

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The Reactivity of Hydroxy Groups in Metal Complexes

Sir:

A recent communication[1] on the complexes of N-2-hydroxyethylethylenediamine (etolen) with cobalt(III), palladium(II), and platinum(II) prompts the author to report work on the general question of hydroxy group reactivity in these systems.

The behavior of 2-hydroxyethyl groups in complexes has been somewhat enigmatic. Apart from a low reactivity of the OH group observed in bis(N-2-hydroxyethyliminodiacetato)chromate(III),[2] studies in other complexes have suggested a total resistance to electrophilic attack.[3,4] The initial studies of Keller and Edwards[3] described the preparation of $[Co(etolen)_3]^{3+}$ by oxidation of the corresponding cobalt(II) complex. The last-mentioned reaction has since been shown to

[1] B. Das Sarma, G. J. Tennenhouse, and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **90**, 1362 (1968).

[2] R. A. Krause and S. D. Goldby, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p 143.

[3] R. N. Keller and L. J. Edwards, *J. Am. Chem. Soc.*, **74**, 215 (1952).

[4] W. C. Drinkard, H. F. Bauer, and J. C. Bailar, Jr., *ibid.*, **82**, 2992 (1960).