pound **2** (and indeed perhaps all related *monohapto*cyclopentadienyl metal compounds[10]) is correctly termed a concerted [1,5] metallotropic rearrangement with conservation of orbital symmetry.

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(3) Bonny, A.; Stobart, S. R. *J. Am. Chem. Soc.* **1979**, *101*, 2247.
(4) Compound **1** has been synthesized previously: Dolgov, B. N.; Borisov, S. N.; Voronkov, M. G. *Zh. Obshch. Khim.* **1957**, *27*, 2062. Found; bp 95-97 °C. This material and compound **2** were thoroughly characterized using IR and mass spectroscopy as well as by ^{1}H and ^{13}C NMR measurements.
(5) Assignment of the pair of lines at higher frequency and showing the larger diastereotopic splitting to $C_{2,5}$ is consistent with our earlier conclusions:[2,3] thus chlorine substitution at Si to give $(R(H)(Cl)Si^*C_5H_5{}^3$ results in a diamagnetic shift of $C_{2,5}$ to a position of low frequency of $C_{3,4}$. It can be seen from the comparison of the present data with those of ref 3 that replacement of alkyl by chlorine at Si also magnifies anisochronous effects. It follows that the unsymmetrical collapse in this region shown in Figure 1 is in accordance with a 1,2 (or 1,5) shift.
(6) Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, 95, 8678.
(7) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 2511.
(8) In which antarafacial migrations cannot occur.
(9) Anastassiou, A. G. *Chem. Commun.* **1968**, 15.
(10) The boat configuration and axial metal substitution established by X-ray crystallography for $Ph_3SnC_7H_7$ (Weidenborner, J. E.; Larrabee, R. B.; Bednowitz, A. L. *J. Am. Chem. Soc.* **1972**, *94*, 4140) clearly constitute a favorable arrangement for an analogous suprafacial [1,5] shift in this fluxional cycloheptatriene system.

Rupert D. Holmes-Smith, Stephen R. Stobart*
Department of Chemistry, University of Victoria
Victoria, British Columbia V8W 2Y2
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^{1}H NMR Assignment of the C-5′ Protons of B_{12} Coenzyme and the Synthesis of B_{12} Coenzyme Chirally Labeled in the C-5′ Position

Sir:

In the course of our study on the mechanism of action of the coenzyme B_{12} dependent enzyme dioldehydrase, we synthesized B_{12} coenzyme chirally labeled in the C-5′ position. To confirm the synthesis of chiral B_{12} coenzyme and subsequently to follow its fate in the enzymatic reactions, it was essential to have the correct NMR assignments for the C-5′ protons. These protons are directly involved in the enzymic reaction. Unfortunately, some uncertainty exists in the literature regarding these assignments. Based on model compound studies, Cockle et al.[1] have tentatively assigned these two protons to be at 0.6 and 0.9 ppm from DSS in D_2O. Brodie and Poe[2] have assigned these two protons to broad resonances at ~0.57 and 1.1 ppm in $(CD_3)_2SO$. However, in a study of the ^{1}H NMR of [5′-^{13}C]adenosylcobalamin, Hogenkamp[3] was unable to observe the expected $^{13}C-^1H$ spin-spin coupling. From this data, he concluded the peaks at 0.6 and 1.1 ppm are not due to the C-5′ protons.

To aid in the assignments, we have used [5′,5′-$^2H_2$]adenosylcobalamin.[4] The spectrum of that compound, as well as that of nonisotopically labeled cobalamin, is shown in Figures 1A and 1B. The spectrum of the nonisotopically labeled coenzyme shows a triplet at 0.6 and a doublet at 1.56 ppm which are not present in the spectrum of the deuterated coenzyme. It is, therefore, reasonable to assign these peaks to the C-5′ protons.

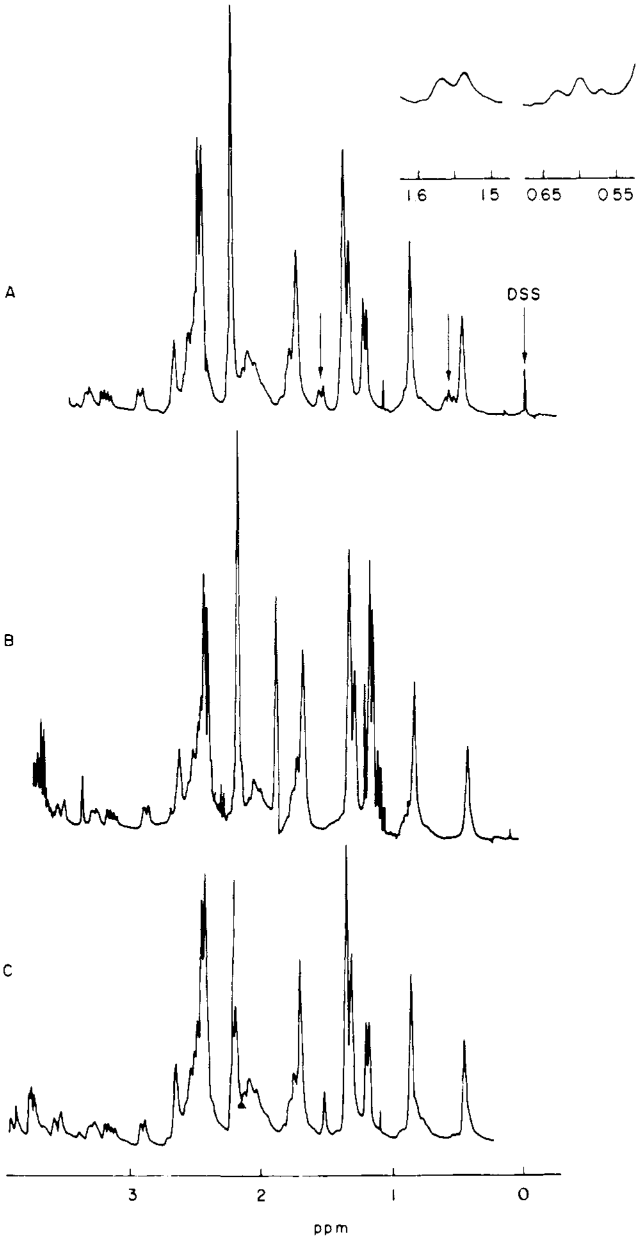

Figure 1. A: 2 mM adenosylcobalamin in D_2O. B: 2 mM [5′,5′-$^2H_2$]adenosylcobalamin in D_2O (it contains contaminants from paper chromatography). C: 2 mM 5′-chiral [5′-^{2}H]adenosylcobalamin in D_2O. The insert in the upper right-hand corner is an expanded spectrum (5.4×) showing the regions of the C-5′ protons. The NMR spectra were taken with a 270-MHz NMR spectrometer at a probe temperature of 20 °C built by A.R.[12]

To confirm these assignments, we have undertaken decoupling experiments. Irradiation at 0.6 ppm changes the doublet at 1.56 ppm into a singlet, and, conversely, irradiation at 1.56 ppm changes the triplet at 0.6 ppm into a doublet. This finding clearly indicates the two peaks in question are spin-spin coupled with each other. With decoupling techniques, we are also able to assign the C-4′ proton. Irradiation at 2.6 ppm causes the triplet at 0.6 ppm to change into a doublet. This suggests the C-4′ proton resonates at 2.6 ppm. These results then confirm our assignment for the two prochiral C-5′ hydrogens.

Figure 1C shows the spectrum of the coenzyme synthesized from (5′-*R*)-[5′-^{2}H]adenosine.[5,6] The absorption at 0.6 ppm is missing and there is now a singlet at 1.56 ppm. These results establish that no significant racemization occurred during the

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synthesis and that we have synthesized B_{12} coenzyme chirally labeled at C-5′.[7]

The coupling constant between the C-4′ proton and the *pro-R* C-5′ proton is ~9 Hz, while the coupling constant between the C-4′ proton and the *pro-S* C-5′ proton is ~0 Hz. This suggests the dihedral angle between the C-4′ proton and the *pro-S* C-5′ proton to be ~90° and the dihedral angle between the C-4′ proton and the *pro-R* C-5′ proton to be ~170°.[8,9]

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(6) The chirally labeled coenzyme was synthesized using a modified procedure of Hogenkamp.[11] In this procedure, 5.5 mg of (5′-*R*)-[5′-^{2}H]adenosine (20.5 μmol)[5] was converted into (5′-*S*)-[5′-^{2}H]-5′-chloro-5′-deoxyadenosine as described. The nucleoside synthesized was reacted with cob(I)alamin generated by the reduction of 50 mg of aquocobalamin (36 μmol) with Zn/NH_4Cl (300 mg of Zn and 625 mg of NH_4Cl) in 5 mL of H_2O for 40 min in the dark. After the excess Zn was filtered off, the coenzyme was purified by phenol extraction, CM cellulose column chromatography (H^+ form, developed with H_2O and eluted with 5 mM acetic acid), and paper electrophoresis on Whatman 3MM paper (using 0.5 N NH_4OH as electrolyte, ~10 V/cm). The final yield was ~15 mg (~50% from adenosine).

(7) The stereochemistry at the C-5′ position of the chiral B_{12} coenzyme is assumed to be of the *R* configuration. This assignment is based on the assumption that the chlorination of adenosine undergoes inversion as suggested by Hogenkamp[11] and that the displacement of the chlorine of 5′-chloroadenosine by cob(I)alamin is by an S_N2 mechanism. With this assumption, one can assign the *pro-R* proton to be at 0.6 ppm and the *pro-S* proton to be at 1.56 ppm.

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Alex Cheung, Ronald Parry, Robert H. Abeles*
Publication No. 1284
Graduate Department of Biochemistry
Brandeis University, Waltham, Massachusetts 02254
Department of Chemistry, Rice University
Houston, Texas 77001

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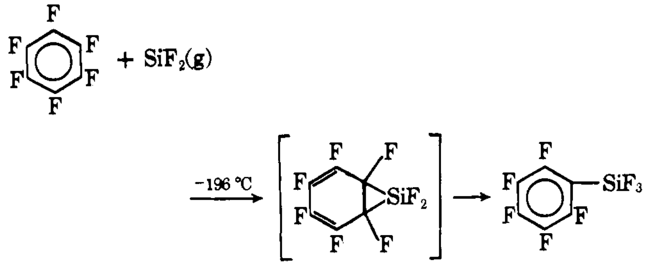
Rediscovery of the Gas-Phase Chemistry of Difluorosilylene Generated by Thermal Reduction

Sir:

Difluorosilylene (silicon difluoride), though often referred to as a carbene analogue, has not shown a behavior quite parallel to that of carbenes.[1-3] Ever since Margrave et al. opened the study of the chemistry some 14 years ago, it has been believed that SiF_2 in the gas phase is not very reactive.[4] As a result, practically all SiF_2 chemistry has been done by cocondensation with other reagents at −196 °C, and reactive diradicals $\cdot(SiF_2)_n\cdot$ (in most cases $n = 2$) are believed to be responsible for much of the observed chemistry:

$$SiF_4(g) + Si(s) \xrightarrow{1200\ °C} 2SiF_2(g) \xrightarrow[-196\ °C]{\text{reagent}} \text{products}$$

There are several reactions[1] ($SiF_2 + H_2O$, $SiF_2 + H_2S$, $SiF_2 + C_6F_6$, etc) which yielded products containing only one SiF_2. In the reaction of SiF_2 with C_6F_6, one gets insertion into the C–F bond, perhaps through the mechanism involving a short-lived siliarane intermediate. Similar mono-SiF_2 reaction products were obtained from SiF_2 reaction with HFC=CH_2, F_2C=CH_2, etc. In most of this cocondensation work, the gas-phase reactants were mixed in the vacuum system before trapping them at −196 °C.



Another exception is the study of the reactions of conjugated dienes with $^{31}SiF_2$ formed in nuclear recoil systems by Tang and his co-workers.[5,6] The $^{31}SiF_2$ molecules generated in such systems possess very high thermal energies and the reaction conditions are very different from those of cocondensation; nonetheless, Tang's work does show that monomeric $^{31}SiF_2$ in gas phase is reactive toward conjugated diene systems. Also, Margrave et al.[1] have reported the gas-phase reactions of SiF_2 with O_2 to form $SiOF_2$ and higher silicon oxyfluorides.

Recently Seyferth's group reported their study on the chemistry of difluorosilirane and reinterpreted our previous results of the reactions with olefins and alkynes through the formation of unstable silirane and silirene intermediates.[7] In supporting Seyferth's view, Thompson's group reported in a recent communication the ^{29}Si NMR spectroscopic evidence for the participation of monomeric SiF_2 in the formation of the copolymer which accounts for 70% of the total products in the cocondensation reaction of SiF_2 and propene.[8]

These results seem to suggest that the observed chemistry of SiF_2 in cocondensation systems could actually be the results of direct reactions between monomeric SiF_2 and unsaturated organic molecules in gas phase. This implication prompted us to reinvestigate the chemistry of SiF_2 in the gas phase, which has not been examined carefully. A natural first choice for such a study is the reaction with 1,3-butadiene, to see how the results compare with those of the nuclear recoil $^{31}SiF_2$ reactions studied by Tang. This is our first report of these studies.

Difluorosilylene was generated by Margrave's method[1] and reacted with butadiene which was introduced into the system from another inlet. The mixture stayed in a closed 12-L bulb for 25 min—ten times the half-life of SiF_2 under a pressure of 0.1 Torr,[4] before it was pumped out and condensed at −196 °C. The evacuated bulb was filled with the gas mixture again and the procedure repeated. Such a procedure ensured that little SiF_2 would be left over when the gas mixture was finally condensed and formation of $\cdot(SiF_2)_n\cdot$ diradicals should be negligible. The wall of the bulb became cloudy during the reaction, presummably owing to the formation of a thin layer of SiF_2-containing material which hydrolyzed immediately on exposure to moisture. However, no polymeric materials were observed on condensation at −196 °C.

The reaction was studied under three different conditions: (i) total pressure of 0.2 ~ 0.4 Torr with approximately equal molar of SiF_2 and C_4H_6, (ii) total pressure of 400 Torr with a SiF_2–C_4H_6 ratio of ~1:2000, and (iii) total pressure of 2 Torr with a SiF_2–C_4H_6 ratio of ~1:1.

Condition i was a simulation of the conditions used in cocondensation experiments; ii and iii were chosen arbitrarily to get a rough idea of pressure effect. However, the results from

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