"formladehyde equivalent". Needless to say, these observations convey attractive mechanistic suggestions for certain types of CO reduction catalysis.[15,16]

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High-Resolution NMR Spectra in Inhomogeneous Magnetic Fields: Application of Total Spin Coherence Transfer Echoes

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The homogeneity of the static magnetic field is the most common limitation on the resolution of NMR spectra, and a variety of spin echo techniques have been devised to extract high-resolution information from inhomogeneously broadened samples.[1-9] In this communication, we demonstrate a novel method for recording high-resolution spectra which, for a coupled spin system, gives transitions at the same frequencies and resolution as would be seen with an absolutely homogeneous field. The method uses multiple quantum coherence transfer echoes[5] and is applicable to both single quantum and multiple quantum spectra of coupled systems consisting of one or more spin species in liquids, liquid crystals, or solids. Unlike previous methods, it is not restricted by the relative size of the shift differences and the spin-spin couplings;[4,7,8] it does not require two-dimensional projections to obtain high resolution;[5,9] and it does not increase the number of transitions nor alter their positions.[6]

As an illustrative example, Figure 1 shows single quantum proton spectra of a nonspinning 10-mm sample of acetaldehyde partially oriented in a nematic liquid crystal. Figure 1a is the normal single-pulse Fourier transform spectrum and shows the inhomogeneity of the magnetic field to be greater than 1 ppm. Figure 1b is the total spin coherence transfer echo spectrum and gives line widths of ~4 Hz (~0.02 ppm). The line positions are governed by both direct and indirect spin-spin couplings and a chemical shift difference, and the spectral simulation in Figure 1c shows that all are preserved. The line widths obtained are independent of magnetic field homogeneity in the limit of negligible diffusion.[1,2]

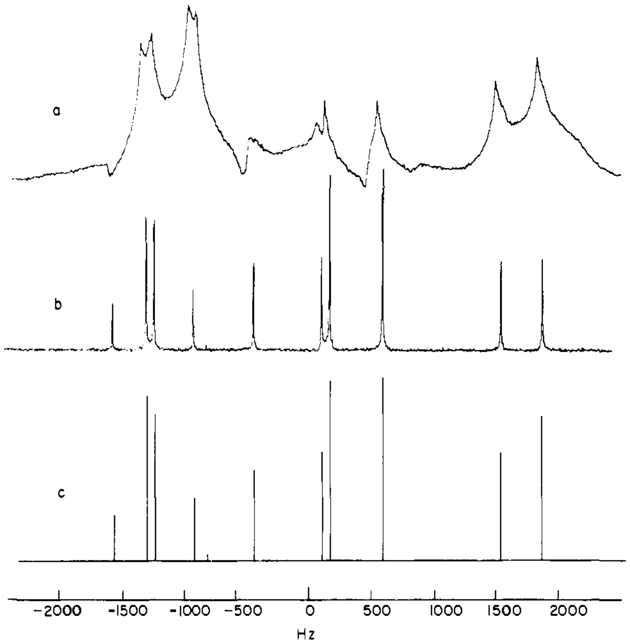

Figure 1. Removal of inhomogeneous broadening by total spin coherence transfer echo spectroscopy. (a) Single quantum Fourier transform proton spectrum of acetaldehyde in a nematic liquid crystal was taken in an inhomogeneous field and then (b) with the pulse sequence of Figure 2. The simulation of this AB$_3$ system is shown in (c) with parameters J_{AB} = 2.8 Hz, ν_{AB} = 1360.9 Hz, D_{AB} = −179.0 Hz, D_{BB} = 458.6 Hz. The lines of E symmetry are absent, because they do not correlate with the total spin transition.

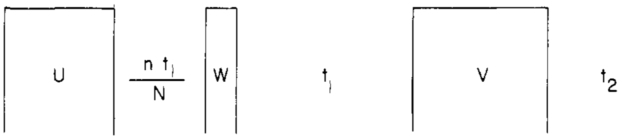

Figure 2. General sequence to use total spin coherence transfer echoes to produce multiple quantum spectra without inhomogeneous broadening. U is a preparation sequence for N-quantum (total spin) coherence. This evolves for a time nt_1/N at which time a pulse or sequence of pulses W transfers the total spin coherence to other n-quantum coherence. At time t_1 echoes are observed through transfer by V to single quantum coherence. Fourier transformation with respect to t_1 gives a homogeneous n-quantum spectrum. For the spectrum in Figure 1b, U was the sequence $(\pi/2)-(\tau/2)-\pi-(\tau/2)-(\pi/2)$, W was a $\pi/2$ pulse, V was omitted, $N = 4$ and $n = 1$. The $\pi/2$ time was 4.5 μs.

To understand the essence of the technique, consider a system of N coupled proton spins. The idea is to exploit the properties of the unique N-quantum coherence, the *total spin coherence*, which connects the extreme eigenstates of the coupled spin system. In the resonant rotating frame (defined so that the sum of the chemical shifts is zero), this coherence evolves only under the inhomogeneous Zeeman term and independently of chemical shift differences and spin-spin couplings. By having the spins evolve for a period in this N-quantum coherence and then in any other n-quantum coherence, the inhomogeneous term can be completely removed from the n-quantum spectrum.

Figure 2 is a general schematic diagram of pulse sequences for total spin coherence transfer echo spectroscopy. The total spin coherence is prepared by a propagator U acting on the equilibrium density operator. Evolution proceeds in the inhomogeneous field for a time nt_1/N where $n = \Delta M$ (difference in Zeeman quantum numbers) is the order of the coherence we wish to observe. At this time a coherence transfer to the lines of order n takes place under the action of the homogeneous propagator W, and evolution proceeds for the time t_1, at the frequencies of interest. At the end of t_1 only that part of the coherence which spent period nt_1/N as $\pm N$ quantum coherence and period t_1 as $\mp n$ quantum coherence has amplitude independent of magnet inhomogeneity. The only modulation of the amplitude of this echo is due to the internal

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Hamiltonian acting during t_1. This modulation is monitored by mixing the coherence back to observable magnetization with the propagator V and detecting during t_2. Fourier transformation of $S(t_1,t_2)$ gives the homogeneous spectrum along the ω_1 axis. No 2-D data manipulation is necessary, and in fact the spectrum of Figure 1b was taken with sampling at $t_2 = 0$ only. The multidimensional analogue of total spin coherence transfer echo spectroscopy would correspond to a projection[5] of cross peaks which correlate the total spin transition with other totally symmetric transitions. When $n \neq 1$ this would involve collecting data over two variable time dimensions in addition to t_2. The sequence presented here shows that this or any other projection is unnecessary.

The method is limited by the necessity of exciting the total spin coherence of the coupled system. To date, this has been achieved for more than a few spins only in oriented molecules.[7,10] In addition lines which belong to an uncoupled subsystem or to other than the totally symmetric irreducible representation do not appear. This can be both an advantage and disadvantage. Resolution is increased, but information is lost that would be available in a perfect magnet, e.g., the shift difference between different uncoupled subsystems.

The propagator U may be as simple as the sequence $(\pi/2)-(\tau/2)-\pi-(\tau/2)-(\pi/2)$ or may be a selective excitation sequence.[10] The other propagators may be single pulses or more elaborate and selective pulse sequences. For the single quantum case ($n = 1$), no mixing is necessary between t_1 and t_2 and Figure 1b was obtained with $V = 1$. When $n \neq 1$ an advantage of more elaborate mixing propagators is that *properly phased lines* of known relative amplitude and homogeneous width may be obtained for multiple quantum transitions. Modulation of the relative rf phases of the propagators allows complete separation of the desired transitions of different orders and eliminates artifacts arising from nonidealities of the pulse sequence.[8] Quantitative aspects of line intensities, phases, widths, separation techniques, and the role of diffusion will be presented in a full paper.

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6-Silafulvene via Silylcarbene Rearrangement from Diazo-2-silacyclohexa-3,5-diene

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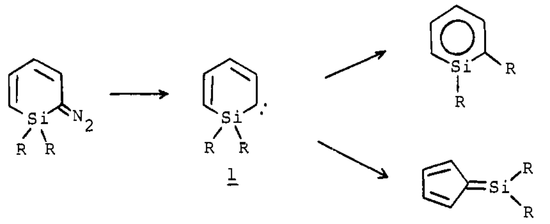
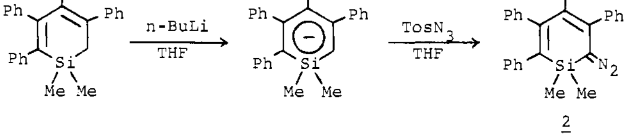
Both silabenzene and silafulvene are attractive molecules in silicon chemistry. The thermally induced retroene route to silabenzene has recently employed by the Barton group,[1] and the existence was confirmed by matrix method at low temperature.[2] More recently, evidence for the intermediacy of 6-silafulvene by retroene reaction was also presented independently by the groups of Barton and Sakurai.[3]

We have reported that α-silylcarbenes undergo 1,2 migration of the substituent from silicon to a carbene center to give reactive silicon-carbon double-bonded intermediates.[4] A failed attempt to obtain silabenzene by 1,4-methyl migration of 4,4-dimethyl-4-silacyclohexadienylidene was reported.[5] One might expect that 2,2-dimethyl-2-silacyclohexadienylidene (**1**) would give silabenzene or/and 6-silafulvene by 1,2 migration of the substituent. We present here strong evidence for the generation of 6-silafulvene from the reaction of diazo-2,2-dimethyl-3,4,5,6-tetraphenyl-2-silacyclohexa-3,5-diene (**2**).



Synthesis of **2** was by a modification of the original method of Doering and Depuy.[6] Treatment of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclohexa-2,4-diene (7.0 g, 16.4 mmol) with equimolar *n*-butyllithium in THF at 0 °C formed the red silacyclohexadienyl anion immediately.[7] Addition of the anion to a solution of *p*-toluenesulfonyl azide (3.9 g, 19.8 mmol) in THF at −77 °C produced, upon workup, **2** in 36% yield. The yellow crystalline diazo compound **2** was stable enough to be recrystallized, mp 134.5–135.5 °C dec; NMR (CCl_4, δ) 0.43 (s, 6 H, $SiMe_2$) and 6.37–7.33 (m, 20 H, ArH); IR (KBr) 2030 (N_2) and 1260 cm^{-1} (SiMe); mass spectrum, *m/e* 426 ($M^+ - 28$).



When a benzene solution of **2** (252 mg, 0.556 mmol) containing excess *tert*-butyl alcohol was refluxed in a sealed Pyrex tube at ca. 100 °C in the presence of catalytic amount of anhydrous cupric sulfate (57 mg), vigorous reaction occurred and ceased in a few minutes. Separation of the reaction mixture by silica gel chromatography gave cyclopentadienyl-*tert*-butoxysilane **4** in 96% yield as white crystals, mp 147–148 °C; NMR (CCl_4, δ) −0.23 (s, 6 H, $SiMe_2$), 0.80 (s, 9 H, *t*-Bu), 4.63 (s, 1 H, SiCH), and 6.83–7.40 (m, 20 H, ArH); IR (KBr) 1240 (SiMe) and 1050 cm^{-1} (SiOC); mass spectrum, *m/e* 500 (M^+). The upfield shift of the silyl methyl groups was observed by the shielding effects of the two phenyl rings at the 1 and 4 positions.

The formation of **4** provides strong evidence for 1,2,3,4-tetraphenyl-6,6-dimethyl-6-silafulvene (**3**) by the migration of the dienyl group to the carbene center. It seems reasonable that the dipolar form of the silafulvene would have enhanced importance because of the stability of the cyclopentadienyl anion. No product from 1,2-dimethyl-3,4,5,6-tetraphenyl-1-silabenzene by the methyl migration was found.

The evidence for the silafulvene **3** was further substantiated by similar reactions with methanol and methanol-*d*. The reaction of **2** with methanol gave 1,2,3,4-tetraphenyl-1,3-cyclopentadiene (**6**)[8] in 91% yield, mp 177–178 °C, probably formed by metha-

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