N(2), 162.6 (1)°; C(9)–Pd(1)–Cl, 174.5 (1)°, and the two virtually equivalent coordination planes are orientated almost perpendicular to each other (88.5 (2)°).[6] The Pd(1)–Cl–Pd(2) angle of 134.8 (1)° is a dominant structural feature, which taken with the two fairly long Pd–Cl distances (2.463 (1) and 2.458 (1) Å) gives rise to a Pd–Pd separation (4.544 (2) Å) that is much greater than that found in complexes where there is a distinct M–M bond.[7] The large deviation of this angle from that expected for a tetrahedral halide atom (two bonds, two long pairs; cf. isoelectronic $[(C_5H_5)(CO)_2Fe(\mu\text{-}I)Fe(CO)_2(C_5H_5)]$, ∠Fe–I–Fe = 110.8 (1)°)[8] is presumably steric in origin.

The solution ^1H NMR data of **1a** [60 MHz; CD_2Cl_2; δ CH_2 4.03, CH_3 2.95] evidences retention of both the Lewis acid–base interaction and coordination of the N donor ligands on the NMR time scale.[9] Since in the solid-state structure there are not only inequivalent CH_2NMe_2 groupings but also diastereotopic CH_2 and Me groups, the NMR solution observation of only single CH_2 and CH_3 signals means that there is a fluxional process, most likely a rotation about the metal–halogen axes, that renders the CH_2NMe_2 environments equivalent. The ^1H NMR data for the other dinuclear species **1b–e** are similar. There is also NMR evidence for a further fluxional process[10] involving a fast reversible dissociation of the dinuclear units initiated by traces of water (a weak coordinating ligand).

Complexes **1a–e** are, as far as we are aware, the first structurally characterized species in which a single halide bridge atom binds two nickel triad metal centers without the support of bidentate phosphine or arsine ligands as found in, for example, A-frame complexes.[11]

To investigate the versatility of the $[M(N\text{–}C\text{–}N)]^+$ system to act as a Lewis acid, we have extended our interest to hydride-containing species (see scheme). From the reaction of $[Pt(N\text{–}C\text{–}N)(CF_3SO_3)]$ and $[Pt(N\text{–}C\text{–}N)(COOH)]$[12] in benzene at 50 °C was isolated the monohydrogen bridge complex $[(N\text{–}C\text{–}N)Pt(\mu\text{-}H)Pt(N\text{–}C\text{–}N)]^+$, **2**,[13] in almost quantitative yield [^1H NMR (CD_2Cl_2) δ –4.54 (Pt,H,Pt), J(Pt,H) = 576 Hz]. This is the first complex containing N donor ligands that has a structural relationship to the unique dihydride $[Ph(PEt_3)_2Pt(\mu\text{-}H)Pt(PEt_3)_2H]^+$,[1] which also contains a three-center two-electron M–H–M bridge bond.

It is also possible to synthesize dihydride-bridged complexes $[N\text{–}C\text{–}N)M(\mu\text{-}H)_2Pt(PPh_3)_2]^+$ (M = Pd (**3a**), Pt (**3b**)) by using a procedure in which a reactive hydride is generated in situ from the reaction of Pt(0) phosphine species and gaseous H_2. From spectroscopic data [^1H NMR (acetone-d_6) δ (**3a**) –3.84 $(\mu\text{-}H)_2$, J(Pt,H) = 818 Hz); (**3b**) –1.86 $(\mu\text{-}H)_2$, $J(Pt_A,H)$ = 707 Hz, $J(Pt_B,H)$ = 385 Hz],[14] these complexes are anticipated to have a geometry in which there is both a four- and a five-coordinate center, a situation also existing in the related tertiary phosphine species $[(PR_3)_2Pt(\mu\text{-}H)_2Pt(PR_3)_2H]BF_4$ (R = Ph, Cy, Et).[15]

The present results emphasize that for mononuclear complexes of the nickel triad Lewis acid–base pairing, via either a halide or hydride ligand, is readily attained, and therefore it may play an important role in the reaction mechanisms of ligand substitution and exchange. It is worth noting that the terdentate ligand (N–C–N) has enabled the isolation of $[(N\text{–}C\text{–}N)Pt(\mu\text{-}RNCHNR)AgX]$ species[16] containing a direct Ag–Pt interaction, and further research in this laboratory is being directed to a better understanding of this ligand's role in stabilizing heteronuclear complexes.

Acknowledgment. Professor K. Vrieze and Professor L. M. Venanzi are thanked for helpful discussions. This investigation was supported in part by the Netherlands Foundation for Chemical Research (SON), with financial aid from the Netherlands Organization for Pure Research (ZWO) (A.L.S.)

Registry No. 1a, 82112-75-2; **1b**, 82112-77-4; **1c**, 82112-79-6; **1d**, 82112-81-0; **1e**, 82112-83-2; **2**, 82112-85-4; **3a**, 82112-87-6; **3b**, 82112-89-8; $Pt(NCN)(CF_3SO_3)$, 82112-90-1; Pt(NCN)(COOH), 82112-91-2; $[Pt(NCN)(H_2O)]BF_4$, 82112-93-4; $[Pt(NCN)(H_2O)]BF_4$, 82112-95-6; Pt(NCN)Cl, 82112-96-7; Pt(NCN)Br, 67507-09-9; Pt(NCN)I, 82112-97-8; Pd(NCN)Cl, 82112-98-9; $Pt(COD)_2$, 12130-66-4.

Supplementary Material Available: Tables of positional and thermal parameters for $[(Pd\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\})_2(\mu\text{-}Cl)]BF_4$ and of bond distances and bond angles (5 pages). Ordering information is given on any current masthead page.

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(6) Calculated from the least-squares planes of the carbon atoms of the two phenyl moieties.

(7) In $[Pd_2(Ph_2PCH_2PPh_2)_2Br_2]$ the M–M separation is only 2.699 (5) Å: Holloway, R. G.; Penfold, B. R.; Colton, R.; McCormick, M. *J. Chem. Soc., Chem. Commun.* **1976**, 485–486.

(8) Cotton, F. A.; Frenz, B. A.; White, A. J. *J. Organomet. Chem.* **1973**, *60*, 147–152.

(9) N donor coordination to palladium centers is established from ^1H NMR shift data, but for platinum species this is subtantiated by the presence of ^{195}Pt couplings with the CH_2NMe_2 signals.

(10) Mixing [Pt(N–C–N)Br] with $[Pt(N\text{–}C\text{–}N)(H_2O)]BF_4$ in CH_2Cl_2 at room temperature in ratios other than 1:1 gives rise to only *one* CH_2NMe_2 ^1H NMR resonance pattern (with ^{195}Pt satellites).

(11) The geometric constraints of bridging bidentate ligands can have a significant influence on the geometry of A-frame complexes. The structure of $[Pd_2(Ph_2PCH_2PPh_2)_2(\mu\text{-}I)(CH_3)I]BF_4$ shows a Pd–I–Pd angle of 67.0 (1) Å: Olmstead, M. M.; Farr, J. P.; Balch, A. L. *Inorg. Chim. Acta* **1981**, *52*, 47–54.

(12) Synthesized from $[Pt(N\text{–}C\text{–}N)(H_2O)]BF_4$ and NaCOOH in H_2O at room temperature (^1H NMR (benzene-d_6) δ 9.78 (COOH, J(Pt,H) = 52 Hz).

(13) The synthesis of a terminal Pt–H bond by thermal elimination of CO_2 from a Pt(COOH) group has been documented. See for example: Catellani, M.; Halpern, J. *Inorg. Chem.* **1980**, *19*, 566–568.

(14) Pt_A is bound to the two PPh_3 groups. The ^{195}Pt satellites arising from Pt_B are significantly broadened owing to incomplete collapse of spin–spin coupling of ^{195}Pt to the ^{14}N donor atoms.

(15) Bracher, G.; Grove, D. M.; Pregosin, P. S.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 155–156; *Angew. Chem.* **1979**, *91*, 169–170.

(16) Van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K. *Inorg. Chem.* **1982**, *21*, 2026.

Multiplet Selection in Crowded ^1H NMR Spectra via Double Quantum Coherence

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We propose a new method for tackling a perennial problem in NMR spectroscopy, that of spectral overcrowding. It allows one to detect specific multiplet resonances in circumstances where they would be partially or totally obscured by line overlap in a conventional ^1H NMR spectrum. All that is required is prior knowledge of the approximate chemical shifts and J couplings of the protons of interest.

Our approach was inspired by recent experiments[1,2] for observing ^{13}C–^{13}C spin–spin coupling in natural-abundance ^{13}C NMR spectra. The method, known as INADEQUATE,[2-4] relies on the momentary creation of double quantum coherence between coupled ^{13}C nuclei to suppress the strong signals from molecules with an isolated ^{13}C. INADEQUATE was later extended into a two-dimensional Fourier transform experiment[5,6] for correlating

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(1) Bax, A.; Freeman, R.; Kempsell, S. P. *J. Am. Chem. Soc.* **1980**, *102*, 4849.

(2) Bax, A. Doctoral Thesis, Technische Hogeschool Delft, The Netherlands, 1981.

(3) Richarz, R.; Ammann, W.; Wirthlin, T. *J. Magn. Reson.* **1981**, *45*, 270.

(4) Sørensen, O. W.; Freeman, R.; Frenkiel, T.; Mareci, T. H.; Schuck, R. *J. Magn. Reson.* **1982**, *46*, 180.

(5) Bax, A.; Freeman, R.; Frenkiel, T. A. *J. Am. Chem. Soc.* **1981**, *103*, 2102.

(6) Bax, A.; Freeman, R.; Frenkiel, T. A.; Levitt, M. H. *J. Magn. Reson.* **1981**, *43*, 478.

(7) Aue, W. P.; Bartholdi, E.; Ernst, R. R. *J. Chem. Phys.* **1976**, *64*, 2229.

(8) Equation 3 and the cosine part of eq 2 are also valid for strong coupling.[7]

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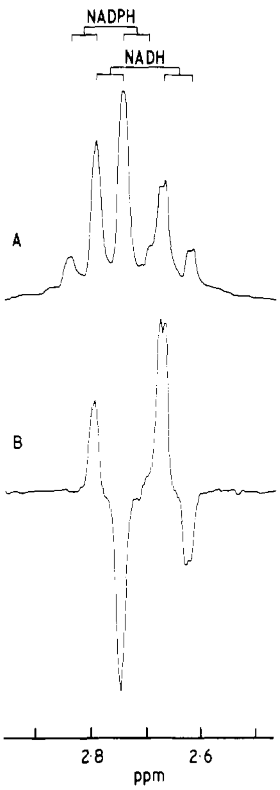

Figure 1. (A) Partial 360-MHz ^{1}H NMR spectrum of NADH and NADPH (10 mM each) in D_2O. (B) DOUBTFUL spectrum obtained with the transmitter placed in the center of the two NADH C(4)H doublets. Seven spectra, obtained with the pulse sequence in eq 1 (t_1 = 0, 6, 12, 18, 24, 30, and 36 ms) were coadded. τ = 12.5 ms ($\simeq (4J)^{-1}$); there were 32 scans for each t_1 value. The small splitting of the higher field NADH doublet probably arises from coupling to the C(5) proton.[12]

coupled ^{13}C nuclei on the basis of their characteristic double quantum frequencies.

We use the following radio-frequency pulse sequence:[1]

$$90°(X)\text{–}\tau\text{–}180°(Y)\text{–}\tau\text{–}90°(X)\text{–}t_1\text{–}90°(X,Y,\text{–}X,\text{–}Y)\text{–}\text{acquisition}(X,\text{–}Y,\text{–}X,Y) \quad (1)$$

Double quantum coherence, created by the initial 90°(X)–τ–180°(Y)–τ–90°(X) sequence, is allowed to precess, as in the two-dimensional experiments[5,6] for a time t_1 (the evolution period). The final 90° mixing pulse then reconverts it to single quantum coherence which is detected as usual. Cycling the phases of the mixing pulse and the receiver in opposite senses as indicated suppresses both longitudinal magnetization and residual single quantum coherence present at the end of the evolution period.[1]

To see how this procedure can be adapted to select specific multiplets, consider the case of two weakly coupled spins (AX). Neglecting relaxation, the amplitude of their double quantum coherence just before the final pulse depends on their spin–spin coupling, J, and on ω_1, the double quantum frequency:

$$I_2(\tau,t_1) = \sin(2\pi J\tau)\cos(\omega_1 t_1) \quad (2)$$

ω_1 is the algebraic sum of the chemical shifts (Ω_A, Ω_X) of the two spins with respect to the transmitter frequency[6-8] ω:

$$\omega_1 = \Omega_A + \Omega_X - 2\omega \quad (3)$$

When the transmitter is placed at the exact center of the AX spectrum, ω_1 is zero and I_2 is independent of t_1. Signals from other multiplets will in general have nonzero double quantum frequencies and hence exhibit cosinusoidal behavior during t_1. Thus the mixing pulse generates transverse magnetization amplitude modulated at a frequency ω_1. By coaddition of a number of spectra obtained with different t_1 times, oscillating components tend to cancel while the desired signals add coherently. In this way one suppresses not only singlet resonances as in ^{13}C INADEQUATE but also the unwanted multiplets.

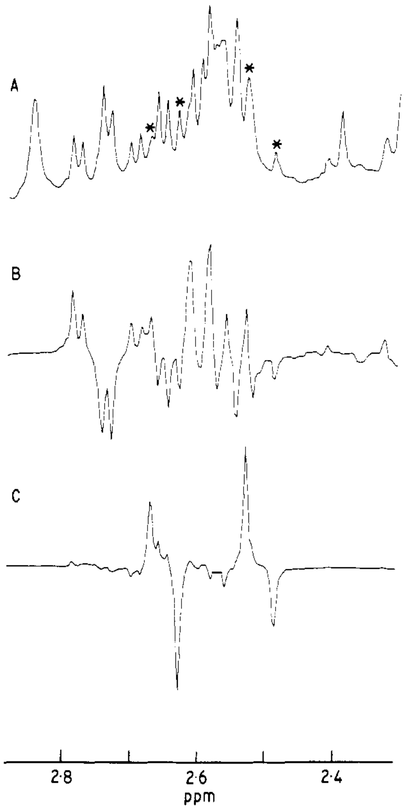

Figure 2. (A) Partial NMR spectrum of a yeast cell extract in D_2O. Citrate peaks are marked with asterisks. (B) DOUBTFUL spectrum, τ = 15.0 ms, t_1 = 10 μs, 32 scans. (C) DOUBTFUL spectrum, t_1 = 1, 2 . . . 40 ms, clearly showing the two citrate doublets. Citrate concentration is $\simeq$1 mM.

Experiments were performed at 360 MHz on a Bruker HX-360 spectrometer controlled by an Aspect 2000 computer. Although good results could be achieved with 4-step phase cycling (eq 1), a 32-step cycle[1,2] giving slightly better suppression was used to obtain the spectra shown in the figures. The phases of the receiver and all four pulses in eq 1 are incremented together in 90° steps, and this 16-step sequence is repeated with the phase of the first pulse and of the receiver inverted. $\tau = (4J)^{-1}$ was chosen in the examples described below even though this is not optimal for sensitivity in strongly coupled spin systems.[9]

Figure 1B shows a spectrum of an equimolar mixture of the coenzymes NADH and NADPH[10] obtained by the above method.[11] The corresponding conventional NMR spectrum (Figure 1A) consists of two strongly overlapping AB patterns from the nicotinamide C(4) methylene protons of the two nucleotides. Good suppression of the NADPH lines is achieved with the transmitter centered on the NADH quartet using evolution times, t_1, of 0, 6, 12, 18, 24, 30, and 36 ms. The up–down intensity pattern is characteristic of this type of experiment.[1-3]

A more severe test of the technique is provided by a yeast cell extract composed of a variety of small metabolites. We have focused on citric acid, a molecule which, like the previous example, has magnetically isolated, nonequivalent CH_2 protons. The NMR spectrum of this mixture is rather cluttered in the 2.5–3.0-ppm range (Figure 2A), and the citrate resonances are largely obscured. A DOUBTFUL[11] spectrum with t_1 = 10 μs is shown in Figure 2B; note the good suppression of singlet resonances at 2.85 and 2.39 ppm but that strong multiplets still overlap the lines of interest. However, when 40 such spectra (t_1 = 1, 2 . . . 40 ms) are added

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[9] Bax, A.; Freeman, R. *J. Magn. Reson.* **1980**, *41*, 507.

[10] NADH, β-nicotinamide adenine dinucleotide; NADPH, NADH C2′ phosphate.

[11] We suggest as a name for this experiment, DOUBTFUL (DOUBle quantum Transitions for Finding Unresolved Lines).

[12] Oppenheimer, N. J.; Arnold, L. J.; Kaplan, N. O. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 3200.

(Figure 2C), the desired lines become well resolved.[13,14]

Although AB spin systems were chosen for these examples, the method is equally successful for two weakly coupled spins. The situation is slightly more complex, however, for three or more coupled nuclei. Several double quantum transitions with different frequencies (which, in general, are not independent of the J couplings) can occur, making the choice of a suitable transmitter position less straightforward. Similarly, the optimum preparation time, τ, is less easily determined.

In practice it is not necessary to have more than an approximate prior knowledge of the shifts and J couplings involved. Given a reasonable choice of transmitter frequency, a few spectra with short t_1 (say <5 ms) once added together often reveal the required line positions. Location of these lines is assisted by the distinctive up–down patterns. Measurements of Ω and J then give the correct ω and τ.

One can envisage a variety of applications for this technique, for example: analysis of complex mixtures such as occur in oil and coal research; detection and monitoring of concentration of metabolites in suspensions of living cells; detection of resonances lying under strong solvent lines; detection of small molecules in the presence of macromolecules. Further work especially on the quantitative aspects of the method is in progress.

Acknowledgment. We are grateful to the Netherlands Organisation for the Advancement of Pure Research (ZWO) for financial support and to the Royal Society, London, for the award of a research fellowship (P.J.H.). It is a pleasure to acknowledge a stimulating discussion with Dr. A. Bax.

Registry No. NADH, 58-68-4; NADPH, 53-57-6.

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[13] Through use of the basic 4-step phase cycling and a 1s relaxation delay between scans, DOUBTFUL spectra of similar quality to Figure 2C could be obtained in 2.5 min.

[14] Previous methods of "editing" NMR spectra[15-20] give subspectra containing, for example, *all* doublets or *all* singlets *and* triplets. DOUBTFUL goes further in selecting *specific* multiplets from such subspectra.

[15] Campbell, I. D.; Dobson, C. M.; Williams, R. J. P.; Wright, P. E. *FEBS Lett.* **1975**, *57*, 96.

[16] Levitt, M. H.; Freeman, R. *J. Magn. Reson.* **1980**, *39*, 533.

[17] Doddrell, D. M.; Pegg, D. T. *J. Am. Chem. Soc.* **1980**, *102*, 6388.

[18] Bodenhausen, G.; Dobson, Ç. M. *J. Magn. Reson.* **1981**, *44*, 212.

[19] Bendall, M. R.; Doddrell, D. M.; Pegg, D. T. *J. Am. Chem. Soc.* **1981**, *103*, 4603.

[20] Bolton, P. H. *J. Magn. Reson.* **1981**, *45*, 418.

Molecular and Crystal Structure of 1,1-Bis(*tert*-butyldimethylsilyl)-2,2-bis(trimethylsilyl)ethylene, the Most Twisted Known Olefin, and Unusual Rearrangement during Its Preparation[1]

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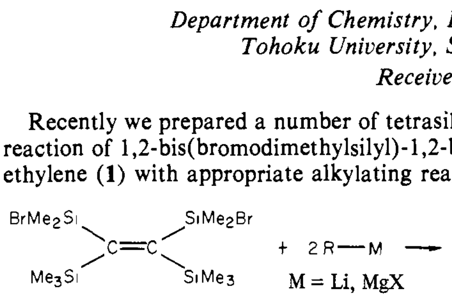
Recently we prepared a number of tetrasilylethylenes by the reaction of 1,2-bis(bromodimethylsilyl)-1,2-bis(trimethylsilyl)ethylene (**1**) with appropriate alkylating reagents.[2]



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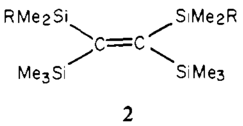

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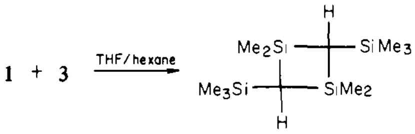
Table I. Bond Lengths and Bond Angles with Estimated Standard Deviations for 1,1-Bis(*tert*-butyldimethylsilyl)-2,2-bis(trimethylsilyl)ethylene (5) at 15 °C

	Bond Lengths (Å)		
Si(1)–C(1)	1.926 (4)	Si(2)–C(10)	1.878 (5)
Si(2)–C(2)	1.915 (5)	Si(2)–C(11)	1.873 (5)
Si(1)–C(3)	1.872 (5)	C(5)–C(6)	1.537 (7)
Si(1)–C(4)	1.885 (5)	C(5)–C(7)	1.531 (7)
Si(1)–C(5)	1.917 (4)	C(5)–C(8)	1.545 (7)
Si(2)–C(9)	1.878 (5)	C(1)–C(2)	1.370 (7)
	Bond Angles (Deg)		
C(1)–Si(1)–C(3)	115.8 (2)	C(9)–Si(2)–C(11)	110.8 (2)
C(1)–Si(1)–C(4)	119.7 (2)	C(10)–Si(2)–C(11)	106.7 (2)
C(1)–Si(1)–C(5)	104.6 (2)	Si(1)–C(1)–C(2)	120.5 (3)
C(2)–Si(2)–C(9)	111.9 (2)	Si(2)–C(2)–C(1)	124.2 (3)
C(2)–Si(2)–C(10)	105.9 (2)	Si(1)–C(5)–C(6)	112.5 (3)
C(2)–Si(2)–C(11)	118.6 (2)	Si(1)–C(5)–C(7)	110.8 (3)
C(3)–Si(1)–C(4)	102.9 (2)	Si(1)–C(5)–C(8)	108.9 (3)
C(3)–Si(1)–C(5)	107.5 (2)	C(6)–C(5)–C(7)	109.2 (4)
C(4)–Si(1)–C(5)	105.4 (2)	C(6)–C(5)–C(8)	107.4 (4)
C(9)–Si(2)–C(10)	101.2 (2)	C(7)–C(5)–C(8)	107.9 (4)
Si(1)–C(1)–Si(1′)	119.0 (2)		
Si(2)–C(2)–Si(2′)	111.6 (2)		

These tetrasilylethylenes are sterically very crowded and show interesting properties; for example, an X-ray crystallographic study on tetrakis(trimethylsilyl)ethylene (**2a**, R = Me) reveals that the double bond of **2a** is twisted by 29.5°.[2c] An obvious approach to more congested olefins involves the reaction of **1** with a bulky alkylating reagent.

However, reactions of **1** with isopropylmagnesium chloride and *tert*-butylmagnesium chloride resulted in the formation of neither expected alkylated products **2** nor hydrosilane (**2b**, R = H). Instead, 1,1,3,3-tetramethyl-2,4-bis(trimethylsilyl)-1,3-disilacyclobutane (**4**) was obtained. The reaction leading to **4** apparently involves an electron-transfer process because lithium anthracenide and even sodium metal can cause the same reaction. Yields in percent and Z/E ratios of **4**, which depend on **3**, were as follows: 22, 9:1 with **3a**; 26, 9:1 with **3b**; 38, 2:1 with **3c**; 14, 1/1 with **3d**.



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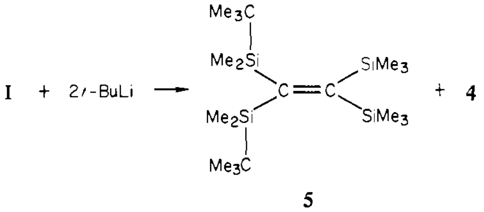
3a, $(CH_3)_2CHMgCl$ (reflux, 8 h)
b, $(CH_3)_3CMgCl$ (reflux, 8 h)
c, [anthracene]$^{-}\cdot$ Li^{+} (reflux, 2.5 h)
d, Na (room temperature, 7 h)

The reaction of **1** with *tert*-butyllithium at 0 °C gave the unexpected 1,1-bis(*tert*-butyldimethylsilyl)-2,2-bis(trimethylsilyl)ethylene (**5**) in 13% yield along with **4** (Z/E 1:1.05) in 13% yield. A very small amount of an isomer of **5** exists in the reaction mixture as detected by GC–MS and NMR but has not yet been separated.



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[1] Chemistry of Organosilicon Compounds. 161.

[2] (a) Sakurai, H.; Nakadaira, Y.; Kira, M.; Tobita, H. *Tetrahedron Lett.* **1980**, *21*, 3077. (b) Sakurai, H.; Tobita, H.; Kira, M.; Nakadaira, Y. *Angew. Chem., Int. Ed. Engl.* **1980**, 19, 620. (c) Sakurai, H.; Nakadaira, Y.; Tobita, H.; Ito, T.; Toriumi, K.; Ito, H. *J. Am. Chem. Soc.* **1982**, *104*, 300.

0002-7863/82/1504-4288$01.25/0