Table III. Selected Interatomic Distances (Å) and Angles (Deg) in $(LiSiMe_3)_2\cdot(TMEDA)_3$

Bond Distances

Li(1)-Si(1)	2.70 (1)	Li(2)-Si(2)	2.69 (1)
Li(1)-N(3)	2.16 (1)	Li(2)-N(2)	2.16 (1)
Li(1)-N(5)	2.18 (1)	Li(2)-N(1)	2.17 (1)
Li(1)-N(6)	2.21 (1)	Li(2)-N(4)	2.15 (1)
Si(1)-C(1)	1.906 (8)	Si(2)-C(15)	1.89 (1)
Si(1)-C(2)	1.957 (9)	Si(2)-C(16)	1.88 (1)
Si(1)-C(3)	1.90 (1)	Si(2)-C(17)	1.92 (1)

Bond Angles

C(1)-Si(1)-C(3)	99.1 (5)	Li(1)-Si(1)-C(3)	119.2 (4)	Li(2)-Si(2)-C(16)	116.3 (5)
C(2)-Si(1)-C(3)	99.0 (5)	C(15)-Si(2)-C(16)	100.9 (4)	Li(2)-Si(2)-C(17)	115.0 (5)
C(1)-Si(1)-C(2)	98.9 (4)	C(16)-Si(2)-C(17)	101.0 (8)	N(1)-Li(2)-N(2)	87.0 (5)
Li(1)-Si(1)-C(1)	118.9 (4)	C(15)-Si(2)-C(17)	98.7 (5)	N(3)-Li(1)-N(6)	84.7 (5)
Li(1)-Si(1)-C(2)	117.2 (4)	Li(2)-Si(2)-C(15)	121.6 (4)		

us to determine its structure in the solid state by single-crystal X-ray diffraction techniques in an attempt to correlate the unusual reactivity of this species with its structural features.

The results of these studies are depicted in Figure 1 which shows an ORTEP diagram of the molecule with the atoms labeled. The features which are of major interest and importance are (1) the fact that there is no Li-Si-Li bridge bonding which shows that the hexameric aggregate, $(LiSiMe_3)_6$, has been completely destroyed, and (2) that the Li-Si bond distance is relatively long with a value of 2.70 Å even when compared to the average Li-Si distance of 2.68 Å, observed in the uncomplexed hexamer.[10] Further, examination of the bond angles around the silicon and lithium atoms (see Table I) shows that the C-Si-C angles are sharp with an average value of 100°. This should be compared with value observed in $(LiSiMe_3)_6$ of 103.3°,[10] of 102.9° in $Mg(SiMe_3)_2\cdot DME$,[11] and 103.0° in $Li_2Hg(SiMe_3)_4$.[12] This further constraint, on the C-Si-C bond, may be interpreted in terms of additional negative charge being transferred to the $SiMe_3$ moiety and, along with the long Li-Si distance, account for both the high and unusual reactivity of this species.

Further work is currently in progress to determine the aggregation state of this species in solution and to determine if other silyl- or organolithium derivatives can be obtained which have both similar reactivity and structures.

$(LiSiMe_3)_6$ was prepared by the methods previously reported.[9] Approximately 1 g of the purified crystalline material was transferred, in an argon-filled drybox, to a reaction vessel which could be closed off and evacuated. This vessel was removed from the drybox, transferred to a vacuum system, and evacuated. Dry cyclopentane (~5 mL) was then distilled into the vessel followed by slow infusion of TMEDA. After several adjustments in concentration, crystals which appeared to be of suitable quality for X-ray study were obtained. Examination of a number of these crystals on the X-ray diffractometer, however, showed that they diffracted only weakly at room temperature. For that reason, data were collected at low temperature (-22 °C) using Cu K$\bar{\alpha}$ radiation on a Syntex $P2_1$ diffractometer. The crystal was found to be monoclinic and was ultimately assigned to the space group $P2_1$ on the basis of the systematic absences. The crystallographic data on the unit cell, and other pertinent data, are collected in Table I. The structure was solved by light atom techniques through the use of MULTAN[13] which gave positions for all of the nonhydrogen atoms except for a portion of one TMEDA unit. The structure was refined by standard techniques.[14] During the refinement, it was found that the TMEDA unit not originally located was disordered. This has been partially treated by assignment of 50% occupancy factors to two positions for one of the carbon atoms—represented by C(24) and C(25). This problem, along with thermal motion, led to initial difficulty in the solution of the structure and so far have prevented a better refinement of the structure.

Atomic coordinates for the nonhydrogen atoms are presented in Table II, and selected interatomic distances and angles are listed in Table III. Anisotropic thermal parameters, a complete listing of bond distances and bond angles, hydrogen positional parameters, and observed and calculated structure amplitudes are available.[15]

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Registry No. $(LiSiMe_3)_2\cdot(Me_2NCH_2CH_2NMe_2)_3$, 81583-50-8.

Supplementary Material Available: Tables containing anistropic thermal parameters, isotropic thermal parameters for hydrogen atoms, hydrogen positional parameters, all interatomic distances and angles, and observed and calculated structure amplitudes (20 pages). Ordering information is given on any current masthead page.

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(15) See the paragraph at the end of the paper regarding supplementary material.

Enhancement of ^{29}Si NMR Signals by Proton Polarization Transfer

Bradley J. Helmer and Robert West*

Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

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Summary: The application of polarization transfer via the INEPT pulse sequence to ^{29}Si NMR has been investigated for a wide variety of silicon compounds. The method was

Table I. Measured and Theoretical Decoupled Enhancements for ^{29}Si NMR of Various Silicon Compounds

	E_d(measd)[7]	E_d(theor)[a]	δ	J, Hz
Me_4Si	9.3	10.8	0	6.6
Me_3SiCl	7.5	9.4	29.87	6.8
Me_2SiCl_2	4.8	7.8	31.66	7.3
$MeSiCl_3$	2.9	5.8	12.34	8.1
t-Bu_2SiCl_2	5.5	13.1	39.10	7.8
t-Bu_2SiF_2	5.8	13.1	−7.76	6.3 (J_{SiF} = 325.3)
t-$BuSiCl_3$	3.6	9.4	17.75	10.4
t-$BuMeSiCl_2$	4.9	10.8	36.85	8.1
Ph_2SiCl_2	3.2	6.5	6.47	6.6 (br)
Ph_2SiH_2	5.0	5.0	−33.19	198.3, 5.9 (ortho), 1.0 (meta)
$PhSiH_3$	5.7	5.8	−59.75	199.9, 6.4 (ortho), 1.1 (meta)
Et_3SiH	3.6	5.0	0.28	185.3, 6.9
$(EtO)_3SiH$	4.7	5.0	−58.82	286.1, 3.4
$(MeO)_4Si$	5.5	10.8	−78.25	3.7
$(HMe_2Si)_2O$	5.1	5.0	−4.42	204.3, 7.0 (sept), 1.3 (d)
$(Me_3\mathit{Si}OMe_2Si)_2O$	6.5	9.4	7.17	6.7
$(Me_3SiOMe_2\mathit{Si})_2O$	6.2	7.8	−21.66	7.3
$(Me_2SiO)_5$	7.1	7.8	−21.14	7.4
p-$(Me_3Si)_2C_6H_4$	7.3	9.4	−4.22	unresol
$(Me_3Si)_2C_2$	8.9	9.4	−19.13	7.1
$(Me_3Si)_2NH$	4.4	9.4	2.40	broad unresol
$(Me_3Si)_2S$	6.6	9.4	14.27	6.8
$(Me_3Si)_2$	7.3	9.4	−19.60	6.5, 2.7
$(HMes_2Si)_2$	4.7	5.0	−53.01	184.1
$(t$-$BuMeSi)_4$	4.2	10.8	−13.41	unresol
$(Me_2Si)_6$	7.3	7.8	−41.86	6.2, 3.3

[a] Calculated from $E_d = \gamma(H)/\gamma(Si)_n{}^{1/2}(1 - 1/n)^{(n-1)/2}$, according to ref 4.

successful for silicon bonded to H, Me, OMe, *t*-Bu, and Ph. The substantial signal enhancement which results from this technique can reduce the time needed to obtain a ^{29}Si NMR spectrum more than 100-fold.

Four characteristics of the ^{29}Si nucleus have made ^{29}Si NMR difficult: (1) it has a low natural abundance (4.7%); (2) it has a relatively small gyromagnetic ratio, resulting in a small energy difference between the spin states and hence a small Boltzmann population difference; (3) it has a negative gyromagnetic ratio, so the nuclear Overhauser effect can give reduced signal intensities; and (4) it has long spin–lattice e relaxation times, T_1, which slow the rate at which FT pulses can be repeated. The final three problems can all be circumvented by employing a method Morris and Freeman[1] have termed "insensitive nuclei enhanced by polarization transfer" or INEPT. This method consists of a multipulse sequence whereby nuclear spin polarization is transferred from protons (large Boltzmann population difference and short relaxation times) to other nuclei to which the protons are coupled (I = ^{13}C,[1] ^{15}N,[2] ^{10,11}B,[3] ^{29}Si,[4] ^{119}Sn,[4] ^{103}Rh,[5] ^{109}Ag[5]).

A typical pulse sequence for obtaining ^{1}H-decoupled I NMR spectra is as follows: 90°[H,x] − τ − 180°[H,x], 180°[I,x] − τ − 90°[H,y], 90°[I,x] − $\Delta/2$ − 180°[H,x], 180°[I,x] − $\Delta/2$ − decouple, acquire, where 90°[H,x] represents a pulse along the x axis of appropriate length (in microseconds) to rotate the H magnetization 90° from its original position parallel to the z axis. τ and Δ represent delay periods (in milliseconds) during which the magnetization vectors are allowed to precess.

The only two parameters to be manipulated in obtaining a spectrum are Δ and τ. The optimum value of Δ (Δ_{opt} = $(\pi J)^{-1}$ arcsin $n^{-1/2})^4$ is dependent on both the number of coupled protons, n, and the coupling constant, J, whereas τ (τ_{opt} = $(4J)^{-1}$) is dependent only on the coupling constant. Because the relationship of Δ and τ to the decoupled enhancement, E_d, is sinusoidal, E_d is fairly insensitive to variations in τ and Δ:

$$E_d = n(\gamma(H)/\gamma(I)) \sin(\pi J\Delta) \cos^{n-1}(\pi J\Delta) \sin(2\pi J\tau)^{4,6}$$

Doddrell et al.[4] have successfully applied polarization transfer to the simple methyl substituted silanes Me_4Si, Me_3SiCl, and Me_2SiCl_2, which gave signal enhancement factors of 9.2, 8.5, and 5.0, respectively. We have found the method to be extremely powerful and generally applicable to a wide variety of mono- and polysilanes (Table I). The substituents found to be useful for polarization transfer include H, Me, OMe, *t*-Bu, and Ph. This illustrates that polarization transer is dependent only on the existence of a sufficiently strong coupling between Si and H and not on the number of bonds separating Si and H.

The enhancement factors[7] obtained vary from 2.9 to 9.3. The deviation of the measured enhancement factors from the theoretical values results from T_2 relaxation during the pulse sequence. This problem is most severe where J_{SiH} is very small, giving long delay period τ and Δ, and where T_2 is very fast, as in compounds containing Si–Cl or Si–N bonds.

The significance of the application of polarization transfer to ^{29}Si NMR can best be seen in terms of time saving. Since the enhanced population difference is "pumped" from ^{1}H to ^{29}Si during each multipulse cycle, only ^{1}H with its relatively fast spin–lattice relaxation (T_1) has to be given time to relax. This allows repetition of

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scans approximately three to six times faster than with the conventional single pulse experiment. Additionally, a given signal/noise level can be attained $(E_d)^2$ times faster from polarization transfer than from the single pulse metods. These factors combine to give time saving factors varying from about 30 to 300.

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Registry No. Me_4Si, 75-76-3; Me_3SiCl, 75-77-4; Me_2SiCl_2, 75-78-5; $MeSiCl_3$, 75-79-6; $t\text{-}Bu_2SiCl_2$, 18395-90-9; $t\text{-}Bu_2SiF_2$, 558-63-4; $t\text{-}BuSiCl_3$, 18171-74-9; $t\text{-}BuMeSiCl_2$, 18147-18-7; Ph_2SiCl_2, 80-10-4; Ph_2SiH_2, 775-12-2; $PhSiH_3$, 694-53-1; Et_3SiH, 617-86-7; $(EtO)_3SiH$, 998-30-1; $(MeO)_4Si$, 681-84-5; $(HMe_2Si)O$, 3277-26-7; $(Me_3SiOMe_2Si)_2O$, 141-62-8; $(Me_2SiO)_5$, 541-02-6; $p\text{-}(Me_3Si)_2C_6H_4$, 13183-70-5; $(Me_3Si)_2C_2$, 14630-40-1; $(Me_3Si)_2NH$, 999-97-3; $(Me_3Si)_2S$, 3385-94-2; $(Me_3Si)_2$, 1450-14-2; $(HMeS_2Si)_2$, 74864-45-2; $(t\text{-}BuMeSi)_4$, 63357-19-7; $(Me_2Si)_6$, 4098-30-0.

Coupling of Iridium-Bound Methylene with Ethylene†

David L. Thorn

Central Research and Development Department
E.I. du Pont de Nemours and Company
Experimental Station, Wilmington, Delaware 19898

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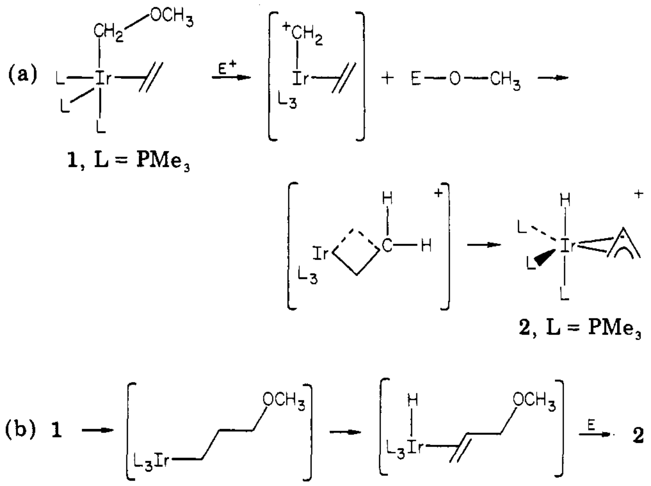
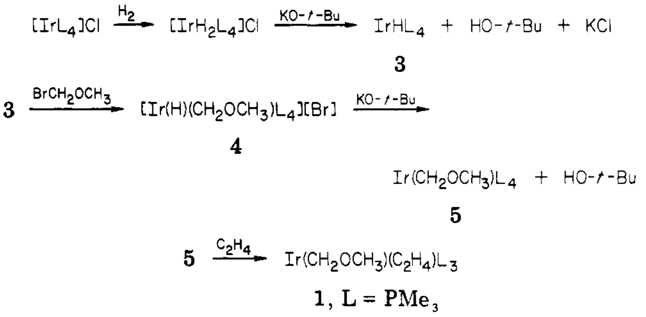
Summary: **The (methoxymethyl)ethyleneiridium(I) complex $Ir(CH_2OCH_3)(C_2H_4)(P(CH_3)_3)_3$ (1) reacts readily with trimethylsilyl trifluoromethanesulfonate to form the hydrido allyl compound $[IrH(C_3H_5)(P(CH_3)_3)_3][CF_3SO_3]$ (2). Suspected intermediates include a methylene ethylene complex which rapidly converts to a metallacyclobutane complex and subsequently undergoes β elimination to form 2.**

The currently favored mechanism for the olefin metathesis reaction requires, as one important step, the coupling of an olefin with a transition-metal carbene ligand to form a metallacyclobutane complex.[1] Examples of the intramolecular reaction of a metal-bound olefin with a metal-bound carbene or alkylidene ligand, in well-characterized metal complexes, are however few[2,3] and are generally confined to complexes of the earlier transition metals.[4,5] Methoxymethyl complexes of the later transition metals have been found to be convenient precursors to methylene complexes, which in turn react with olefins to form cyclopropanes.[6,7] Some of these latter reactions are believed to occur by a stepwise process in which the olefin is never directly bonded to the metal in the usual η^2 fashion.[7,8]

Scheme I



Scheme II



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† Contribution No. 2981.

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