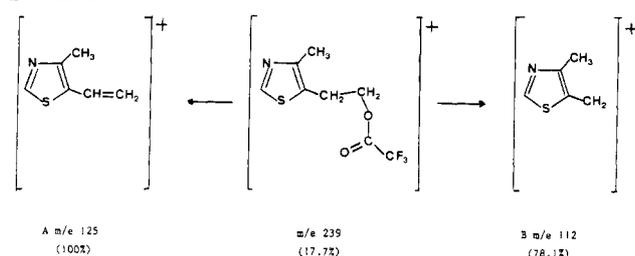
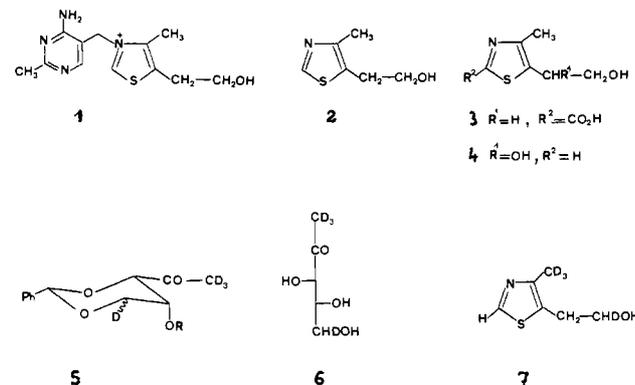


Scheme I



dication of incorporation of 1-deoxy-D-threo-pentulose without carbon-carbon bond cleavage.



The labeled precursor utilized in the present investigation, 1-deoxy-D-threo-[1-<sup>2</sup>H<sub>3</sub>,5-<sup>2</sup>H<sub>1</sub>]pentulose (**6**) was synthesized from 2,4-O-benzylidene-D-[4-<sup>2</sup>H<sub>1</sub>]threose, which is available from D-[1-<sup>2</sup>H<sub>1</sub>]arabinitol by standard methods.<sup>10,11</sup> Reaction of the threose derivative with trideuteriomethylmagnesium iodide in ether then gave a mixture of protected, epimeric pentane tetrols, which was oxidized by the stannylene procedure<sup>12</sup> to 3,5-O-benzylidene-1-deoxy-D-threo-2-[1-<sup>2</sup>H<sub>3</sub>,5-<sup>2</sup>H<sub>1</sub>]pentulose **5**.<sup>13</sup> The labile, free pentulose **6** was prepared just before use by mild, acidic hydrolysis of **5** (4:1 water-acetic acid, 45 min at 80 °C).<sup>14</sup>

Nongrowing, washed cells of *Escherichia coli*, derepressed for the biosynthesis of thiamine, were incubated in the presence of the labeled pentulose **6** in a medium containing the pyrimidine of thiamine, L-tyrosine, and glucose. The thiamine was then extracted, and cleaved by bisulfite to give HET in the usual way. This was converted to the trifluoroacetic ester for MS examination.<sup>15</sup>

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(13) Crystals, mp 96-97 °C (cyclohexane-ethyl acetate), [ $\alpha$ ]<sub>D</sub><sup>20</sup> -90° (c 2.2, methanol);  $\nu_{\text{max}}^{\text{film}}$  1715 (CO), 3400 cm<sup>-1</sup> (OH); *m/e* (relative intensities) 225 (0.4, M - H), 181 (20), 180 (100, M - CD<sub>3</sub>CO), 46 (64, CD<sub>3</sub>CO<sup>+</sup>); the validity of this interpretation was checked by comparison with the fragmentation of the undeuterated analogue. A satisfactory analysis was found, and the 250-MHz <sup>1</sup>H NMR spectrum was compatible with the conformation as in **5**. Compound **5** in its unlabeled form was further characterized by its O-acetate, mp 100 °C (ethyl acetate-cyclohexane), [ $\alpha$ ]<sub>D</sub><sup>20</sup> -101° (c 2.2, methanol).

(14) <sup>1</sup>H NMR spectra show that **6** is a 3:2 mixture of pentuloses epimeric at C-5.

(15) A shikimate auxotroph mutant of *E. coli* (strain 83-1) was cultivated according to a described procedure<sup>1</sup> in the presence of adenosine. The cells were washed and resuspended in a minimal medium without glucose. This suspension (105 mL, dry weight of cells 2 mg/mL) was added to the labeled pentulose **6** (0.46 mmol) in water (5 mL), and then stirred for 5 min at 37 °C. The pyrimidine of thiamine (50  $\mu$ g), tyrosine (2  $\times$  10<sup>-4</sup> M) and glucose (to a final concentration of 0.4%) were added, and the suspension was stirred again for 1 h at 37 °C. Thiamine was extracted, and HET was obtained as described before.<sup>9</sup> The crude thiazole was taken over in a mixture of carbon tetrachloride (50  $\mu$ L) and trifluoroacetic anhydride (5  $\mu$ L) and stirred for 5 min. Then phosphate buffer (0.5 M, pH 6; 0.5 mL) was added, the mixture was stirred, and the organic layer recovered with a syringe through the aqueous layer.

The relevant fragmentations of HET trifluoroacetate, according to ref 7 are given in Scheme I. In the present investigation, the observed incorporations<sup>16</sup> were as follows: species with four deuterium atoms were present to the extent of ca 19% in the molecular ion and 22% in fragment A. On the other hand, there was 21% of a species with three deuterium atoms in fragment B. Species with one to five deuterium atoms, other than those mentioned above, were only present to an insignificant extent in the molecular ion and fragments A and B. Now fragment A retains the hydrogen atoms of the CH<sub>3</sub> and CH<sub>2</sub>OH groups of HET, while, in fragment B, the CH<sub>2</sub>OH group is lost. Thus, this fragmentation shows the presence of species **7** in biosynthetic HET.

From an estimation of the total amount of HET biosynthesized during the incubation, one can calculate that ca. 25% originated from deoxypentulose **6**. The identity of the distributions of the label in the five-carbon chains of both the precursor **6** and the HET indicated incorporation without rupture. Otherwise, fragments of **6** would have mixed with the unlabeled precursors of the thrice as much abundant, unlabeled HET to give a completely different pattern. A Schiff base of tyrosine and **6** seems a probable intermediate.<sup>17</sup> The presence in cells of 1-deoxy-D-threo-pentulose or a phosphorylated derivative has not been recorded so far.

(16) A Ribermag R 10-10 gas chromatograph-mass spectrometer equipped with a 25-m  $\times$  0.34-mm Girdel capillary column packed with CPSIL 5 was used at 150°C. Volume of injections 1.5  $\mu$ L.

(17) In purely chemical experiments, incubation of 1-deoxy-D-threo-pentulose, tyrosine, or glycine and hydrogen sulfide in DMF solution gave traces of thiazoles **2** and **4**, which could be detected by bioautography.

## Sonochemistry and Sonocatalysis of Iron Carbonyls

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The chemical effects of high-intensity ultrasound have long been known to arise from cavitation: the creation, expansion, and adiabatic compression of gas vacuoles in solution during sonication.<sup>1</sup> The intense, but transient, local heating and compression produced during cavitation have been calculated<sup>2,3</sup> to reach as high as 10 000 °C and 10 000 atm, thus producing a variety of high-energy species in solution. The effects of high-intensity ultrasound on transition-metal and organometallic complexes have not been previously studied. We report herein the observed sonochemistry of the neutral iron carbonyls and the use of high-intensity ultrasound to initiate catalysis of olefin isomerization by these complexes. The iron carbonyls were chosen for our initial studies because of their well-studied thermal and photochemical reactivities.<sup>4-6</sup>

The thermolysis, ultraviolet photolysis, and multiphoton infrared photolysis of Fe(CO)<sub>5</sub> serve as a useful backdrop to this present work. Thermolysis<sup>7</sup> of Fe(CO)<sub>5</sub> above 100 °C gives pyrophoric, finely divided iron powder; ultraviolet photolysis<sup>8</sup> yields Fe(CO)<sub>4</sub>,

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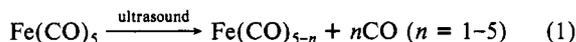
Table I

| system <sup>a</sup>                                   | d[Fe <sub>3</sub> (CO) <sub>12</sub> ]/dt,<br>mM/h | d[Fe]/dt,<br>mmol/h | relative yield <sup>b</sup> of<br>Fe <sub>3</sub> (CO) <sub>12</sub> , % |
|---|--|---------------------|--|
| neat Fe(CO) <sub>5</sub>                              | 1.59   | 1.19                | 3.8  |
| 0.77 M Fe(CO) <sub>5</sub> in decalin                 | 1.27   | 2.45                | 1.5  |
| 0.10 M Fe(CO) <sub>5</sub> in decalin                 | 1.11   | 0.68                | 4.7  |
| 0.10 M Fe(CO) <sub>5</sub> in decane                  | 0.45   | 0.55                | 2.4  |
| 0.10 M Fe(CO) <sub>5</sub> in octane                  | 0.32   | 0.13                | 6.9  |
| 0.10 M Fe(CO) <sub>5</sub> in 0.5M heptane in decalin | 0.54   | 0.15                | 9.8  |
| 0.10 M Fe(CO) <sub>5</sub> in heptane                 | 0.15   | <0.001 <sup>c</sup> | >82  |

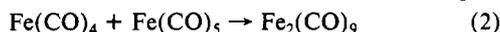
<sup>a</sup> 0 °C, 20 kHz, ~150 W, 10-mL volume, under Ar atmosphere. <sup>b</sup> Based on equiv of Fe. <sup>c</sup> None detected.

which reacts in solution with Fe(CO)<sub>5</sub> to form Fe<sub>2</sub>(CO)<sub>9</sub>; multiphoton infrared photolysis<sup>8</sup> in the gas phase yields isolated Fe atoms. Multiple ligand dissociations, producing Fe(CO)<sub>3</sub>, Fe(CO)<sub>2</sub>, etc., are not generally possible by ordinary thermal or photochemical processes (although this can occur in low-temperature inert matrices<sup>9</sup> and by gas-phase laser photolysis<sup>10</sup>). These observations underline the dual difficulties inherent in creating controlled multiple ligand dissociation: first, to deliver sufficient energy in a utilizable form and, second, to quench the highly energetic intermediates before complete ligand loss occurs.

Sonication of Fe(CO)<sub>5</sub>, neat or in decalin, decane, octane, or heptane, yields Fe<sub>3</sub>(CO)<sub>12</sub> and finely divided iron as shown in Table I.<sup>11</sup> The primary process induced by sonication of iron carbonyl may be described by reaction 1. Several observations allow us

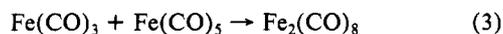


to comment on the distribution of CO loss. For example, any Fe(CO)<sub>4</sub> produced would react<sup>2</sup> with the remaining Fe(CO)<sub>5</sub> according to reaction 2. We do not, however, observe the pro-



duction of Fe<sub>2</sub>(CO)<sub>9</sub> during sonolysis of Fe(CO)<sub>5</sub>. Sonolysis of Fe<sub>2</sub>(CO)<sub>9</sub> in decalin yields Fe(CO)<sub>5</sub> and finely divided iron at rates fast compared to Fe<sub>3</sub>(CO)<sub>12</sub> formation. Sonolysis of Fe<sub>2</sub>(CO)<sub>9</sub> in decalin in the presence of Fe(CO)<sub>5</sub> similarly does not yield Fe<sub>3</sub>(CO)<sub>12</sub>. Thus we conclude that production of Fe(CO)<sub>4</sub> may occur during sonolysis of Fe(CO)<sub>5</sub> to yield Fe<sub>2</sub>(CO)<sub>9</sub>, which is rapidly sonochemically cleaved but that it certainly is *not* an intermediate on route to Fe<sub>3</sub>(CO)<sub>12</sub>. Direct sonication of Fe<sub>3</sub>(CO)<sub>12</sub> leads to neither detectable declusterification nor formation of iron.

The production of Fe<sub>3</sub>(CO)<sub>12</sub> probably results from initial sonochemical production of Fe(CO)<sub>3</sub>, which may then react according to reactions 3 and 4. An alternate mechanism would



produce Fe<sub>2</sub>(CO)<sub>8</sub> by dimerization of Fe(CO)<sub>4</sub>. Since cavitation produces rather localized hot spots, the local concentration of Fe(CO)<sub>4</sub> during sonolysis may be high enough to make this alternative plausible. The reaction of Fe<sub>2</sub>(CO)<sub>8</sub> with Fe(CO)<sub>5</sub> may proceed through initial dissociation to form Fe<sub>2</sub>(CO)<sub>7</sub>, by analogy to the photochemistry of Fe(C<sub>4</sub>H<sub>4</sub>)(CO)<sub>3</sub> which produces Fe<sub>2</sub>(C<sub>4</sub>H<sub>4</sub>)<sub>2</sub>(CO)<sub>3</sub> at subambient temperature.<sup>12</sup>

The metallic iron produced from sonication of Fe(CO)<sub>5</sub> may be due to initial loss of all carbonyls or spontaneous loss of CO from clusterification of Fe(CO)<sub>2</sub> and Fe(CO). Since production of these intermediates clearly requires greater activation of Fe-

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(11) All sonications were performed by using a Heat Systems Model W-375 sonicator equipped with a titanium immersion tip. The sonicator was in continuous mode at 30% power at 20 KHz. The sonications were carried out in a glass-lined brass cell equipped for inert atmosphere and cryogenic capabilities. Products were identified by IR, UV-VIS, and mass spectroscopy, capillary vapor phase chromatography, and elemental analysis, as needed.

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Table II

| precatalyst <sup>a</sup><br>(amount, M)                 | length<br>of<br>sonica-<br>tion, h | av rate of<br>2-pentene<br>formation, <sup>c</sup><br>M/h | initial turnover<br>rate <sup>d</sup> |
|---|------------------------------------|---|---------------------------------------|
| Fe(CO) <sub>5</sub> (0.01)                              | 1                                  | 1.5 × 10 <sup>-1</sup>                                    | 17                                    |
| Fe(CO) <sub>5</sub> (0.1)                               | 1                                  | 2.0 × 10 <sup>-1</sup>                                    | 4                                     |
| Fe(CO) <sub>5</sub> (0.1)                               | 0 <sup>b</sup>                     | <1 × 10 <sup>-6</sup>                                     | <10 <sup>-5</sup>                     |
| Fe <sub>2</sub> (CO) <sub>9</sub> (0.01 <sup>e</sup> )  | 1                                  | 1.7 × 10 <sup>-1</sup>                                    | 51                                    |
| Fe <sub>2</sub> (CO) <sub>9</sub> (0.01 <sup>e</sup> )  | 0 <sup>b</sup>                     | <2 × 10 <sup>-4</sup>                                     | <2 × 10 <sup>-2</sup>                 |
| Fe <sub>3</sub> (CO) <sub>12</sub> (0.001)              | 1                                  | 7.1 × 10 <sup>-3</sup>                                    | 86                                    |
| Fe <sub>3</sub> (CO) <sub>12</sub> (0.01 <sup>e</sup> ) | 1                                  | 1.3 × 10 <sup>-2</sup>                                    | 15                                    |
| Fe <sub>3</sub> (CO) <sub>12</sub> (0.01 <sup>e</sup> ) | 0 <sup>b</sup>                     | <2 × 10 <sup>-4</sup>                                     | <2 × 10 <sup>-2</sup>                 |
| none  | 1                                  | <2 × 10 <sup>-4</sup>                                     |                                       |

<sup>a</sup> 0.5 M 1-pentene in decane, T = 0 °C, ~100 W/cm<sup>2</sup>, 10-mL volume, under Ar atmosphere; similar results are observed in toluene, heptane, and di-*n*-butyl ether. <sup>b</sup> Controls were run under identical conditions for ≥60 min, but without ultrasonic irradiation. *No 2-pentene was observable* (<0.05% of 1-pentene) under these conditions. <sup>c</sup> Trans/cis ratio is always ~3.0. <sup>d</sup> Initial turnover rates during sonication have been calculated as moles of 1-pentene isomerized per mole of precatalyst per hour, as determined during the first 5 min of sonication. <sup>e</sup> Undissolved precatalyst is present.

(CO)<sub>5</sub> than Fe(CO)<sub>4</sub> or Fe(CO)<sub>3</sub>, one expects that conditions which reduce the peak temperatures generated during cavitation, such as increased vapor pressure of the solvent system,<sup>1,3</sup> would reduce the relative yield of iron. As seen in Table I, this has proved to be the case; simply by changing solvent volatility we can alter the ratio of products over a 100-fold range. Thus, we can exert significant control over the extent of ligand dissociation created by ultrasonic cavitation.

In addition to clusterification, sonochemical ligand substitution has been observed for both Fe(CO)<sub>5</sub> and Fe<sub>3</sub>(CO)<sub>12</sub>. For example, in the presence of triphenylphosphine, Fe(CO)<sub>4</sub>(PPh<sub>3</sub>), Fe(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>, and small amounts of Fe(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> are produced in high yields, as occurs both thermally<sup>13</sup> and photochemically.<sup>5,12</sup> Due to the thermal cleavage<sup>13</sup> of Fe<sub>2</sub>(CO)<sub>9</sub> and Fe<sub>3</sub>(CO)<sub>12</sub> by phosphines, however, such trapping studies are mechanistically ambiguous in establishing the production of Fe(CO)<sub>3</sub>. Note that while Fe<sub>3</sub>(CO)<sub>12</sub> is sonochemically stable in the absence of phosphines, in their presence it does undergo declusterification and ligand substitution.

The transient, coordinatively unsaturated species produced from sonolysis of iron carbonyls are likely candidates for active homogeneous catalysts, since similar species produced photochemically show olefin isomerization activity.<sup>6,14-16</sup> Sonication of Fe(CO)<sub>5</sub>, Fe<sub>2</sub>(CO)<sub>9</sub>, or Fe<sub>3</sub>(CO)<sub>12</sub> in decane solutions of 0.5 M 1-pentene produce *trans*- and *cis*-2-pentene in approximately a 3:1 ratio (i.e., the thermodynamic ratio), as shown in Table II.

For Fe(CO)<sub>5</sub>, isomerization of 1-pentene is roughly linear for 60 min and continues for several hours before activity is gradually lost as finely divided Fe and small amounts of Fe<sub>3</sub>(CO)<sub>12</sub> are produced. Fe<sub>2</sub>(CO)<sub>9</sub> shows greater initial activity, which is lost as the Fe<sub>2</sub>(CO)<sub>9</sub> is rapidly sonochemically converted to Fe(CO)<sub>5</sub>.

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$\text{Fe}_3(\text{CO})_{12}$  also shows high initial activity which diminishes during the sonication. In this case, however, no iron species other than  $\text{Fe}_3(\text{CO})_{12}$  are detected even after prolonged sonication. As shown in Table II, the rate of 1-pentene isomerization can be enhanced by  $>10^5$  by sonolysis of the iron carbonyls.

In the photocatalyzed isomerization of 1-pentene by  $\text{Fe}(\text{CO})_5$ , the catalytically active species is proposed<sup>15,16</sup> to be  $\text{Fe}(\text{CO})_3$ - (pentene) which is obtained by sequential photodissociation of CO in the presence of pentene. Isomerization would then occur via  $\beta$ -hydrogen abstraction, forming  $\text{Fe}(\text{CO})_3(\text{H})(1\text{-ethyl-}\pi\text{-allyl})$  which produces the 2-pentenes. A similar mechanism has been demonstrated<sup>17</sup> for the thermal catalysis of olefin isomerization by  $\text{Fe}_3(\text{CO})_{12}$ . In the photocatalysis by both  $\text{Fe}(\text{CO})_5$  and  $\text{Fe}_3(\text{CO})_{12}$  the trans/cis ratio of the 2-pentene produced is always  $\sim 3$ , which is consistent with a common, mononuclear catalytic species.<sup>18</sup> The sonocatalysis produces the same trans/cis ratio, which does not change during sonication, as expected if the same catalysis species is produced.

Ultrasonic cavitation creates extremely intense thermal heating but for only very brief (submicrosecond) duration. This can produce unusual chemistry, distinct from both photochemical and thermal processes. The use of high-intensity ultrasound to initiate ligand dissociation is a novel method of catalyst activation with unique potential. The potential ability to induce ligand dissociation from complexes inert to photochemical or low-energy ( $<200^\circ\text{C}$ ) thermal processes suggests that sonocatalysis may be produced by intermediates not normally accessible. Further work is in progress to explore this hypothesis.

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**Registry No.**  $\text{Fe}(\text{CO})_5$ , 13463-40-6;  $\text{Fe}_2(\text{CO})_9$ , 15321-51-4;  $\text{Fe}_3(\text{CO})_{12}$ , 17685-52-8; 1-pentene, 109-67-1; *cis*-2-pentene, 627-20-3; *trans*-2-pentene, 646-04-8.

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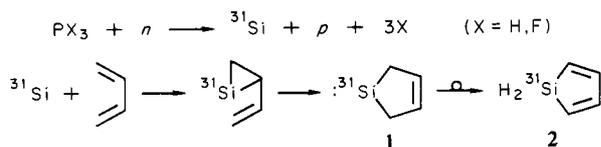
### 1-Silacyclopent-3-en-1-ylidene, a Cyclic Silylene from the Reactions of Silicon Atoms, and a Silicon Atom Synthron<sup>†,‡</sup>

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The suggestion that 1-silacyclopent-3-en-1-ylidene (**1**) is produced as a reactive intermediate from recoiling silicon atoms and 1,3-butadiene has been made to explain the formation of 1-silacyclopenta-2,4-diene (**2**).<sup>1-3</sup>



<sup>†</sup> We dedicate this communication to George Hammond with gratitude for the inspiration, both human and scientific, that he has always provided.

<sup>‡</sup> This research has been made possible by financial support from the United States Department of Energy. This is technical report C00-1713-98.

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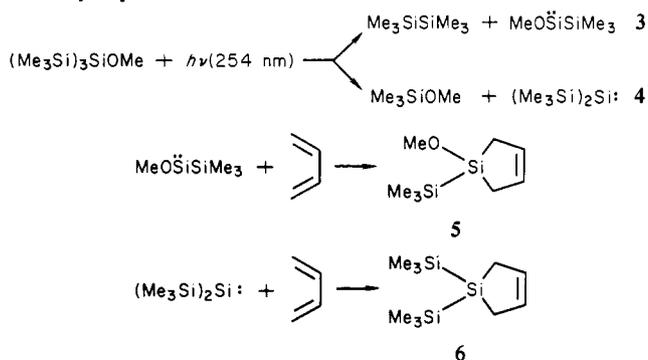
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Since unsubstituted silole **2** has *not* been prepared by other means,<sup>4-6</sup> its identification as a product in hot-atom experiments remains, in our view, controversial.<sup>2,5</sup>

It has now been possible, however, to generate silylene **1** directly, and it reacts with butadiene to form in high yield a product which we have also found from recoiling silicon atoms and from the cocondensation of silicon vapor with the same substrate. We are thus reporting new evidence for the intermediacy of 1-silacyclopent-3-en-1-ylidene (**1**) in the reactions of silicon atoms, the first fruitful reaction of thermally evaporated silicon with a hydrocarbon, and a silicon atom synthron.

1-Silacyclopent-3-en-1-ylidene (**1**) was produced by pyrolysis of 1-methoxy-1-(trimethylsilyl)-1-silacyclopent-3-ene (**5**). This silylene precursor was itself the product of a silylene reaction in the photolysis of methoxytris(trimethylsilyl)silane in butadiene solution.

While the photochemistry of alkyl- and mixed alkylarylpoly-silanes has received considerable attention,<sup>7,8</sup> this seems to be the first report of the photolysis of an alkoxy polysilane. In this case, photoinduced  $\alpha$  elimination is nonspecific, forming both methoxy(trimethylsilyl)silylene (**3**) and bis(trimethylsilyl)silylene (**4**) in ca. 2:1 ratio.<sup>9</sup> The trapping of silylenes by 1,3-dienes to give 1-silacyclopent-3-enes is well established.<sup>7,10,11</sup>



In a typical experiment 49% of **5** and 23% of the bis(trimethylsilyl)silacyclopentene (**6**) were obtained, together with 17% recovered methoxytris(trimethylsilyl)silane.

When such a reaction mixture, containing excess butadiene, was heated at  $310^\circ\text{C}$  for 2.5 h following 6 h of irradiation, **5** underwent thermally induced  $\alpha$  elimination which was, as expected, specific to the removal of methoxytrimethylsilane. Reaction of the resulting cyclic silylene **1** with butadiene gave the spiro adduct 5-silaspiro[4.4]nona-2,7-diene (**7**), a known compound,<sup>12</sup> in 32% overall yield.<sup>13</sup>

The spiro compound **7** is also formed in low (ca. 0.5%) yield in the gas phase from reactions of recoiling <sup>31</sup>Si atoms in mixtures of phosphine and butadiene. It had previously eluded detection recoil experiments<sup>2</sup> but has now been identified by comparison

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