a listing of observed and calculated structure factor amplitudes are available.[27]

Acknowledgment. We are grateful to the National Science Foundation for the support of this work at MIT, to the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for support at the University of Alberta, and to Dr. R. G. Ball for X-ray data collection.

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[27] Supplementary material.

Registry No. 2 (R = allyl), 91993-58-7; **2a**, 85534-04-9; **2b**, 85534-05-0; **5a**, 91993-59-8; **5b**, 91993-60-1; 8, 91993-61-2; (μ-$CH_2{=}CHCH_2S)_2Fe_2(CO)_6$, 74438-37-2; ($\eta^5$-$C_5H_5)Fe(CO)_2SC(S)H$, 91993-62-3; ($\eta^5$-$C_5H_5)Fe(CO)_2I$, 12078-28-3; $S_2Fe_3(CO)_9$, 22309-04-2; $Fe_2(CO)_9$, 15321-51-4; $LiBEt_3H$, 22560-16-3; CS_2, 75-15-0; MeI, 74-88-4; C_2H_5I, 75-03-6; $CH_2{=}CHCH_2Cl$, 107-05-1; $CH_3C(S)OEt$, 926-67-0; $C_2H_5C(S)OEt$, 924-45-8; HC(S)OEt, 29392-46-9.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen parameters, and observed and calculated structure amplitudes (8 pages). Ordering information is given on any current masthead page.

Silacyclopropenes. 2. "Two-Atom" Insertion Reactions of 1,1-Dimethyl-2,3-bis(trimethylsilyl)silirene[1,2]

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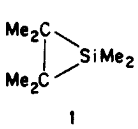
Received May 14, 1984

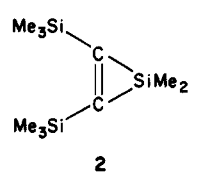
The silacyclopropene 1,1-dimethyl-2,3-bis(trimethylsilyl)silirene reacts with aldehydes, ketones, styrenes, conjugated terminal acetylenes, benzyne, terminal 1,3-dienes, and a conjugated imine to give five-membered cyclic organosilicon products in which the C=O, C=C, C≡C, or C=N bonds of the organic reactants have inserted into the Si—C bond of the silirene ring. In the case of the C=C and C≡C insertions, acyclic products, isomeric with the cyclic products, are formed as well. The available evidence suggests that a radical mechanism is operative.

Introduction

A characteristic reaction of the hyperreactive hexamethylsilirane, 1, is the "two-atom" insertion that it undergoes with aryl olefins such as styrene, terminal 1,3-dienes, terminal conjugated acetylenes, aldehydes, ketones, imines, and *cis*-azobenzene.[3,4] Some of these reactions occur at room temperature; most require mild heating; those involving aliphatic aldehydes and ketones require UV irradiation. We have prepared and isolated a number of silacyclopropenes (silirenes) that appeared to be even more reactive than hexamethylsilirane, and it was of interest to see if these too would undergo such two-atom insertion reactions. We describe here such reactions of 1,1-dimethyl-2,3-bis(trimethylsilyl)silirene, 2.



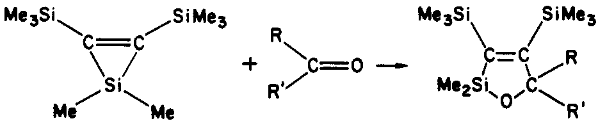
1



2

Results and Discussion

1,1-Dimethyl-2,3-bis(trimethylsilyl)silirene, 2, was found to react exothermally with a number of aromatic, heterocyclic, and α,β-unsaturated aldehydes and ketones when the reactants were mixed in benzene solution. According to their spectroscopic properties, the products were the respective 1-oxa-2-silacyclopent-3-enes, 3 (eq 1). The



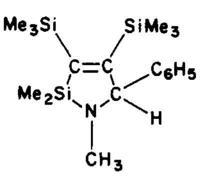
(1)

3

reactions proceeded well in normal laboratory lighting in benzene and diethyl ether solution and only poorly or not at all in pentane. The reaction with 2-acetylfuran was carried out in the dark to check whether normal laboratory fluorescent lighting was a requirement. An 18-h reaction at room temperature with complete exclusion of light gave the expected two-atom insertion product in 89% yield. Acetaldehyde and acetone did not react with 2 at room temperature, but low yields of products of type 3 were obtained when the respective reaction mixtures were heated at ~70 °C for 18 h. Results are given in Table I.

The insertion of aliphatic aldehydes and ketones into the Si–C bond of silirene 2 was facilitated by UV irradiation (100-W UV lamp, quartz flask) for ~2 h in pentane. Longer irradiation times resulted in diminished yields. The results of these experiments are given in Table II.

One compound with a C=N bond, benzaldehyde *N*-methylimine, also underwent insertion into the SiC_2 ring of silirene 2 at room temperature, giving 4 in 77% yield.



4

Inspection of the results in Tables I and II shows that the nature of the carbonyl substrate in these two-atom insertions into silirene 2 is of great importance. The most

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[1] Part 1: Seyferth, D.; Annarelli, D. C.; Vick, S. C. *J. Organomet. Chem.*, in press.

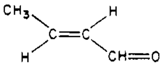
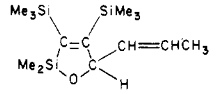
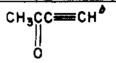
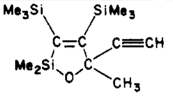
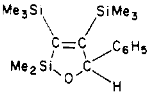
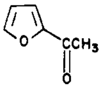
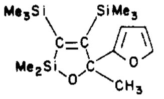
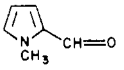
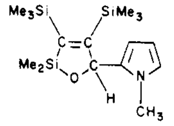
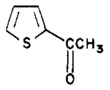
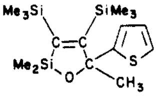
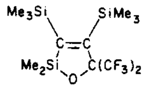
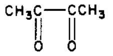
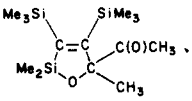
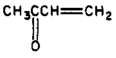
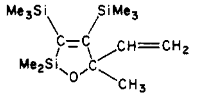
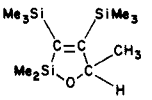
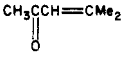
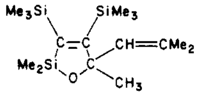
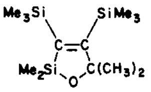
[2] Preliminary communications: (a) Seyferth, D.; Duncan, D. P.; Vick, S. C. *J. Organomet. Chem.* 1977, *125*, C5. (b) Seyferth, D.; Vick, S. C.; Shannon, M. L.; Lim, T. F. O.; Duncan, D. P. *J. Organomet. Chem.* 1977, *135*, C37.

[3] Seyferth, D.; Duncan, D. P.; Shannon, M. L.; Goldman, E. W. *Organometallics* 1984, *3*, 574–578.

[4] Seyferth, D.; Duncan, D. P.; Shannon, M. L. *Organometallics* 1984, *3*, 579–583.

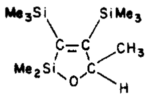
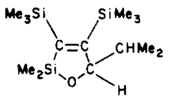
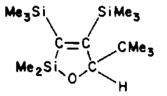
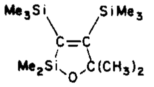
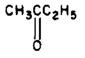
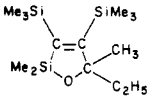
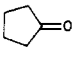
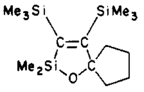
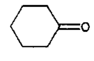
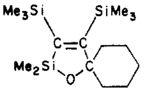
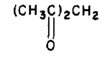
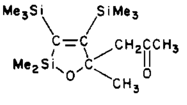
0276-7333/84/2303-1897$01.50/0

Table I. Thermal Reactions of Silirene 2 with Aldehydes and Ketones[a]

CO compd	solv	product (% yield)	CO compd	solv	product (% yield)
	benzene	 (93)	 $CH_3\underset{O}{\underset{\|}{C}}C\equiv CH$[b]	C_6H_6	 (62)
$C_6H_5CH=O$	benzene	 (77)		Et_2O	 (100)
	Et_2O	 (41)		Et_2O[c]	 (46)
$(CF_3)_2C=O$	C_6H_6	 (56)	 $CH_3\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}CH_3$	Et_2O[d]	 (100)
 $CH_3\underset{O}{\underset{\|}{C}}CH=CH_2$	C_6H_6	 (44)	$CH_3CH=O$	benzene[e]	 (26)
 $CH_3\underset{O}{\underset{\|}{C}}CH=CMe_2$	C_6H_6	 (43)	$(CH_3)_2C=O$	benzene[e]	 (14)

[a] Reactions at room temperature for 18 h. [b] Experiment by Dr. T. Lim. [c] 30% yield after 1 h. [d] 1-h reaction time. [e] Reaction at 70 °C for 18 h.

Table II. UV-Induced Reactions of Silirene 2 with Aliphatic Aldehydes and Ketones[a]

CO compd	product (% yield)
$CH_3CH=O$	 (92)
$Me_2CHCH=O$	 (28)
$Me_3CCH=O$	 (33)
$Me_2C=O$	 (73)
 $CH_3\underset{O}{\underset{\|}{C}}C_2H_5$	 (57)[b]
	 (78)
	 (73)
 $(CH_3\underset{O}{\underset{\|}{C}})_2CH_2$	 (20)

[a] 2-h reaction time in pentane solution. [b] 51% yield after 1 h; 35% yield after 1.5 h of irradiation in Et_2O solution.

reactive carbonyl compounds are those that bear substituents (aromatic or vinylic) that are capable of stabilizing a radical center at the carbonyl carbon atom. Such stabilization is not possible in aliphatic aldehydes and ketones. However, UV irradiation is known to produce an excited state of the aliphatic carbonyl compound (n → π^* excitation),[5] and thus UV irradiation would provide a more reactive species that could react with the silirene. Examination of the position of the absorption band corresponding to the n → π^* transition in the electronic spectra of various carbonyl compounds is informative.

Those aldehydes and ketones that reacted exothermally with silirene 2 at room temperature in the absence of UV irradiation all have n → π^* absorption bands at wavelengths greater than 3000 Å.[6,7] Thus accessibility of the n → π^* excited state would appear to be an important factor in the two-atom insertion reaction. Similar observations have been made in the case of analogous "two-atom" insertions of various aldehydes and ketones into the strained, highly reactive SiC_2 ring of hexamethylsilirane.[4] In the case of the latter the reactions with α,β-unsaturated and aromatic carbonyl compounds also occurred at room temperature but they were not exothermic. UV irradiation also was required to effect insertions of aliphatic aldehydes and ketones into the silirane ring. We suggested that these reactions are similar in mechanism to the UV-induced cycloaddition of carbonyl compounds to simple alkenes, dienes, and acetylenes. Such formation of oxetanes, it has been proposed, may proceed by way of an initial exiplex, with subsequent formation of a diradical resulting from attack on the alkene by the electron-deficient oxygen atom of the excited C=O group (n,π^* triplet state).[8] The more energetically stable of the two possible diradicals will then lead to formation of the product. Such "molecule-induced homolysis" is well-known.[5b]

In the case of the C=O insertions into the SiC_2 ring of silirene 2 one would expect the 1,5-diradical with the more stable Si–O bond 5 to be favored (eq 2). The stabilization

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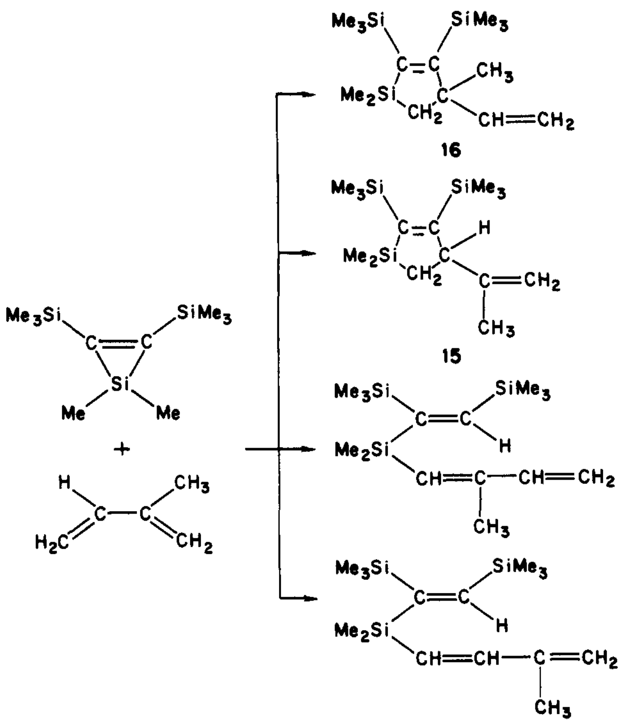
[5] (a) Bartrop, J. A.; Coyle, J. D. "Excited States in Organic Chemistry"; Wiley: New York, 1975. (b) Pryor, W. A. "Free Radicals": McGraw-Hill: New York, 1966; Chapters 6 and 8.

[6] Pitts, J. N.; Wan, J. K. S. In "The Chemistry of the Carbonyl Group": Patai, S., Ed.; Wiley: New York, 1966; 828.

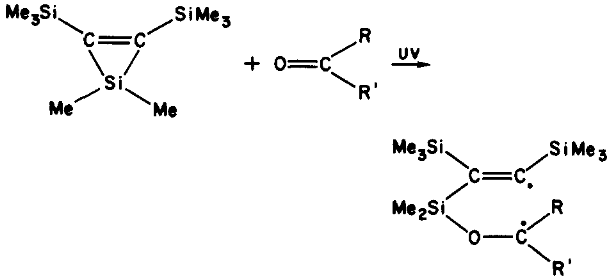
[7] Ayscough, P. D.; Steacie, E. W. R. *Proc. R. Soc. London, Ser. A* 1956, *234*, 476.

[8] Reference 5, pp 208–212.

Scheme I



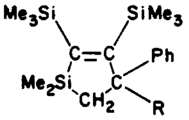
of this radical by unsaturated groups on the carbon atom to which the oxygen atom is bound also will be a contributing factor to making diradical 5 the favored one. Ring closure of 5 then would give the observed 1-oxa-2-silacyclopent-3-enes, 3.



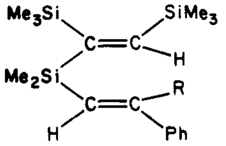
(2)

5

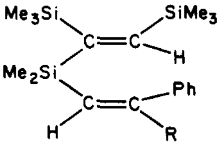
As noted in the Introduction, various substrates containing activated C═C and C≡C bonds underwent two-atom insertion reactions with hexamethylsilirane. As might be expected, 1,1-dimethyl-2,3-bis(trimethylsilyl)silirene reacts even more readily with the same substrates. A reaction of silirene 2 with styrene and with α-methylstyrene in benzene for 18 h at 70 °C gave in each case three products, 6, 7, and 8. In the case of α-methylstyrene, a 36% combined yield of 6, 7, and 8 (R = CH_3) in 45:30:25 relative ratio was obtained. In the case of styrene, an 87% combined yield of 6, 7, and 8 (R = H) in 40:40:10 relative ratio was obtained. The formation of the acyclic products 7 and 8 is mechanistically significant and will be discussed below. Trimethylvinylsilane did not react in this manner with silirene 2.



6

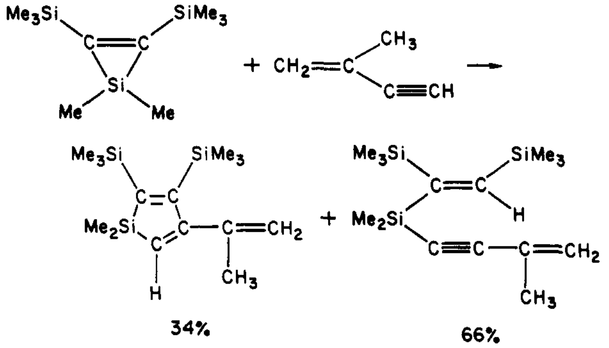


7

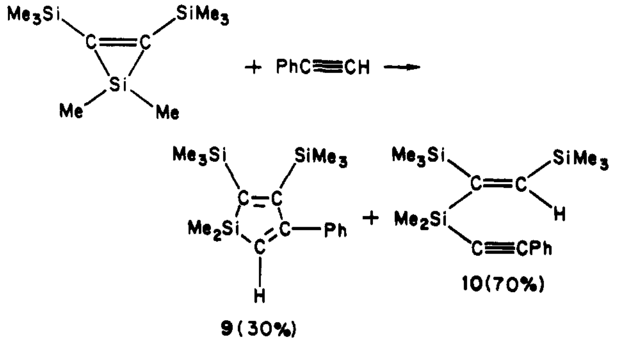


8

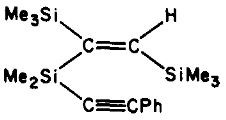
Conjugated terminal acetylenes reacted with silirene 2 at room temperature (eq 3 and 4). When the reaction was carried out in the presence of a hydrogen atom donor, diphenylmethane, neither the absolute nor the relative product yields in the latter reaction were changed. No silacyclopentadiene 9 was formed when a pentane solution of silirene 2 and phenylacetylene was irradiated (100-W UV lamp) in a quartz flask for 4 h. Two GC-separable products, 10 (3 parts) and its trans isomer 11 (2 parts), were obtained in 66% combined yield. (Both pure 10 and pure 11 were shown to undergo photoinduced isomerization to a 50/50 mixture of 10 and 11.) Unconjugated terminal acetylenes such as $Me_3CC{\equiv}CH$ and $Me_3SiC{\equiv}CH$ did not appear to react with silirene 2 at 70 °C.



(3)

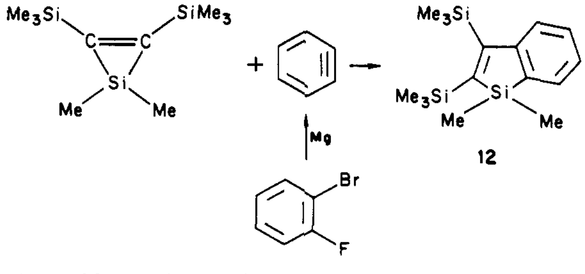


(4)



11

Benzyne is a very reactive cyclic "acetylene", and this intermediate, when generated in the presence of silirene 2 by the action of magnesium on *o*-bromofluorobenzene in THF at 65 °C, also inserted into the SiC_2 ring (eq 5). The expected silaindene 12 was obtained in 37% yield.



(5)

As had been observed with hexamethylsilirane, terminal 1,3-dienes also inserted into the SiC_2 ring of silirene 2.

Table III. Reaction of Silirene 2 with Some Unsaturated Compounds

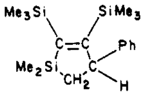
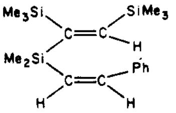
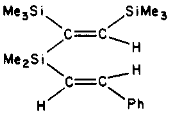
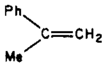
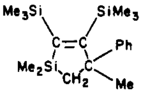
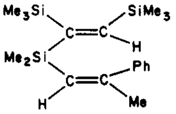
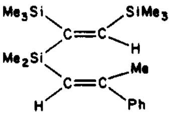
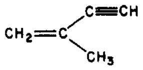
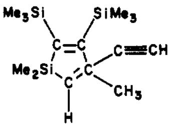
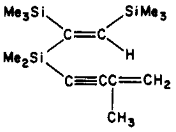
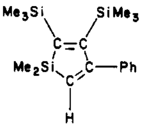
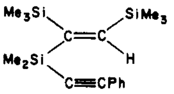
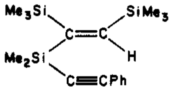
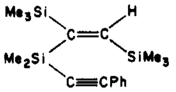
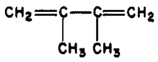
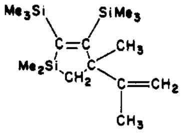
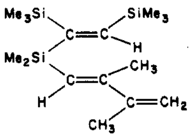
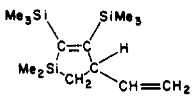
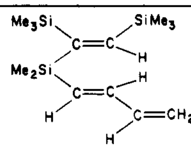
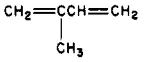
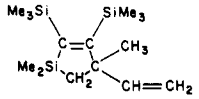
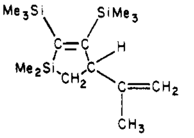
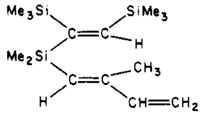
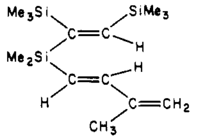
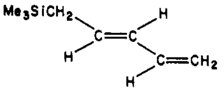
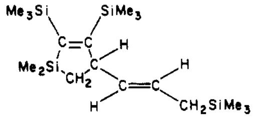
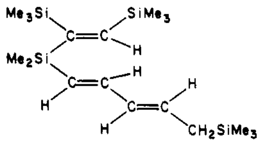
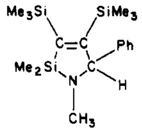
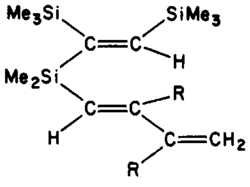
substrate	solv	reaction temp, °C (time)	product (% yield)
$PhCH{=}CH_2$	benzene	70 (18 h)	 (35)
			 (17)
			 (35)
	benzene	70 (18 h)	 (16)
			 (9)
			 (11)
	benzene	rt (18 h)	 (34)
			 (66)
$PhC{\equiv}CH$	benzene	rt (18 h)	 (22.5)
			 (52.5)
$PhC{\equiv}CH$	pentane	UV (4 h)	 (40)
			 (26)
	benzene	70 (3 days)	 (36)
			 (13)
$CH_2{=}CHCH{=}CH_2$	benzene	70 (18 h) (bomb tube)	 (45)

Table III (*Continued*)

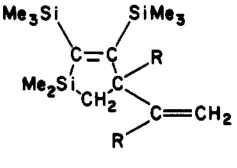
substrate	solv	reaction temp, °C (time)	product (% yield)
			 (20)
 $CH_2{=}C(CH_3)CH{=}CH_2$	benzene	70 (18 h)	 (24)
			 (24)
			 (low)[a]
			 (low)[a]
	benzene	75 (18 h)	 (15) +  (31)
PhCH=NCH$_3$	Et$_2$O	rt (18 h)	 (77)

[a] Not isolated; assumed product on basis of results obtained with other 1,3-dienes.

Here also both cyclic and acyclic products were obtained. Thus a sealed tube reaction of silirene **2** and an excess of 1,3-butadiene in benzene at 70 °C for 18 h gave two products: the acylic triene **13** (R = H) (20% yield) and vinylsilacyclopentene **14** (R = H) (45% yield). A reaction of silirene **2** with 2,3-dimethyl-1,3-butadiene in benzene proceeded similarly, giving **13** and **14** (R = CH$_3$) in 13% and 36% yield, respectively. Isoprene was not regioselective in its reaction with silirene **2** and gave two cyclic and two acylic products (Scheme I). The cyclic products were present in 1:1 ratio in 48% combined yield.

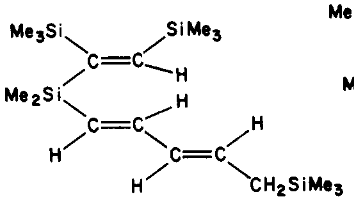


13

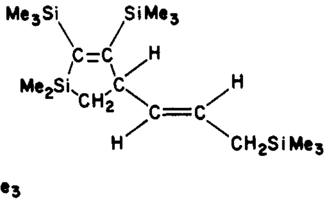


14

Another 1,3-diene that reacted with silirene **2** was (*E*)-2,4-pentadienyltrimethylsilane. Under the usual reaction conditions (18 h at ~75 °C in benzene solution) an inseparable mixture of two isomeric products was obtained in 46% combined yield. These were identified on the basis of the proton NMR spectrum of the mixture as **17** and **18**.



17



18

By comparison of the integrated area ratio of the signal at δ 7.31 (vinyl proton of the trisilylethylene unit of **17**) and at δ 5.67 and 5.73 (vinyl protons of **18**) and **17**/**18** ratio was determined to be 2.

Only terminal 1,3-dienes appear to react. No products were formed when reactions of silirene **2** with 2,4-hexadiene and with cyclopentadiene were attempted.

The mechanism of these two-atom insertion reactions is of interest. The fact that in the case of aldehyde and ketone C=O insertion into the 1,1-dimethyl-2,3-bis(trimethylsilyl)silirene ring it was the excited n,π^* triplet state of the carbonyl compound that was implicated suggests

Table IV. Products of Two-Atom Insertion Reactions of Silirene 2

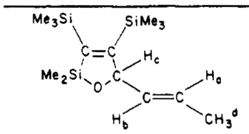
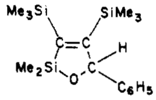
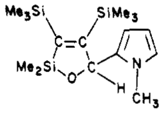
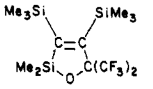
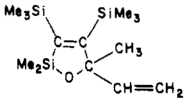
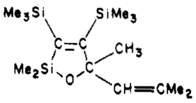
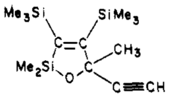
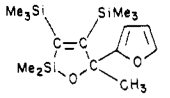
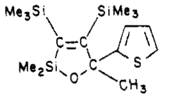
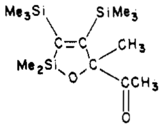
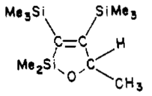
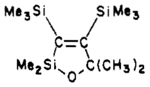
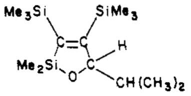
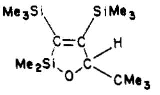
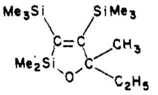
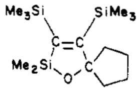
compd	$n^{25}{}_D$ or mp (°C)	anal. found (calcd) C	anal. found (calcd) H	^{1}H NMR, δ (in CCl_4 soln with CH_2Cl_2 int std)
	1.4870	56.28 (56.30)	10.17 (10.13)	0.25 (br s, 24 H, $SiCH_3$), 1.74 (d, J = 6 Hz, $=CCH_3$), 5.00–5.80 (complex m, 3 H, H_a, H_b, H_c); 270-MHz spectrum H_a (two overlapping q, 5.671, J_{ab} = 14.71 Hz, J_{ad} = 6.62 Hz), H_b, H_c (perturbed AB pattern, H_b 5.233, J_{bd} = 1.47 Hz, H_c 5.153, J_{bc} = 7.35 Hz)
	61–62	61.20 (61.01)	9.17 (9.03)	0.02 (s, 9 H, $SiCH_3$), 0.32 (br s, 15 H, $SiCH_3$), 5.68 (s, 1 H, ring CH), 7.22 (br s, 5 H, Ph)
	68–69	57.24 (56.90)	8.94 (9.25)	0.03, 0.09 (2 s, 12:3 ratio, 15 H, Me_3Si, Me_2Si), 0.24 (s, 9 H, Me_3Si), 3.36 (s, 3 H, NMe), 5.58, 5.80, 6.44 (AA′B m, 1 H, each, pyrrole), 5.67 (s, 1 H, ring CH)
	52–53	39.57 (39.57)	6.24 (6.13)	0.32, 0.35, 0.42 (s, 24 H, total, $SiCH_3$)
	31.5–32	56.54 (56.30)	10.04 (10.13)	0.34, 0.37 (s, 24 H, total, $SiCH_3$), 1.49 (s, 3 H, CMe), 4.89–6.22 (ABX, 3 H, vinyl)
	1.4876	58.96 (58.82)	10.43 (10.49)	0.28, 0.30, 0.35 (s, 24 H total, $SiCH_3$), 1.38 (s, 3 H, ring CH_3), 1.58 (d, J = 1 Hz, 3 H, =CMe), 1.77 (d, J = 1 Hz, 3 H, =CMe), 5.27–5.45 (m, 1 H, =CH)
	57–58	57.02 (56.68)	9.82 (9.51)	0.37, 0.47 (s, 24 H total, $SiCH_3$), 1.47 (s, 3 H, CCH_3), 2.37 (s, 1 H, ≡CH)
	1.4931	56.90 (56.73)	8.97 (8.93)	0.04 (s, 9 H, $SiCH_3$), 0.27 (s, 15 H, $SiCH_3$) 1.67 (s, 3 H, CCH_3), 6.01, 6.26, 7.26 (3 complex m, 1 H each, furan)
	1.5138	54.14 (54.17)	8.60 (8.52)	−0.01, 0.25, 0.26 (s, 24 H total, $SiCH_3$) 1.74 (s, 3 H, CCH_3), 6.76, 7.03, 7.53 (3 complex m, 1 H each, thiophene)
	33–34	53.58 (53.43)	9.67 (9.61)	0.16, 0.21, 0.23 (s, 24 H total, $SiCH_3$), 1.30 (s, 3 H, ring CCH_3), 1.91 (s, 3 H, $C(O)CH_3$)
	1.4774	52.94 (52.87)	10.47 (10.35)	0.20, 0.25 (s, 24 H total, $SiCH_3$), 1.23 (d, J = 6 Hz, 3 H, CCH_3), 4.87 (q, J = 6 Hz, 1 H, ring CH)
	52–52.5	54.62 (54.47)	10.49 (10.55)	0.30, 0.33 (s, 24 H total, $SiCH_3$), 1.37 (s, 6 H, CCH_3)
	1.4766	56.07 (55.92)	10.75 (10.73)	0.15, 0.21 (s, 24 H total, $SiCH_3$), 0.51 (d, J = 7 Hz, 3 H, $CHCH_3$), 1.03 (d, J = 7 Hz, 3 H, $CHCH_3$), 1.86 (m, J = 7 Hz, 1 H, $CHMe_2$), 4.68 (d, J = 1 Hz, ring CH)
	1.4789	57.24 (57.24)	10.64 (10.89)	0.10, 0.22, 0.29, 0.32 (s, 3:9:9:3 ratio, 24 H total, $SiCH_3$), 0.89 (s, 9 H, Me_3C), 4.64 (s, 1 H, ring CH)
	34–34.8	56.22 (55.92)	10.84 (10.73)	0.23, 0.27 (s, 24 H total, $SiCH_3$), 0.76 (t, J = 4 Hz, 3 H, CH_3 of Et), 1.27 (s, 3 H, ring CH_3), 1.68 (q, J = 4 Hz, CH_2)
	73–74.5	57.38 (57.62)	10.35 (10.32)	0.11, 0.14, 0.17 (s, 24 H total, $SiCH_3$), 1.20–1.89 (complex m, 8 H, ring CH_2)

Table IV (*Continued*)

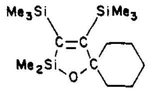
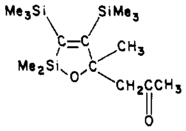
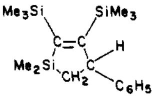
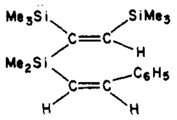
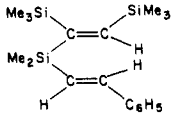
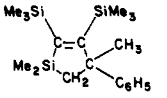
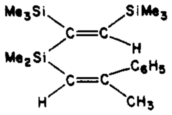
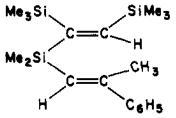
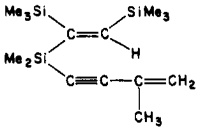
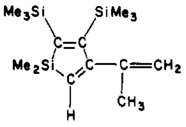
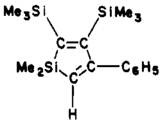
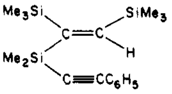
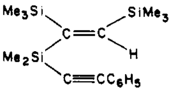
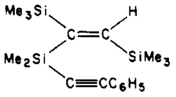
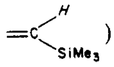
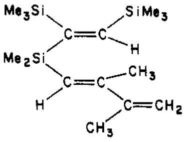
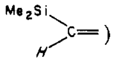
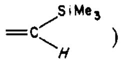
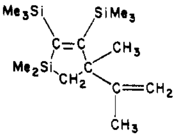
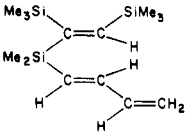
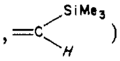
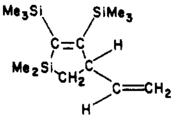
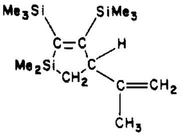
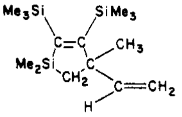
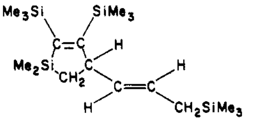
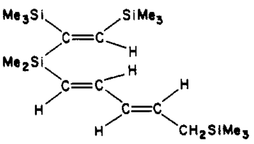
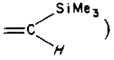
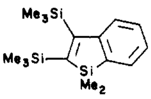
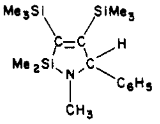
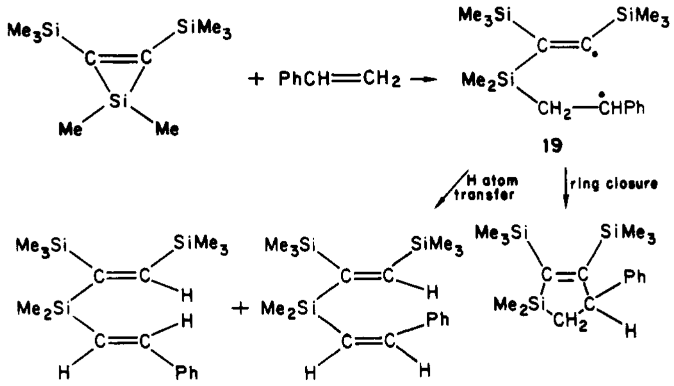
compd	$n^{25}{}_D$ or mp (°C)	anal. found (calcd) C	H	^{1}H NMR, δ (in CCl$_4$ soln with CH$_2$Cl$_2$ int std)
	62-64	58.97 (58.83)	10.04 (10.49)	0.21, 0.27 (s, 24 H total, SiCH$_3$), 1.01-1.96 (complex m, 10 H, ring CH$_2$)
	1.4792	54.93 (54.82)	9.80 (9.81)	0.16, 0.23 (s, 24 H total, SiCH$_3$), 1.29 (s, 3 H, ring CCH$_3$), 2.05 (s, 3 H, C(O)CH$_3$), 2.65 (s, 2 H, CH$_2$)
 6-H +  8-H	1.5296[b]	65.30[b] (64.98)	9.63[b] (9.70)	0.00, 0.14, 0.16, 0.18, 0.29 (s, SiCH$_3$ of **6**-*H* and **8**-*H*), 0.45-1.34 (complex m, ring CH$_2$ of **6**-*H*), 4.39 (broadened d, *J* = 10 Hz, ring CH of **6**-*H*), 5.86 (d, *J* = 15.6 Hz, $\begin{smallmatrix}Si & & Ph\\ & C=C & \\ H & & H\end{smallmatrix}$ of **8**-*H*), 6.83-7.34 (m, C$_6$H$_5$ of **6**-*H* and **8**-*H* + =C*H*Ph of **8**-*H*), 7.46 (s, $=C\begin{smallmatrix}SiMe_3\\H\end{smallmatrix}$ of **8**-*H*)
	1.5319	65.24 (64.98)	9.58 (9.70)	0.18, 0.25 (s, 24 H total, SiCH$_3$), 6.26-6.90 (AB, J_{AB} = 19.2 Hz, 2 H, =CH), 7.09-7.48 (m, 6 H, Ph and $=C\begin{smallmatrix}SiMe_3\\H\end{smallmatrix}$)
 6-Me +  8-Me	1.5313[b]	65.85[b] (65.81)	10.00[b] (9.88)	−0.22, 0.14, 0.16, 0.23, 0.25 (s, SiCH$_3$, **6**-*Me* and **8**-*Me*), 0.59-1.01 (AB, J_{AB} = 15 Hz, ring CH$_2$ of **6**-*Me*), 1.48 (s, CCH$_3$ of **6**-*Me*), 2.05 (br s, =CCH$_3$), 5.86 (br s, =CH), 6.99-7.35 (m, Ph of **6**-*Me* and **8**-*Me*), 7.46 (s, $=C\begin{smallmatrix}SiMe_3\\H\end{smallmatrix}$ of **8**-*Me*)
	1.5172	65.22 (65.81)	9.95 (9.88)	−0.21 (s, 6 H, SiMe$_2$), 0.09, 0.10 (s, 18 H, SiMe$_3$), 2.17 (d, *J* = 1.5 Hz (trans allylic coupling, 3 H, =CCH$_3$), 5.57 (q, *J* = 1.5 Hz, 1 H, =CH), 7.03-7.25 (m, 6 H, Ph and $=C\begin{smallmatrix}SiMe_3\\H\end{smallmatrix}$)
	1.4930	61.25 (61.14)	10.17 (10.26)	0.14, 0.17, 0.20 (s, 24 H total, SiCH$_3$), 1.86 (t, *J* = 1 Hz, 3 H, CCH$_3$), 5.22 (dq, J_d = 8 Hz, J_q = 1 Hz, 2 H, =CH$_2$), 7.48 (s, 1 H, $=C\begin{smallmatrix}SiMe_3\\H\end{smallmatrix}$)
	48.5-49.5	61.06 (61.14)	10.46 (10.26)	0.15, 0.16 (s, 24 H, SiCH$_3$), 1.91 (br s, 3 H, =CCH$_3$), 4.79 (br s, 2 H, =CH$_2$), 5.75 (s, 1 H, ring =CH)
 9 +  10	1.5372[b]	65.50[b] (65.37)	9.20[b] (9.14)	−0.08, 0.02, 0.29, 0.33 (s, 24 H, SiCH$_3$ of **9** and **10**), 7.18-7.51 (m, maxima at 7.26, 7.33, 7.40, 5 H, C$_6$H$_5$ of **9** and **10**), 5.89 and 7.58 (s, 1 H, total, =CH of **9** and **10**), 5.89 and 7.58 (s, 1 H, total, =CH of **9** and **10**, respectively)
 pure 10	1.5315	65.24 (65.37)	9.35[c] (9.14)	0.23, 0.29 (s, 18 H total, Me$_3$Si), 0.33 (s, 6 H, Me$_2$Si), 7.22-7.45 (m, 5 H, Ph), 7.55 (s, 1 H, $=C\begin{smallmatrix}SiMe_3\\H\end{smallmatrix}$)

Table IV (*Continued*)

compd	$n^{25}{}_{D}$ or mp (°C)	anal. found (calcd)		¹H NMR, δ (in CCl$_4$ soln. with CH$_2$Cl$_2$ int std)
		C	H	
 11	1.5304			0.17, 0.24 (s, 18 H total, Me$_3$Si), 0.39 (s, 6 H, Me$_2$Si), 7.15-7.39 (m, 6 H, Ph and )
	1.4987	61.79 (61.85)	11.13 (11.03)	0.07, 0.10, 0.13 (s, 24 H total, SiCH$_3$), 1.57 (s, 3 H, SiC=CCH_3), 1.80 (br s, 1 H, CH$_2$=CCH_3), 4.80 and 4.88 (br s, 1 H, each, =CH$_2$), 5.45 (s, 1 H, ) 7.20, (s, 1 H, )
	1.5029	61.97 (61.85)	10.87 (11.03)	0.20, 0.25 (s, 24 H total, SiCH$_3$), 0.67 (AB, J_{AB} = 14 Hz, 2 H, ring CH$_2$), 1.27 (s, 3 H, ring CH$_3$), 1.70 (br s, 3 H, =CCH$_3$), 4.55 (br s, 2 H, =CH$_2$)
 13	1.4931	59.62[b] (59.49)	10.77[b] (10.70)	0.12 0.15 (s, 24 H total, SiCH$_3$), 4.85-6.50 (m, 5 H, dienyl H), 7.28 (s, 1 H, )
 14	45-46			0.17, 0.20 (s, 24 H total, SiCH$_3$), 0.64-0.80 (m, 2 H, ring CH$_2$), 3.34-4.04 (m, 1 H, ring CH), 4.34-5.04 (m, 3 H, vinyl H)
 15 +  16	1.4984[b]	61.04[b] (60.72)	10.88[b] (10.87)	0.20, 0.26, 0.29 (s, 24 H total, SiCH$_3$), 0.51-0.87 (m, 2 H, ring CH$_2$ of **15** and **16**), 1.26 (s, 1.5 H, CCH$_3$ of **16**), 1.90 (br s, 1.5 H, =CCH$_3$ of **15**), 3.58-3.62 (m, 0.5 H, ring CH of **15**), 4.40-5.28 (m, 2.5 H, vinyl H of **15** and **16**)
 17 +  18	1.4958[b]	58.48[b] (58.60)	10.82[b] (10.93)	−0.03, 0.01, 0.15, 0.17, 0.18 (s, SiCH$_3$), 0.68 (m, 2 H, CH$_2$ of **18**), 1.37 (dd, J = 7 Hz, J = 1 Hz, 2 H, SiCH$_2$ of **17**), 1.51 (dd, J = 7 Hz, J = 1 Hz, 2 H, SiCH$_2$ of **18**), 3.58-3.98 (m, 1 H, ring CH of **18**), 5.07, 5.12, 5.18, 5.87 (four m, 4 H, dienyl CH of **17**), 5.67, 5.73 (two m, vinyl H of **18**), 7.31 (s, 1 H, )
	1.5477	63.02 (63.07)	9.27 (9.26)	0.25 (s, 9 H, Me$_3$Si), 0.28 (s, 6 H, Me$_2$Si), 0.36 (s, 9 H, Me$_3$Si), 6.92-7.54 (m, 4 H, benzo H)
	60-61	62.22 (62.17)	9.70 (9.56)	−0.13 (s, 9 H, Me$_3$Si), 0.16 (s, 15 H, SiCH$_3$), 1.17 (s, 3 H, NCH$_3$), 5.67 (s, 1 H, ring CH), 7.19 (m, 5 H, Ph)

[a] IR and 70-eV mass spectra are given in the MIT Ph.D. theses of S. C. Vick and M. L. Shannon. In almost all cases, the mass spectra showed the molecular ion and an M$^+$ − 15 fragment ion. The IR spectra of the aldehyde and ketone insertion products all showed a band in the region 1000-1070 cm^{-1}, characteristic of the presence of an Si-O bond. [b] Data for a mixture of the cyclic and acyclic products indicated. [c] Data for a mixture of **10** and **11**.

Scheme II



the operation of a radical mechanism as shown in eq 2. Indirect confirmation was provided by the isolation of the acyclic products in the reactions of the silirene with the styrenes, the conjugated terminal acetylenes, and the terminal 1,3-dienes. Their formation could be rationalized in terms of hydrogen atom transfer processes in an intermediate 1,5-diradical. This is shown in Scheme II for the silirene/styrene reaction. Furthermore, the formation of both *cis*- and *trans*-β-styryl isomers would be explained: in diradical **19** there would be free rotation about the C–C single bond, so both isomers might be expected. The fact that such reactions have been seen only with conjugated systems also would find an explanation by the mechanism shown in Scheme II. Such a radical mechanism also would explain the formation of only the acyclic product when the silirene **2**/phenylacetylene reaction mixture is irradiated. All experimental observations thus are consistent with a radical mechanism as shown in eq 2 and Scheme II.

Other research groups, as mentioned in part 1, have prepared other silirenes by a photochemical route. In two of these papers similar ketone insertion into the Si–C bonds of 1,1-dimethyl-2-phenyl-3-(trimethylsilyl)silirene were reported.[9,11]

Experimental Section

General Comments. The "general comments" of part 1[1] are applicable here. The need to carry out all operations involving hexamethylsilirane and 1,1-dimethyl-2,3-bis(trimethylsilyl)silirene in the complete absence of air and moisture must be stressed again. All solvents used should be rigorously dried and degassed.

Large-scale preparations of silirene **2** were carried out as described in part 1.

Thermal Reactions of Silirene 2. A flame-dried, 25-mL, two-necked, round-bottomed flask equipped with a magnetic stir bar, a no-air septum stopper, and an argon inlet tube was charged with a solution of the other reactant (a large excess, usually 5–15 molar equiv/equiv of silirene) and then the silirene was added slowly by syringe (either neat or as a solution). The mixture was stirred for a time (1–18 h, depending on how strong an exotherm had been observed), at room temperature or with heating. Subsequently, the mixture was analyzed by GLC and samples of the product(s) were collected by GLC.

In the case of the reactions of 1,3-butadiene with silirene **2**, a solution of the reactants (1.69 mmol of the silirene and 2.0 mL (liquid) of the diene) in 5 mL of benzene was cooled and sealed in a thick-walled Pyrex bomb tube and then was heated at 70 °C for 18 h.

The thermal reactions of the silirene with carbonyl compounds are summarized in Table I and those with other substrates in Table III. Characterization data (n_D^{25} if a liquid, mp if a solid; C/H analysis and ^{1}H NMR spectrum) for new compounds are given in Table IV. In those cases where separation of pure compounds could not be effected by GLC, data for compound mixtures are given.

UV-Induced Reactions of Silirene 2 with Carbonyl Compounds. The same procedure was used, except that the reactants, in pentane solution in a quartz flask, were irradiated with a 100-W mercury UV lamp (Hanovia Lamp Division, Catalog No. 30600). These reactions are summarized in Table II.

Reaction of Silirene 2 with Benzyne.[11] A 50-mL, three-necked flask equipped with a magnetic stir bar, a no-air rubber septum, a glass stopper, and a reflux condenser topped with an argon inlet tube was charged with 0.245 g (10.1 mmol) of magnesium (Alfa, 99.99%) and then was flame-dried under a brisk stream of argon. A solution of 0.402 g (1.76 mmol) of silirene **2** in 10 mL of THF was added by syringe, and the flask was immersed in an oil bath at 65 °C. To the stirred mixture was added 1.81 g (10.3 mmol) of *o*-bromofluorobenzene, dropwise over a period of 1 h. After the reaction mixture had cooled to room temperature, it was filtered and the filtrate was trap-to-trap distilled at 0.05 mmHg (heat gun) into a cooled receiver. Analysis of the distillate by GLC (4 ft SE-30, 180 °C) showed the presence of one product, **12**, in 37% yield.

Acknowledgment. We are grateful to the U.S. Air Force Office of Scientific Research (NC)-AFSC for generous support of this work.

Registry No. **2**, 61059-04-9; **3** (R = CH=CHCH$_3$, R′ = H), 92014-07-8; **3** (R = C$_6$H$_5$, R′ = H), 62346-55-8; **3** (R = 2-(1-methylpyrrole), R′ = H), 92014-08-9; **3** (R = R′ = CF$_3$), 92014-09-0; **3**(R = CH=CH$_2$, R′ = CH$_3$), 92014-10-3; **3** (R = CH=CMe$_2$, R′ = CH$_3$), 92014-11-4; **3** (R = C≡CH, R′ = CH$_3$), 92014-12-5; **3** (R = 2-furyl, R′ = CH$_3$), 92014-13-6; **3** (R = 2-thienyl, R′ = CH$_3$), 92014-14-7; **3** (R = C(O)CH$_3$, R′ = CH$_3$), 92014-15-8; **3** (R = CH$_3$, R′ = H), 64588-29-0; **3** (R = R′ = CH$_3$), 64588-21-2; **3** (R = CHMe$_2$, R- = H), 64588-33-6; **3** (R = CMe$_3$, R′ = H), 64588-34-7; **3** (R = CH$_3$, R′ = C$_2$H$_5$), 64588-31-4; **3** (R = R′ = (CH$_2$)$_4$), 64588-22-3; **3** (R = R′ = (CH$_2$)$_5$), 64588-30-3; **3** (R = CH$_2$COCH$_3$, R′ = CH$_3$), 64588-32-5; **4**, 92014-21-6; **6** (R = H), 64588-09-6; **6** (R = CH$_3$), 64588-12-1; **7** (R = H), 64588-11-0; **7** (R = CH$_3$), 64588-14-3; **8** (R = H), 64588-10-9; **8** (R = CH$_3$), 64588-13-2; **9**, 62346-60-5; **10**, 62346-61-6; **11**, 92014-17-0; **12**, 92014-22-7; **13** (R = H), 64588-16-5; **13** (R = CH$_3$), 64588-18-7; **14** (R = H), 64588-15-4; **14** (R = CH$_3$), 64588-17-6; **15**, 64588-20-1; **16**, 64588-19-8; **17**, 92054-72-3; **18**, 92014-20-5; C$_6$H$_5$CH=O, 100-52-7; (CF$_3$)$_2$C=O, 684-16-2; CH$_3$CH=O, 75-07-0; (CH$_3$)$_2$C=O, 67-64-1; Me$_2$CHCH=O, 78-84-2; Me$_3$CCH=O, 630-19-3; PhCh=NCH$_3$, 622-29-7; PhCH=CH$_2$, 100-42-5; PhC≡CH, 536-74-3; CH$_2$=CHCH=CH$_2$, 106-99-0; (*E*)-(Me$_3$Si)CH=C(Me$_3$Si)Si(Me$_2$)C≡CC(CH$_3$)=CH$_2$, 92014-16-9; (*E*,*E*)-(Me$_3$Si)CH=C(Me$_3$Si)Si(Me$_2$)CH=C(CH$_3$)CH=CH$_2$, 92014-18-1; (*E*,*E*)-(Me$_3$Si)CH=C(Me$_3$Si)Si(Me$_2$)CH=CHC(CH$_3$)=CH$_2$, 92014-19-2; 4-ethynyl-1,1,4-trimethyl-2,3-bis(trimethylsilyl)-2-silacyclopentene, 92078-14-3; (*E*)-2-butenal, 123-73-9; 1-methyl-1*H*-pyrrole-2-carboxaldehyde, 1192-58-1; 3-buten-2-one, 78-94-4; 4-methyl-3-penten-2-one, 141-79-7; 3-butyn-2-one, 1423-60-5; butanone, 78-93-3; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; 2,4-pentanedione, 123-54-6; 2-propenylbenzene, 98-83-9; 2-methyl-1-buten-3-yne, 78-80-8; 2,3-dimethyl-1,3-butadiene, 513-81-5; 2-methyl-1,3-butadiene, 78-79-5; (*E*)-2,4-pentadienyltrimethylsilane, 72952-73-9; benzyne, 462-80-6; 2-acetylfuran, 1192-62-7; 1-(2-thienyl)ethanone, 88-15-3; biacetyl, 431-03-8.

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