4824 *Organometallics* **1997,** *16,* 4824−4827

# Synthesis of Silirenes by Palladium-Catalyzed Transfer of Silylene from Siliranes to Alkynes

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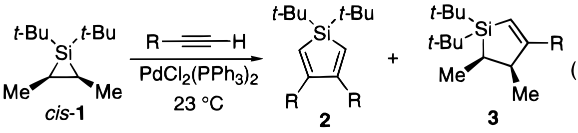
*Received June 10, 1997*⊗

Palladium-catalyzed reactions of *cis*-1,1-di-*tert*-butyl-2,3-dimethylsilirane with disubstituted alkynes produced thermally stable silirenes in high yields (81−86%). Alkyl-, aryl-, trimethylsilyl-, and heteroatom-substituted alkynes were employed. The silirenes reacted with phenylacetylene and <3 mol % of $PdCl_2(PPh_3)_2$ to produce trisubstituted siloles. A common catalytic cycle involving palladasilacyclobutene accounts for both the formation of silirene and the trisubstituted silole. The palladium-catalyzed extrusion of silylene effectively transfers silylene from one strained ring (a silirane) to form another strained ring (a silirene) and represents an unusual metal-mediated process.

Metal-catalyzed silylene transfer has been postulated to occur in oligosilane rearrangements,[1] disproportionations,[2] and the degradation of a trisilane to disilane[3] and has been used in the synthesis of siloles[4−6] and disilacyclohexadienes.[7] We recently reported that palladium-catalyzed silylene transfer reactions of silirane *cis*-**1**[8] with terminal alkynes produced silole **2** as the major product along with silacyclopentene **3** when the reaction was carried out at ambient temperature (eq 1).[4]



(1)

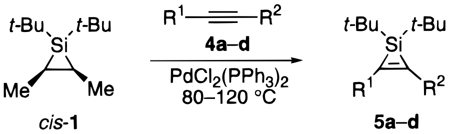
Under these conditions, no identifiable products were produced with internal alkynes as substrates. In this paper, we describe an unusual metal-mediated transfer of silylene from a silirane to an internal alkyne[9] as a practical method for the synthesis of silirenes. Although there have been several methods for the preparation of these strained silanes,[10−12] none involve the use of transition metal catalysis. This situation contrasts dramatically with the methods for the synthesis of other three-membered ring systems, in which metal catalysis plays a dominant role.[13] The silirene products were further treated with a terminal alkyne in the presence of palladium catalyst to produce trisubstituted siloles. These experiments demonstrate that oxidative addition of palladium into the C−Si bond of silirenes is a reversible process, and a common catalytic cycle can account for the production of both silirenes and siloles.

**Table 1. Synthesis of Silirenes 5a−d from Silirane *cis*-1 (Eq 2)**

| alkyne | **5a−d** (yield %) | $^{29}$Si NMR (δ)[a] |
|---|---|---|
| **4a**: $R^1 = Ph, R^2 = SiMe_3$ | 81 | −71.7 |
| **4b**: $R^1 = CH_3, R^2 = CH_2OSiMe_2$*t*-Bu | 85 | −65.3 |
| **4c**: $R^1 = R^2 = Et$ | 86 | −66.3 |
| **4d**: $R^1 = R^2 = Ph$ | 84[b] | −66.7 |

[a] Chemical shift of the ring-bearing Si atom (99.3 MHz in $C_6D_6$). [b] Isolated as an 88:12 mixture of **5d**:**4d**.

The reaction of *cis*-**1** with various disubstituted alkynes **4a−d** in the presence of <3 mol % $PdCl_2(PPh_3)_2$ produced silirenes **5a−d** in high yields (eq 2, Table 1).



(2)

Although silirenes with heteroatom-containing functional groups have not been previously synthesized, this method can be applied to prepare silirene **5b** bearing a *tert*-butyldimethylsilyl ether group in 85% yield. The $^{29}$Si NMR chemical shifts of the ring-bearing silicon atom of silirenes **5a−d** are in the region from −65 to

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⊗ Abstract published in *Advance ACS Abstracts,* October 1, 1997.

(1) Tamao, K.; Sun, G.-R.; Kawachi, A. *J. Am. Chem. Soc.* **1995**, *117*, 8043−8044.

(2) Yamamoto, K.; Okinoshima, H.; Kumada, M. *J. Organomet. Chem.* **1971**, *27*, C31−C32.

(3) Tamao, K.; Tarao, Y.; Nakagawa, Y.; Nagata, K.; Ito, Y. *Organometallics* **1993**, *12*, 1113−1120.

(4) Palmer, W. S.; Woerpel, K. A. *Organometallics* **1997**, *16*, 1097−1099.

(5) Ishikawa, M.; Sugisawa, H.; Harata, O.; Kumada, M. *J. Organomet. Chem.* **1981**, *217*, 43−50.

(6) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9263−9264.

(7) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1977**, 352.

(8) Boudjouk, P.; Samaraweera, U.; Sooriyakumaran, R.; Chrusciel, J.; Anderson, K. R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1355−1356.

(9) Ohshita and Ishikawa demonstrated an equilibrium between two silirenes in the presence of an alkyne, although silirene products were not isolated, see: Ohshita, J.; Ishikawa, M. *J. Organomet. Chem.* **1991**, *407*, 157−165.

(10) Pyrolysis of 1,2-dimethoxy-1,1,2,2-tetramethyldisilane with 2-butyne afforded a stable silirene, although this synthesis provided mixtures of products, see: Conlin, R. T.; Gaspar, P. P. *J. Am. Chem. Soc.* **1976**, *98*, 3715−3716.

(11) The first silirenes that could be isolated in pure form and fully characterized were prepared by Seyferth. The synthesis involved thermal silylene transfer from a silirane to an alkyne, see: (a) Seyferth, D.; Annarelli, D. C.; Vick, S. C. *J. Am. Chem. Soc.* **1976**, *98*, 6382−6384. (b) Seyferth, D.; Annarelli, D. C.; Vick, S. C. *J. Organomet. Chem.* **1984**, *272*, 123−139.

(12) For other examples of silirene syntheses using thermal and photochemical methods, see: (a) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3879−3880. (b) Reference 8. (c) Belzner, J.; Ihmels, H. *Tetrahedron Lett.* **1993**, *34*, 6541−6544. (d) Ando, W.; Shiba, T.; Hidaka, T.; Morihashi, K.; Kikuchi, O. *J. Am. Chem. Soc.* **1997**, *119*, 3629−3630.

(13) For example, metal-mediated cyclopropane synthesis has been well-investigated, see: Brookhart, M.; Studebaker, W. B. *Chem. Rev.* **1987**, *87*, 411−432.

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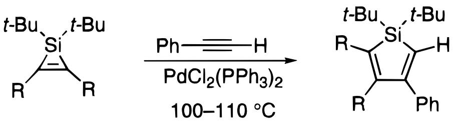
−72 ppm, indicating highly shielded silicon nuclei. These values are slightly lower but are consistent with previously reported $^{29}$Si NMR data on aryl-,[12c] dimethyl-,[11] and di-*tert*-butyl-substituted silirenes.[14] Silirenes **5a**−**c** were thermally stable and could be routinely purified by distillation at temperatures of up to 160 °C with little to no decomposition. However, silirene **5d** was thermally unstable and was isolated as an 88:12 mixture of **5d** and alkyne **4d** upon distillation at 124−138 °C (0.05 Torr).

Several experiments indicated that the transfer of di-*tert*-butylsilylene from *cis*-**1** to disubstituted alkynes required palladium catalysis. Under thermal conditions, silirane *cis*-**1** liberates silylene[8] at a much slower rate. A sealed NMR tube reaction of *cis*-**1** with **4d** in the absence of $PdCl_2(PPh_3)_2$ showed no product formation after 1.5 h at 115 °C. When the temperature was increased to 125 °C for 3 h, less than 10% conversion of *cis*-**1** was observed; complete consumption of *cis*-**1** required 2 days at 130 °C. The slow thermal reaction of *cis*-**1** contrasts with its complete consumption in the presence in $PdCl_2(PPh_3)_2$ at 110 °C within 2.5 h.

Control experiments indicated that *trans*-**1** underwent silylene extrusion to form silirenes by a thermal process. The reaction of *trans*-**1** with **4d** produced *trans*-2-butene and silirene **5d** only after several days at increased temperatures (>140 °C), both with and without $PdCl_2(PPh_3)_2$ present. The contrasting reactivity of *trans*-**1** versus *cis*-**1** does not arise from the inability of Pd(0) to undergo oxidative addition into the ring: we have previously shown that *trans*-**1** readily gives silole **2** on treatment with phenylacetylene and $PdCl_2(PPh_3)_2$ at ambient temperatures.[4] The difference in reactivity between the two silirane starting materials, therefore, must arise from a prohibitively slow step later in the catalytic cycle.

Silirenes **5c** and **5d** react with phenylacetylene in the presence of <3 mol % $PdCl_2(PPh_3)_2$ at 100−110 °C to give trisubstituted siloles **6c** (78%) and **6d** (99%), respectively (eq 3).[15,16] These results demonstrate that silirenes react with the palladium catalyst under the conditions of their formation. Interestingly, no products of their reactions with internal alkynes (such as tetrasubstituted siloles **7** or disilacyclohexadienes **8**) were observed during the formation of silirenes **5a**−**d**. In contrast, 1,1-dimethyl-substituted silirenes undergo metal-catalyzed insertion of mono- and disubstituted acetylenes to produce siloles[5,17] and readily dimerize in the presence of $PdCl_2(PEt_3)_2$ to form disilacyclohexadienes.[7] Ishikawa and Kumada have shown that the bulkier the substituents on the silicon atom of the silirene, the more difficult was the insertion of disubstituted acetylenes to form siloles[5] as well as dimerization to form disilacyclohexadienes.[18] The results shown in eq 3 demonstrate that oxidative addition of palladium into the silirene ring is not obviated by the bulky *tert*-butyl substituents on the silicon atom. Rather, the inability of silirenes **5** to insert another disubstituted acetylene to form a silole **7** must be due to the inaccessibility of a more advanced reactive intermediate.

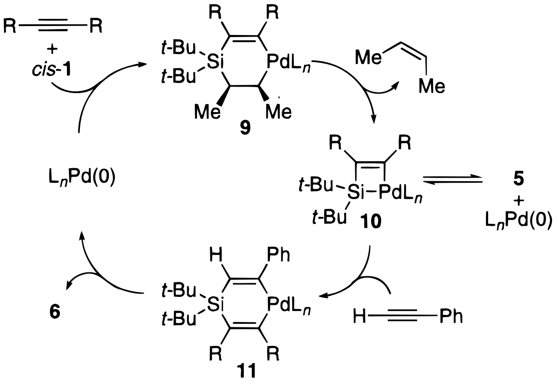


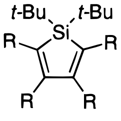
(3)

**5c**: R = Et
**5d**: R = Ph

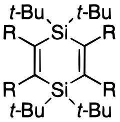
**6c**: R = Et (78%)
**6d**: R = Ph (99%)

**Scheme 1**





**7**



**8**

The formation of silirenes (eq 2) and siloles (eq 3) can be accounted for by a common reaction mechanism (Scheme 1). Oxidative addition of *in situ* generated Pd(0)[17] into the C−Si bond of *cis*-**1** occurs with stereospecific retention of configuration,[4] and subsequent insertion of a disubstituted acetylene would provide the *cis*-palladasilacyclohexene **9**. Migratory deinsertion to liberate *cis*-2-butene[4] would give the palladasilacyclobutene **10**.[19] Our data indicate that disubstituted acetylenes cannot form intermediates leading to tetrasubstituted siloles, so instead, reductive elimination forms silirene **5** exclusively. However, when a silirene **5** is exposed to a terminal acetylene, such as phenylacetylene, rapid formation of the trisubstituted silole **6**, via the palladasilacyclohexadiene **11**,[20] is observed. The formation of silirene and the subsequent elaboration to a silole demonstrates the reversible formation of the palladasilacyclobutene **10** and silirene **5**.

A question that arises from this work is whether silirenes possess less ring strain than the siliranes from which they are made. Recent calculations by Clark and co-workers on phosphirenium cations and the isolobal silirenes suggest that $\sigma^*$-aromaticity can overcome the inherent strain energy that would otherwise destabilize

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[14] Boudjouk reported di-*tert*-butyl-substituted silirene (where $R^1 = R^2 = SiMe_3$) which showed a $^{29}$Si NMR chemical shift of −86.2 ppm. The $SiMe_3$ substituents appear to increase the shielding of the ring-bearing silicon atom, hence this chemical shift would be consistent with data reported in Table 1. See ref 8.

[15] The regiochemistry indicated for **6c** was indicated by a 12% NOE between the *tert*-butyl group and the hydrogen on the ring.

[16] Control experiments where **5c** and **5d** were treated with phenylacetylene in the absence of palladium gave only unidentifiable degradation products.

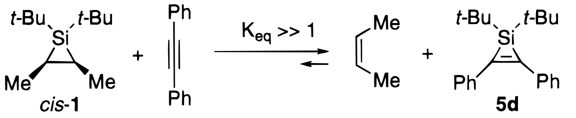
[17] Seyferth, D.; Shannon, M. L.; Vick, S. C.; Lim, T. F. O. *Organometallics* **1985**, *4*, 57−62.

[18] Ishikawa, M.; Sugisawa, H.; Kumada, M.; Higuchi, T.; Matsui, K.; Hirotsu, K. *Organometallics* **1982**, *1*, 1473−1477.

[19] A related nickelasilacyclobutene has been observed, see: Ishikawa, M.; Ohshita, J.; Ito, Y.; Iyoda, J. *J. Am. Chem. Soc.* **1986**, *108*, 7417−7419.

[20] A platinasilacyclohexadiene has been characterized and shown to reductively eliminate to form a silole, see: Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 3227−3232.

the unsaturated three-membered ring of a silirene.[21,22] A reversible reaction between a silirane and a silirene has not been reported, although reversible tungsten-catalyzed silylene transfer between two different silirenes has been reported.[9] Although the demonstration of an equilibrium between *cis*-**1** and **5d** would allow the measurement of the relative stability of these two strained rings, the formation of silirene **5d** from *cis*-**1** is an irreversible process (eq 4). No silirane was detected by $^1$H NMR spectroscopy when silirene **5d** was treated with an excess (>500 equiv) of *cis*-2-butene and heated to 130 °C in a sealed vessel, either with or without $PdCl_2(PPh_3)_2$. Therefore, experimental evidence indicates that the equilibrium strongly favors the silirene and alkene over the silirane and alkyne.



(4)

In conclusion, the palladium-catalyzed silylene transfer from siliranes to alkynes represents an unusual metal-mediated process that can be utilized for the synthesis of isolable silirenes. The bulky *tert*-butyl substituents hinder formation of tetrasubstituted siloles and disilacyclohexadienes and impart stability to the silirene structure. The silirenes can be further reacted with a monosubstituted acetylene to produce a trisubstituted silole. This reactivity suggests reversible formation of a palladasilacyclobutene and a silirene, and shows that the production of siloles and silirenes can be accounted for by a common reaction mechanism.

## Experimental Section

**General.** $^1$H and $^{13}$C NMR spectra were recorded at ambient temperature at 300, 500, and 125 MHz, respectively, using Nicolet QE-300, Omega 500, and GN-500 spectrometers. The $^1$H NMR data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the $\delta$ scale, multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration, and assignments. When uncertain, assignments were made with the assistance of decoupling, NOE, or DEPT (for $^{13}$C NMR) experiments. Chemical shifts are reported in ppm from tetramethylsilane on the $\delta$ scale, with the solvent resonance employed as the internal standard ($CDCl_3$ at 77.0 ppm and $C_6D_6$ at 128.0 ppm). $^{29}$Si NMR spectra were recorded at ambient temperature at 99.3 MHz using a Nicolet Omega 500 spectrometer, and chemical shifts are reported in ppm from tetramethylsilane resonance employed as the external standard on the $\delta$ scale at 0 ppm. High-resolution mass spectra were acquired on a VG Analytical 7070E or Fisons Autospec spectrometer and were obtained by peak matching. Microanalyses were performed by Atlantic Microlab (Atlanta, GA) or by Micrролytics (S. Deerfield, MA). Melting points are reported uncorrected. Analytical thin layer chromatography was performed on EM Reagents 0.25 mm silica gel 60-F plates. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on EM Reagents silica gel ($SiO_2$) 60 (230−400) mesh. All reactions were carried out under an atmosphere of nitrogen in glassware which had been flame-dried under a stream of nitrogen. Siliranes and silirenes were stored and handled in an Innovative Technologies nitrogen atmosphere drybox. Solvents were dried and distilled prior to use. NMR tube experiments were carried out with 5 mm Wilmad J. Young tubes or by flame-sealing NMR tubes, with $C_6D_6$ distilled from $CaH_2$ then sodium/benzophenone ketyl. Commercially available $PdCl_2(PPh_3)_2$ was used. Commercially available alkynes **4a**, **4c**, **4d**, and 2-butyn-1-ol were dried prior to use. Siliranes *cis*-**1** and *trans*-**1** were prepared according to the method of Boudjouk.[8]

**4-(*tert*-Butyldimethylsilyloxy)-2-butyne (4b).** 2-Butyn-1-ol (2.6 g, 37 mmol) and imidazole (5.1 g, 74 mmol) were dissolved in DMF (10 mL). The mixture was cooled in an ice bath, and *tert*-butyldimethylsilyl chloride (5.6 g, 37 mmol) was added. The reaction mixture was slowly warmed to ambient temperature, and 40 mL of water was added. The mixture was extracted with diethyl ether (2 × 40 mL), and the combined organic layers were washed with 1 N HCl (2 × 40 mL) and saturated aqueous NaCl (2 × 40 mL), concentrated *in vacuo*, dissolved in $CH_2Cl_2$ (50 mL), dried ($Na_2SO_4$), filtered, and concentrated to a yellow liquid. Purification by short-path distillation (54−57 °C/30 Torr) gave 5.27 g (78%) of **4b** as a clear liquid: bp 54−57 °C/30 Torr; TLC $R_f$ = 0.56 (15:85 EtOAc:hexanes); $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 4.18 (m, 2H, $CH_2O$), 1.74 (m, 3H, $CH_3CC$), 0.82 (s, 9H, *t-Bu*), 0.02 (s, 6H, $SiMe_2$); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 80.7, 77.7, 51.9, 25.8, 18.3, 3.5, −5.3; IR (thin film) 2930, 2858, 1255, 1081, 838, cm$^{-1}$; HRMS (CI/isobutane) *m/z* calcd for $C_{10}H_{19}OSi$ $(M - H)^+$ 183.1205, found 183.1201; LRMS (CI) *m/z* (relative intensity) 183 ($M^+ - H$, 23), 141(100). Anal. Calcd for $C_{10}H_{20}OSi$: C, 65.15; H, 10.94. Found: C, 61.77; H, 10.36.[23,24]

**1,1-Di-*tert*-butyl-2-phenyl-3-(trimethylsilyl)silirene (5a).** To a 20 mL bomb was added *cis*-**1** (533 mg, 2.69 mmol), 1-phenyl-2-(trimethylsilyl)acetylene (483 mg, 2.77 mmol), $PdCl_2(PPh_3)_2$ (10 mg, 0.5 mol %), and 3.7 mL of benzene. The bomb was sealed and heated in a 117 °C oil bath for 17 h. The reaction mixture was concentrated *in vacuo*, and purification by bulb-to-bulb distillation (90−120 °C/0.05 Torr) gave a mixture of **5a** and **4a**. A subsequent bulb-to-bulb distillation (92 °C/0.05 Torr) separated **4a** from **5a** to give **5a** as a clear liquid (694 mg, 81%): $^1$H NMR ($C_6D_6$, 500 MHz) $\delta$ 7.60 (m, 2H, Ar*H*'s), 7.24 (m, 2H, Ar*H*'s), 7.09 (m, 1H, Ar*H*), 1.09 (s, 18H, *t-Bu*$_2$), 0.32 (s, 9H, $SiMe_3$); $^{13}$C NMR ($C_6D_6$, 125 MHz) $\delta$ 174.0, 157.6, 137.4, 129.5, 128.7, 128.0,[25] 30.6, 21.1, 0.6; $^{29}$Si NMR ($C_6D_6$, 99.3 MHz) $\delta$ −13.6, −71.7; IR (thin film) 3060, 2956, 1470, 1246, 837 cm$^{-1}$; HRMS (CI/isobutane) *m/z* calcd for $C_{19}H_{32}Si_2$ ($M^+$) 316.2042, found 316.2036; LRMS (CI) *m/z* (relative intensity) 316 ($M^+$, 48), 259 ($M^+ - C_4H_9$, 48), 159 (100). Anal. Calcd for $C_{19}H_{32}Si_2$: C, 72.07; H, 10.19. Found: C, 71.97; H, 10.25.

**1,1-Di-*tert*-butyl-2-methyl-3-(*tert*-butyldimethylsilyloxymethyl)silirene (5b).** The procedure described for the synthesis of **5a** was used. Purification by bulb-to-bulb distillation (85−105 °C/0.05 Torr) gave 0.60 g (85%) of **5b** as a clear liquid: $^1$H NMR ($C_6D_6$, 500 MHz) $\delta$ 4.67 (q, *J* = 1.4, 2H, $CH_2O$), 2.27 (t, *J* = 1.4, 2H, $CCH_3$), 1.07 (s, 18H, Si*t-Bu*$_2$), 1.00 (s, 9H, OSi*t-Bu*), 0.10 (s, 6H, $SiMe_3$); $^{13}$C NMR ($C_6D_6$, 125 MHz) $\delta$ 150.0, 146.3, 62.6, 29.2, 25.2, 20.6, 17.6, 14.7, −6.1; $^{29}$Si NMR ($C_6D_6$, 99.3 MHz) $\delta$ 18.4, −65.3; IR (thin film) 2929, 1471, 1255, 1080, 836 cm$^{-1}$; HRMS (CI/isobutane) *m/z* calcd for $C_{14}H_{29}OSi_2$ $(M - C_4H_9)^+$ 269.1757, found 269.1755; LRMS (CI) *m/z* (relative intensity) 269 ($M^+ - C_4H_9$, 23), 147 (100). Anal. Calcd for $C_{18}H_{38}OSi_2$: C, 66.18; H, 11.73. Found: C, 64.41; H, 11.90.[24]

**1,1-Di-*tert*-butyl-2,3-diethylsilirene (5c).** The procedure described for the synthesis of **5a** was used. Purification by

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[21] Goller, A.; Heydt, H.; Clark, T. *J. Org. Chem.* **1996**, *61*, 5840−5846.

[22] Wild has recently reported the reaction of a phosphiranium ion with an alkyne to afford a phosphirenium ion, see: Hockless, D. C. R.; McDonald, M. A.; Pabel, M.; Wild, S. B. *J. Organomet. Chem.* **1997**, *529*, 189−196.

[23] The alkyne was thermally unstable and readily formed 1-(*tert*-butyldimethyl)silyl-2-butyn-1-ol.

[24] Repeated attempts to obtain satisfactory elemental analysis failed.

[25] Overlap of the aryl-CH with $C_6D_6$ was confirmed by a DEPT experiment.

bulb-to-bulb distillation (60−90 °C/0.05 Torr) gave 0.247 g (86%) of **5c** as a clear liquid: $^1$H NMR ($C_6D_6$, 500 MHz) $\delta$ 2.44 (q, $J$ = 7.6, 4H, C$H_2$), 1.13 (t, $J$ = 7.6, 6H, $CH_2CH_3$), 1.09 (s, 18H, *t-Bu*$_2$); $^{13}$C NMR ($C_6D_6$, 125 MHz) $\delta$ 152.8, 30.5, 22.5, 21.3, 15.3; $^{29}$Si NMR ($C_6D_6$, 99.3 MHz) $\delta$ −66.3; IR (thin film) 2964, 1470, 822 cm$^{-1}$; HRMS (CI/isobutane) *m/z* calcd for $C_{14}H_{28}Si$ ($M^+$) 224.1955, found 224.1960; LRMS (CI) *m/z* (relative intensity) 224 ($M^+$, 100), 167 ($M^+ - C_4H_9$, 93). Anal. Calcd for $C_{14}H_{28}Si$: C, 74.91; H, 12.57. Found: C, 72.30; H, 12.11.[24]

**1,1-Di-*tert*-butyl-2,3-diphenylsilirene (5d).** The procedure described for the synthesis of **5a** was used. Purification by bulb-to-bulb distillation (124−138 °C/0.05 Torr) gave 741 mg (84%) of a clear liquid as an 88:12 mixture of **5d**:**4d**. Further purification by vacuum sublimation gave 94 mg (12%) of a white solid that was pure by $^1$H and $^{13}$C NMR spectroscopy: mp 69−80 °C; $^1$H NMR ($C_6D_6$, 500 MHz) $\delta$ 7.65 (m, 4H, Ar*H*'s), 7.18 (m, 4H, Ar*H*'s), 7.06 (m, 2H, Ar*H*'s), 1.16 (s, 18H, Si*t-Bu*$_2$); $^{13}$C NMR ($C_6D_6$, 125 MHz) $\delta$ 151.8, 136.6, 129.1, 128.8, 127.6, 30.3, 21.8; $^{29}$Si NMR ($C_6D_6$, 99.3 MHz) $\delta$ −66.7; IR (thin film) 3057, 2928, 1469, 762, 691 cm$^{-1}$; HRMS (EI) *m/z* calcd for $C_{22}H_{28}Si$ ($M^+$) 320.1960, found 320.1955; GCMS (EI) *m/z* (relative intensity) 320 ($M^+$, 73), 263 ($M^+ - C_4H_9$, 69), 207 (100). Anal. Calcd for $C_{22}H_{28}Si$: C, 82.43; H, 8.80. Found: C, 81.98; H, 8.80.

**1,1-Di-*tert*-butyl-4,5-diethyl-3-phenylsilacyclopentadiene (6c).** To a bomb was added silirene **5c** (59 mg, 0.26 mmol), phenylacetylene (113 mg, 1.11 mmol), $PdCl_2(PPh_3)_2$ (2 mg, 1 mol %), and benzene (5 mL). The bomb was sealed and heated in a 115 °C oil bath for 12 h. The brown mixture was concentrated *in vacuo*, and purification by column chromatography (hexanes) gave **6c** as a clear liquid (66 mg, 78%): TLC $R_f$ = 0.48 (hexanes); $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.33−7.21 (m, 5H, Ar*H*), 5.71 (s, 1H, C*H*=C), 2.37 (q, $J$ = 7.6 Hz, 2H, C$H_2$), 2.25 (q, $J$ = 7.6, 2H, C$H_2$), 1.14 (t, $J$ = 7.6, 3H, $CH_2CH_3$), 1.10 (s, 18H, *t-Bu*), 0.66 (t, $J$ = 7.6, 3H, $CH_2CH_3$); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 163.8, 155.5, 143.3, 139.6, 127.7, 127.6, 126.7, 126.5, 29.1, 23.0, 21.1, 19.5, 15.1, 13.8; IR (thin film) 3025, 2964, 1468, 821, 700 cm$^{-1}$; HRMS (CI/isobutane) *m/z* calcd for $C_{22}H_{34}Si$ ($M^+$) 326.2430, found 326.2427; LRMS (CI) *m/z* (relative intensity) 326 ($M^+$, 85), 269 ($M^+ - C_4H_9$, 80), 135 (100). Anal. Calcd for $C_{22}H_{34}Si$: C, 80.91; H, 10.49. Found: C, 79.19; H, 10.33.[24]

**1,1-Di-*tert*-butyl-3,4,5-triphenylsilacyclopentadiene (6d).** A procedure similar to that used for the preparation of **6c** was employed. Purification by column chromatography (hexanes) gave **6d** as a clear viscous oil (74 mg, 99%): TLC $R_f$ = 0.22 (hexanes); $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.10 (m, 5H, Ar*H*), 6.98 (m, 8H, Ar*H*), 6.76 (m, 2H, Ar*H*), 6.22 (s, $^2J_{Si-H}$ = 11.1, 1H, SiC*H*=C), 1.15 (s, 18H, *t-Bu*); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 163.0, 154.8, 143.4, 142.2, 141.5, 138.8, 130.2, 129.4, 129.2, 128.0, 127.7, 127.3, 127.2, 126.6, 126.1, 125.0, 29.1, 20.1; IR (thin film) 3058, 2855, 1470, 697 cm$^{-1}$; HRMS (CI/isobutane) *m/z* calcd for $C_{30}H_{34}Si$ ($M^+$) 422.2430, found 422.2415; LRMS (CI) *m/z* (relative intensity) 422 ($M^+$, 100), 365 ($M^+ - C_4H_9$, 95). Anal. Calcd for $C_{30}H_{34}Si$: C, 85.25; H, 8.11. Found: C, 84.99; H, 8.07.

**Acknowledgment.** This research was supported by the National Institutes of Health (Grant No. GM-54909). K.A.W. thanks the American Cancer Society (for a Junior Faculty Research Award) and the Research Corporation (for a Cottrell Scholars Award). We thank the National Science Foundation and Pharmacia & Upjohn for generous support of our research. We thank Dr. John Greaves and Dr. John Mudd for mass spectrometric data.

**Supporting Information Available:** Spectra ($^1$H and $^{13}$C NMR) for compounds **4b**, **5b**, **5c**, and **6c** (8 pages). Ordering information is given on any current masthead page.

OM9704861