2,3-Disilaoxetanes from Tetramesityldisilene: Synthesis and Photolysis

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Tetramesityldisilene (1) reacts with acetone, 3-pentanone, 2,4-dimethyl-3-pentanone, benzophenone, butyraldehyde, benzaldehyde, tetraphenylcyclopentadienone, acrolein, methyl vinyl ketone, and ethyl vinyl ketone by [2 + 2] cycloaddition to the carbonyl group, yielding **2a–j**. Methyl furoate reacts similarly to give **6**, but other esters do not react with **1**. Photolysis of **2a,b,d** in the presence of ethanol gives trapped products corresponding to silenes **8a,b,d** and silanone **7**, which are postulated to arise from retro-[2 + 2] cleavage of the oxetane ring. Photolysis of **2a** without the presence of a trapping agent also leads to cleavage of the ring, producing allylsilane **11** and allyldisiloxane **13**.

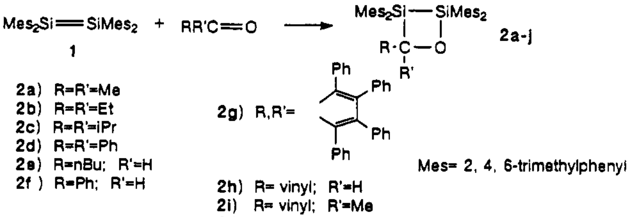
Introduction

Synthesis and Characterization of 2,3-Disilaoxetanes. Following the discovery of stable disilenes,[1] one of the first reactions to be reported was the 2 + 2 cycloaddition reaction with ketones.[2,3] An example is the reaction of tetramesityldisilene (**1**) with acetone to give the disilaoxetane **2a**. Subsequently, Schäfer and Weidenbruch showed that tetra-*tert*-butyldisilene, formed by the photolysis of hexa-*tert*-butylcyclotrisilane, reacts similarly with ketones to give cycloaddition products **3a–c** (Scheme I).[4]

In this paper we explore the generality of the reaction of **1** with various ketones, aldehydes, and α,β-unsaturated carbonyl compounds and describe the photolysis of the disilaoxetane **2a**.

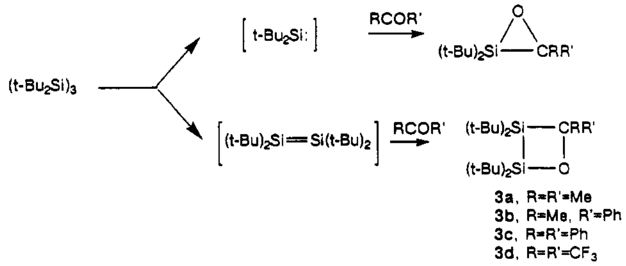
Results and Discussion

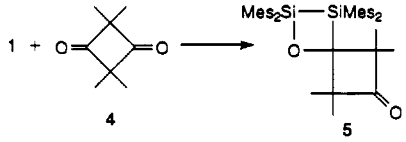
Reactions of tetramesityldisilene (**1**) with acetone, 3-pentanone, 2,4-dimethyl-3-pentanone, benzophenone, butyraldehyde, benzaldehyde, and tetraphenylcyclopentadienone all led to [2 + 2] cycloadducts as shown in eq 1. Both enolizable and nonenolizable ketones reacted similarly.[5] The rate of the reaction depended on the steric shielding at the carbonyl group. The reaction of **1** with acetone was complete within a few minutes at 25 °C, but the cycloaddition with 2,4-dimethyl-3-pentanone required heating for 12 h at 80 °C. The very hindered di-*tert*-butyl ketone failed to react with **1** at 80 °C, and at higher temperatures only the thermolysis product[2] of **1** was isolated. Reaction with the diketone **4** gave only the monocycloaddition product **5**; even long heating with excess **1** produced none of the bis cycloadduct, perhaps for steric reasons.



(1)

Scheme I. Photolysis of Hexa-*tert*-butylcyclotrisilane in the Presence of Ketones



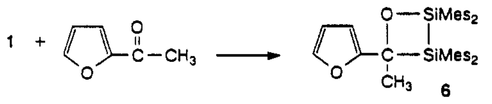


(2)

Disilenes do not react with 1,3-dienes such as isoprene[6] but are known to undergo [2 + 4] cycloaddition with 1,2-diketones (eq 3).[7] When **1** was treated with α,β-unsaturated aldehydes and ketones, [2 + 4] cycloaddition was not observed; instead, [2 + 2] addition took place to the carbonyl group to give products **2h–j**.

(3)

Although the [2 + 2] cycloaddition reaction between **1** and aldehydes or ketones appears to be quite general, **1** was unreactive toward most esters. Ethyl acetate, methyl benzoate, and ethyl *p*-(dimethylamino)benzoate all failed to react with **1** either at room temperature or after 3 days at 80 °C. Reaction was observed only with the activated carbonyl group in methyl furoate, to give the [2 + 2] cycloadduct **6**. The decreased reactivity of esters toward **1** compared with that of ketones can be accounted for by



(4)

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[1] For reviews on disilenes see: West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

[2] Fink, M. J.; DeYoung, D. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 1070.

[3] Even earlier, a [2 + 2] cycloaddition between transient tetramethyldisilene and benzophenone was proposed: Barton, T. J.; Kilgour, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 7631. Marchand, A.; Gerval, P.; Duboudin, F.; Joanny, M.; Mazerolles, P. *J. Organomet. Chem.* **1984**, *267*, 93.

[4] Schäfer, A.; Weidenbruch, M. *J. Organomet. Chem.* **1985**, *282*, 305.

[5] No products corresponding to an "ene" reaction were isolated, although these have been observed in reaction of Si═C compounds with ketones. See: Ando, W.; Ikeno, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **1977**, *99*, 6447 and references therein.

[6] Tetramesityldisilene was found to be unreactive toward alkenes and conjugated dienes: DeYoung, D. J.; Winslow, R.; West, R. Unpublished results.

[7] Boudjouk, P.; Han, B.-H.; Anderson, K. R. *J. Am. Chem. Soc.* **1982**, *104*, 4992.

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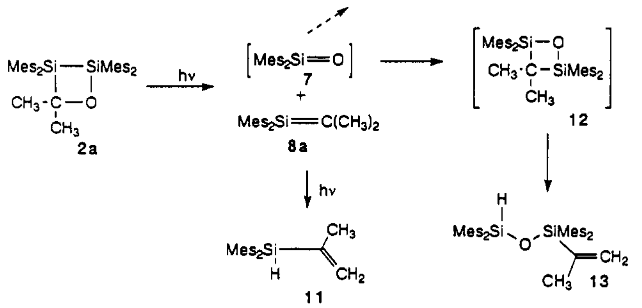
Scheme II. Proposed Pathway for Photolysis of Disilaoxetane 2a



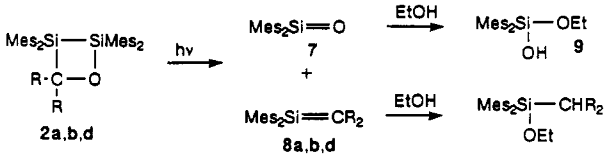
the lower polarity of the C=O bond in esters. A moderately strongly polarized multiple bond is apparently necessary for reaction to take place. This explanation is consistent with the fact that 1 does not react with alkenes and reacts only with polarized alkynes.[8]

Compounds **2a–c** and **2e–j** are all colorless or pale yellow solids, stable in air and in refluxing benzene. The ^{1}H NMR spectra of **2a–j** showed either two or four nonequivalent mesityl groups, depending on the presence or absence of a plane of symmetry. The barrier to rotation of the mesityl group increased with increasing size of the substituents R and R′. For instance, the ^{1}H NMR spectrum of **2a** at room temperature showed a sharp singlet for the *o*-Me resonance of the mesityl group attached to the silicon atom adjacent to oxygen, while the other *o*-Me resonance was quite broad. In **2b** the rotation was restricted enough to show two different resonances for the methylene unit of the ethyl groups. Finally for **2c**, the *o*-Me resonances were observed only as broad lumps. Additionally, in the spectra of the aldehyde cycloaddition products **2e,f**, the protons directly attached to the oxetane ring at the 4-position appeared very far downfield (deshielded), considering that they are in a saturated environment at carbon (5.35 and 6.12 ppm, respectively).

In the ^{29}Si NMR spectra, the cycloadducts showed two resonances, both falling between +14 and +35 ppm. Silicon atoms in four-membered rings are typically rather strongly deshielded; for example, the 2-silaoxetanes of Brook and co-workers have ^{29}Si chemical shifts of 42–65 ppm.[9] For compound **2a**, which has ^{29}Si resonances at 17.08 and 19.88 ppm, a two-dimensional ^{29}Si–^{1}H correlation experiment (H, X-COSY)[10] was performed, showing that the more downfield resonance was due to the silicon adjacent to the oxygen atom.

The $^{1}J_{^{29}\mathrm{Si}-^{29}\mathrm{Si}}$ value of **2a** was determined to be 84 Hz by using the INEPT-INADEQUATE pulse sequence adapted for the ^{29}Si nucleus.[11] Three- and four-membered-ring heterocycles formed from reactions involving tetramesityldisilene have tended to show large $^{1}J_{^{29}\mathrm{Si}-^{29}\mathrm{Si}}$ values (95–108 Hz), and it has been inferred that this is due to some degree of π-bonding between the silicon atoms.[12] However, the $^{1}J_{^{29}\mathrm{Si}-^{29}\mathrm{Si}}$ value of **2a** corresponds more closely to those of organodisilanes (85 Hz),[13] which suggests that little or no π-bonding is present.

Photolysis. Our results confirm earlier preliminary experiments which had suggested that **2a** photolyzed by retro-[2 + 2] ring cleavage to give the silene and silanone.[2] Photolysis of **2a** in pentane in the presence of ethanol produces a 1.0:1.0 mixture of compounds **9** and **10a**. As shown in eq 5, these products can reasonably be interpreted as resulting from the trapping of silanone **7** and silene **8a** by ethanol. Similar reactions with **2b,d** led to the analogous products **9** and **10b,d**, identified by GC/MS methods.



(5)

10a, R= Me
10b, R= Et
10c, R= Ph

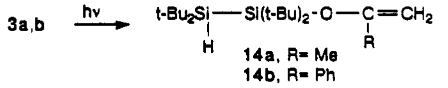
Photolysis of **2a** at −60 °C in pentane without ethanol produced a yellow solution, stable at room temperature, but it instantly decolorized upon exposure to air. When ethanol was added to this solution, decolorization also occurred and the major volatile product was **10a**.

After the yellow solution produced by photolysis of **2a** was exposed to air, two products in a 3:1 ratio were obtained by preparative gel permeation chromatography. The minor product was silane **11**, on the basis of the ^{1}H and ^{29}Si NMR and mass spectral data. The product may result from a 1,3-hydrogen shift of silene **8a**. If so, this appears to be the first example of a 1,3-hydrogen shift in silenes, although 1,3-alkyl shifts have been observed.[14]

The major product from the photolysis was identified as **13**. This product may arise from an ene reaction between **7** and **8a**, or alternatively, **7** and **8a** might undergo a [2 + 2] cycloaddition to the intermediate 1,3-disilaoxetane **12**. Ring opening of either Si–C bond of **12** followed by a hydrogen shift[2] could then yield **13**.

The photolysis of **2a** is summarized in Scheme II. In the proposed pathway, initial retro-[2 + 2] cleavage produces **7** and **8a**, which may be trapped with ethanol as shown in eq 5. In the absence of ethanol, part of silene **8a** undergoes rearrangement to **11** and part reacts with **7** to produce **13**. Much of the silane **7** must be lost by formation of as yet unidentified high-molecular-weight products.

Photolysis of tetra-*tert*-butyldisilaoxetanes **3a,b** was reported[4] to take a quite different course, displayed in eq 6, to give disilane products **14a,b**. A structure analogous to that of **14a** might be possible for our product **13** but is ruled out by a detailed consideration of the NMR spectrum.



$$\mathbf{3a,b} \xrightarrow{h\nu} \underset{\mathrm{H}}{\mathrm{t\text{-}Bu_2Si}}\text{—}\mathrm{Si(t\text{-}Bu)_2\text{-}O}\text{—}\underset{\mathrm{R}}{\mathrm{C}}\mathrm{=CH_2} \qquad (6)$$

14a, R= Me
14b, R= Ph

The ^{29}Si NMR spectrum of **13** showed peaks at −16.5 and −30.3 ppm. When the spectrum was acquired with the decoupler gated off, the −30 ppm peak split into a doublet ($^{1}J_{^{29}\mathrm{Si}-^{1}\mathrm{H}}$ = 213 Hz), indicating that this resonance was due to the terminal silicon nucleus. The other resonance was broadened to 33 Hz at half-height. This broadened peak was caused by coupling from the methyl and methylene

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[8] DeYoung, D. J.; Fink, M. J.; Michl, J.; West, R. *Main Group Met. Chem.* **1987**, *1*, 19.

[9] Brook, A. G.; Chatterton, W. J.; Sawyer, J. F.; Hughes, S. W.; Vorspohl, K. *Organometallics* **1987**, *6*, 1246.

[10] Maxka, J.; Huang, L. M.; West, R. *Organometallics* **1991**, *10*, 656.

[11] Maxka, J.; Adams, B. R.; West, R. *J. Am. Chem. Soc.* **1989**, *111*, 3447.

[12] Gillette, G. R.; Maxka, J.; West, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 54.

[13] Marsmann, H. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin and New York, 1981; Vol. 17, p 128.

[14] Eaborn, C.; Hopper, D. A. R.; Hitchcock, P. B.; Hopper, S. P.; Safa, K. D.; Washburne, S. S.; Walton, D. M. *J. Organomet. Chem.* **1980**, *186*, 309.

[15] Brook, A. G.; Harris, J. W.; Lennon, J.; El Sheik, M. *J. Am. Chem. Soc.* **1979**, *101*, 1584.

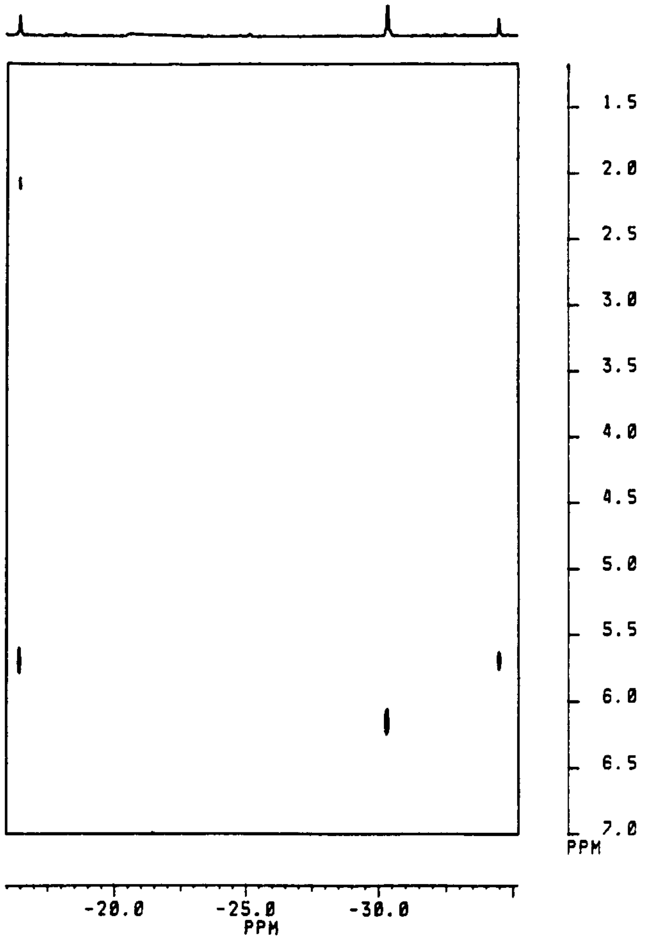

Figure 1. Two-dimensional ^{1}H, ^{29}Si COSY experiment of the reaction mixture from the photolysis of **2a**. Resonances at −16.5 and −30.3 ppm in the ^{29}Si spectrum are due to **13**: the −30.3 ppm peak is correlated with the Si–H proton at 6.179 ppm. The resonance at −34.5 is from **11**.

protons. The multiplet was not resolved because of line broadening caused by long-range coupling from the protons on the mesityl groups. If the reaction had occurred to give a product with a backbone like **14**, the signal at −16 ppm should have been split into a doublet with a $^{2}J_{^{29}Si-^{1}H}$ coupling of about 4 Hz. Furthermore, a two-dimensional ^{29}Si–^{1}H correlation NMR experiment was performed on the photolysis mixture (Figure 1). This spectrum shows that the silicon nucleus at −30 ppm is correlated with its attached proton at 6.1 ppm, while the other silicon nucleus at −16 ppm is coupled to both the methyl and methylene protons (2.06 and 5.65 ppm). If a structure analogous to **14** were present, a correlation from a $^{2}J_{^{29}Si-^{1}H}$ coupling should have been observed for the downfield silicon resonance, and no correlation should have been observed from the methyl protons at 2.0 ppm.

It is curious that the photolysis of **2a** takes such a different course from that of **3a,b**. The difference may reflect the greater steric crowding in the *tert*-butyl compounds. The X-ray crystal structure of the disilaoxetane **3c** shows an elongated Si–Si bond (240 pm) and a highly stretched Si–C bond (202 pm), which may favor Si–C bond breaking.[4]

Experimental Section

Solvents were distilled from Na/benzophenone immediately prior to use. Alcohols were distilled from sodium alkoxide. Aldehydes were distilled from K_2CO_3. Gas chromatography (GLC) was performed on a Hewlett-Packard Model 5720A gas chromatograph equipped with a flame ionization detector using a 3 ft × $^{1}/_{8}$ in. Dexsil column (5% on Chromosorb W), while a Gow-Mac Model 550P gas chromatograph equipped with a thermal conductivity detector and 9 ft × 1.4 in. Dexsil column (5% on Chromosorb W) was used for preparative work. Preparative gel permeation chromatography (GPC) was done on a Japan Analytical Industry Co. Model LC-908 instrument using a Jaigel-1H column of cross-linked polystyrene and refractive index detection. Toluene was used as an eluent with a flow rate of 3.5 mL/min.

NMR spectra were determined in benzene-d_6 unless otherwise noted. ^{1}H NMR spectra were recorded on a Bruker WP-200 spectrometer. ^{29}Si and ^{13}C spectra were recorded on either a Bruker AM-500 or an AM-360 spectrometer. All ^{29}Si spectra were collected by use of the INEPT pulse sequence with a ^{1}H refocusing pulse (standard Bruker program INEPTRD: D1 = 3.0 s, D2 = 0.085 s, D3 = 0.15 s). The two-dimensional ^{1}H, ^{29}Si COSY spectrum was run with use of the standard Bruker program XHCORR without futher modification (D1 = 3.0 s, D2 = 0.17 s, D3 = 0.30 s). Mass spectra were obtained with a Kratos MS-80 mass spectrometer, and GC/MS measurements were carried out on a Kratos MS-25 spectrometer.

Solutions for photolysis were made up in deolefinated pentane distilled from LAH and degassed with use of fine freeze–thaw–degas cycles. Solvents were similarly degassed before all reactions involving disilenes. Photolyses were carried out at 254 nm under vacuum in a Rayonet Model RPR-100 photoreactor. All other reactions were run under either dry nitrogen or argon.

Disilene **1** was prepared as either the solvent-free compound or **1**·2THF according to the modified literature preparation.[16] All other starting materials were purchased from Aldrich and used without further purification. Melting points are reported uncorrected.

4,4-Dimethyl-2,2,3,3-tetramesityl-2,3-disilaoxetane (2a). To 25 mL of degassed benzene was added 0.63 g (1.18 mmol) of **1** along with 1 mL of freshly distilled acetone. The solution was stirred until the solution was pale yellow. Evaporation of the solvents and recrystallization gave 0.42 g (60%) of **2a** as a white solid: mp 239–242 °C; ^{1}H NMR δ 1.62 (s, 6 H, Me_2C), 2.08 (s, 6 H, *p*-Me), 2.09 (s, 6 H, *p*-Me), 2.30 (s, 12 H, *o*-Me), 2.36 (br s, 12 H, *o*-Me), 6.66 (s, 4 H, Ar H), 6.70 (s, 4 H, Ar H); ^{29}Si NMR δ 17.08 (*Si*–CMe_2), 19.88 (*Si*–O), assignments made by 2-D ^{29}Si–H correlation (XHCORR); ^{13}C NMR δ 21.01, 25.60, 25.86, 33.54, 83.38, 129.2, 135.45, 136.32, 138.80, 138.45, 143.71; HRMS (EI) *m/z* $M^+ - (CH_3)_2C$ calcd for $C_{36}H_{44}Si_2O$ 548.2915, found 548.2931. Anal. Calcd for $C_{39}H_{50}Si_2O$: C, 79.3; H, 8.47. Found: C, 78.92; H, 8.33.

4,4-Diethyl-2,2,3,3-tetramesityl-2,3-disilaoxetane (2b). The same conditions were used as for **2a**. To 2 mL of Et_2CO in benzene was added 0.65 g (1.22 mmol) of **1**, giving 0.39 g (52%) of **2b** after recrystallization: mp 256–257 °C; ^{1}H NMR δ 0.89 (t, 6 H, CH_3CH_2), 1.97 and 2.11 (2 q, 4 H, CH_3CH_2), 2.07 (s, 6 H, *p*-Me), 2.08 (s, 6 H, *p*-Me), 2.32 (s, 12 H, *o*-Me), 2.56 (br s, 12 H, *o*-Me), 6.67 (s, 4 H, Ar H), 6.69 (s, 4 H, Ar H); ^{29}Si NMR δ 21.25, 21.03; ^{13}C NMR δ 20.88, 20.96, 23.8 br, 25.64, 32.73, 90.14, 128.6, 129.0, 135.72, 136.33, 138.0, 138.2, 143.3, 143.4; HRMS (EI) *m/z* $M^+ - (CH_3)_2C$ calcd for $C_{36}H_{44}Si_2O$ 548.2915, found 548.2924. Anal. Calcd for $C_{41}H_{54}Si_2O$: C, 79.55; H, 8.79. Found: C, 79.33; H, 9.00.

4,4-Diisopropyl-2,2,3,3-tetramesityl-2,3-disilaoxetane (2c). To 2 mL of 2,4-dimethyl-3-pentanone in benzene was added 0.65 g (1.22 mmol) of **1**. The mixture was refluxed overnight. A white product, **2c** (0.31 g, 40%), was obtained by recrystallization from hexane: mp 272–273 °C; ^{1}H NMR δ 0.97 (d, J = 6.7 Hz, 12 H, Me_2CH), 2.08 (s, 12 H, *p*-Me), 2.36 (br s, 12 H, *o*-Me), 2.92 (br s, 12 H, *o*-Me), 2.61 (sept, J = 6.7 Hz, Me_2CH), 6.66 (m, 8 H, Ar H); ^{29}Si NMR δ 17.05, 34.08; HRMS (EI) *m/z* $M^+ - (iPr)_2C$ calcd for $C_{36}H_{44}Si_2O$ 548.2915, found 548.2933.

2,2,3,3-Tetramesityl-4,4-diphenyl-2,3-disilaoxetane (2d). To 0.5 g of benzophenone in benzene was added 0.6 g (1.13 mmol) of **1**. The solution was heated to 50 °C for 1 h, but the yellow color persisted. Exposure of the solution to air did not cause decoloration of the solution. Kugelrohr distillation was used to remove the excess benzophenone. The residue was chromatographed on a silica gel column with 90:10 hexane–ether as eluent,

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[16] The chemistries in solution for **1** and **1**·2THF are identical. For the synthesis of tetramesityldisilene see: Yokelson, H. B.; Gillette, G. R.; Tan, R. P. K.; Millevolte, A. J.; West, R. *Inorg. Synth.*, in press.

yielding 0.10 g (12%) of the yellow fraction (**2d**): mp 282–284 °C; ^{1}H NMR δ 2.02 (s, 6 H, *p*-Me), 2.04 (s, 6 H, *p*-Me), 2.28 (s, 12 H, *o*-Me), 2.60 (s, 12 H, *o*-Me), 6.83–6.89 (m, 6 H, Ph), 7.49–7.56 (m, 4 H, Ph); ^{29}Si NMR δ 22.93, 23.61; HRMS (EI) *m/z* M$^+$ calcd for $C_{49}H_{54}Si_2O$ 714.3713, found 714.3728.

4-*n*-Butyl-2,2,3,3-tetramesityl-2,3-disilaoxetane (2e). The reaction of butanal (0.5 mL, >5× excess) with 0.6 g of **1** (1.13 mmol) in 13 mL of benzene was completed in less than 5 min at room temperature. Recrystallization from hexane afforded 0.46 g (67%) of **2e**: mp 209–211 °C; ^{1}H NMR δ 0.90 (pseudo-t, 3 H, $CH_3CH_2CH_2CH$), 1.60 (m, 2 H, $CH_3CH_2CH_2CH$), 1.90 (m, $CH_3CH_2CH_2CH$), 2.02, 2.03, 2.10, 2.14 (4 s, 12 H, *p*-Me), 2.20, 2.33 (2 s, 12 H, *o*-Me), 2.40 (br s, 6 H, *o*-Me), 2.70 (s, 6 H, *o*-Me), 5.33–5.37 (dd, $|J_{AX} + J_{BX}|$ = 13.7 Hz, 1 H, $CH_3CH_2CH_2CH$), 6.63, 6.76 (m, 8 H, Ar H); ^{29}Si NMR δ 14.55, 24.86. Anal. Calcd for $C_{40}H_{52}Si_2O$: C, 79.41; H, 8.66. Found: C, 79.10; H, 8.39.

2,2,3,3-Tetramesityl-4-phenyl-2,3-disilaoxetane (2f). To an excess of benzaldehyde in benzene was added 0.7 g (1.32 mmol) of **1**. The reaction was completed in about 1 min. Recrystallization from hexane afforded 0.59 g (70%) of **2f**: mp 228–229 °C; ^{1}H NMR δ 1.99 (s, 6 H, *o*-Me), 2.00, 2.05, 2.09, 2.12 (4 s, 12 H, *p*-Me), 2.43 (s, 12 H, *o*-Me), 2.75 (s, 6 H, *o*-Me), 6.12 (s, 1 H, PhC*H*), 6.52 (s, 2 H, Ar H), 6.66 (s, 4 H, Ar H), 6.75 (s, 2 H, Ar H), 6.95–7.0 (m, 3 H, Ph), 7.20–7.25 (m, 2 H, Ph); ^{29}Si NMR δ 15.69, 22.52; HRMS (EI) *m/z* M$^+$ calcd for $C_{43}H_{50}Si_2O$ 638.3400, found 638.3392.

Reaction of 1 with Tetraphenylcyclopentadienone (2g). A Schlenk flask was charged with 107 mg of **1**·2THF (0.17 mmol), 67 mg of tetraphenylcyclopentadienone (0.17 mmol), and 4 mL of benzene. After the mixture was stirred for 3 h at room temperature, a clear red solution had formed. The solvent was removed under vacuum, and the violet residue was suspended in 10 mL of ether, the suspension filtered, and the residue washed thoroughly with ether aliquots until the washing liquors were colorless to give 129 mg of **7** (89%): mp 207–208 °C; ^{1}H NMR (C_6D_6) δ 2.00, 2.06 (2 s, 6 H, *p*-Me), 2.12 (s, 6 H, *p*-Me), 2.23, 2.25, 2.38, 2.59 (4 s, 24 H, *o*-Me), 6.54–7.78 (m, 28 H, Ph); ^{29}Si NMR ($CDCl_3$) δ 0.21, 25.80; IR ($CHCl_3$) 3016 (s), 2921 (m), 1603 (m) cm^{-1}; low-resolution MS (EI) *m/z* 916 (M$^+$, 15%), 514 (15), 444 (15), 325 (18), 267 (20), 83 (100). Anal. Calcd for $C_{65}H_{64}Si_2O$: C, 85.09; H, 7.05. Found: C, 85.16; H, 6.98.

2,2,3,3-Tetramesityl-4-vinyl-2,3-disilaoxetane (2h). To 64 mg of **1** (0.12 mmol) in 5 mL of C_6D_6 at 10 °C was added 9 μL of acrolein (0.18 mmol). After the addition the yellow color of the solution faded immediately. The solution was stirred briefly to ensure that **1** was completely reacted. Removal of solvent in vacuo afforded 63 mg of **2h** (91%) as a waxlike solid: ^{1}H NMR (C_6D_6) δ 2.02 (s, 6 H, *p*-Me), 2.07, 2.11 (2 s, 6 H, *p*-Me), 2.18 (s, 6 H, *o*-Me), 2.29 (s, 6 H, *o*-Me), 2.33 (br s, 6 H, *o*-Me), 2.61 (s, 6 H, *o*-Me), 4.85 (ddd, *J* = 11, 1, <1 Hz, 1 H, HC=C*H*H′), 5.32 (ddd, *J* = 17, 1, 1 Hz, 1 H, HC=CH*H*′), 5.66 (ddd, *J* = 7, 1, 1, <1 Hz, 1 H, $Mes_2SiCHRO$), 6.22 (ddd, *J* = 17, 11, 7 Hz, 1 H, *H*C=CH_2), 6.60 (s, 2 H, Ar H), 6.64 (s, 4 H, Ar H), 6.70 (s, 2 H, Ar H); ^{29}Si NMR (C_6D_6) δ 14.41, 25.29; HRMS (EI) *m/z* calcd for $C_{38}H_{45}Si_2O$ 573.3009, found 573.4027.

4-Methyl-2,2,3,3-Tetramesityl-4-vinyl-2,3-disilaoxetane (2i). The same procedure as above with 89 mg of **1** (0.17 mmol) and 33 mL of methyl vinyl ketone gave 96 mg of **2i** (94%) as the major product: ^{1}H NMR (C_6D_6) δ 1.53 (s, 3 H, Me), 2.03, 2.05, 2.09, 2.12, 2.21, 2.31, 2.68 (7 s, 3:3:6:3:9:6:6, 36 H, *p*-Me and *o*-Me), 4.91 (m, 1 H, HC=C*H*H′), 5.31 (m, 1 H, HC=CH*H*′), 6.40 (m, 1 H, *H*C=CHH′), 6.64, 6.66, 6.70, 6.73 (5 s, 8 H, Ar H); ^{29}Si NMR (C_6D_6) δ 21.07, 23.99; HRMS (EI) *m/z* calcd for $C_{40}H_{50}Si_2O$ 602.3400, found 602.3417.

4-Ethyl-2,2,3,3-Tetramesityl-4-vinyl-2,3-disilaoxetane (2j). The same procedure with 67 mg of **1**·2THF (0.10 mmol) and 20 mL of ethyl vinyl ketone (0.20 mmol) gave 61 mg of **2j** (98%) as a pale yellow solid: ^{1}H NMR (C_6D_6) δ 0.98 (t, 3 H, CH_3), 1.02 (q, 2 H, CH_2CH_3), 2.02, 2.04, 2.08, 2.12 (4 s, 12 H, *p*-Me), 2.10, 2.23, 2.37, 2.66 (4 s, 24 H, *o*-Me), 4.92 (m, 1 H, HC=C*H*H′), 5.23 (m, 1 H, HC=CH*H*′), 5.98 (m, 1 H, *H*C=CHH′), 6.64, 6.67, 6.69, 6.73 (4 s, 8 H, Ar H); ^{29}Si NMR (C_6D_6) δ 21.68, 25.19; HRMS (EI) *m/z* calcd for $C_{41}H_{52}Si_2O$ 616.3557, found 616.3587.

Reaction of 1 with 2,2,4,4-Tetramethyl-1,3-cyclobutanedione (4). In a Schlenk flask a suspension of 630 mg of **1**·2THF (0.93 mmol) and 330 mg of **4** (2.35 mmol) in 10 mL of benzene was stirred at 40 °C for 3 h. The solvent was removed in vacuo from the pale yellow solution and the excess diketone sublimed at 40 °C/0.05 Torr into a cooled tube. The pale yellow residue was suspended in 12 mL of ether, the suspension filtered, and the residue washed with ether, to give 669 mg (93%) of **5** as a colorless powder: ^{1}H NMR δ 1.21 (s, 6 H, CH_3), 1.48 (s, 6 H, CH_3), 2.06 (s, 12 H, *p*-Me), 2.12 (s, 12 H, *o*-Me), 2.55 (s, 12 H, *o*-Me), 6.60 (s, 4 H, Ar H), 6.65 (s, 4 H, Ar H); ^{29}Si NMR δ 20.25, 24.08; IR ($CHCl_3$): 3014 (m), 2922 (m), 1761 (s), 1605 (m), 1456 (m), 1025 (w) cm^{-1}; MS (FAB) *m/e* 673 (M$^+$ + H, 1%), 547 (20), 445 (25), 385 (28), 283 (50), 119 (100).

Reaction of 1 with Methyl Furoate. A Schlenk flask was charged with 281 mg of **1**·2THF (0.41 mmol), 523 mg of methyl furoate (4.45 mmol), and 6 mL of benzene. After the mixture was heated to 80 °C for 15 min, a pale yellow solution had formed. The excess ester was removed under vacuum at 50 °C, leaving behind 224 mg of **5** (83%) as a yellow residue, which was recrystallized from hexane. Further recrystallizations did not improve the purity because of the large solubility of the product in benzene, ether, and pentane: ^{1}H NMR (C_6D_6) δ 1.98, 2.04 (2 s, 6 H, *p*-Me), 2.07 (s, 6 H, *p*-Me), 2.18, 2.46, 2.79, 2.95 (4 s, 24 H, *o*-Me), 3.40 (s, 3 H, OCH_3), 5.98 (m, 1 H, =CH), 6.08 (m, 1 H, =CH), 6.57 (s, 2 H, Ar H), 6.64 (s, 4 H, Ar H), 6.78 (s, 2 H, Ar H), 7.02 (m, 1 H, =CH); ^{29}Si NMR (C_6D_6) δ 14.99, 24.37; HRMS (EI) calcd for $C_{42}H_{50}Si_2O_3$ 658.3298, found 658.3311.

Photolysis of 2a with EtOH. A photolysis tube was charged with 60 mg (0.10 mmol) of **2a**, 10 mL of pentane, and 1 mL of ethanol. The solution was cooled to −60 °C and photolyzed at 254 nm for 2 h. The solution, which remained clear, was analyzed by GC/MS methods, and the products were isolated by preparative GLC. The yields were nearly quantitative, on the basis of the results of the gas chromatography. $Mes_2Si(OEt)(OH)$ (**9a**): GC/MS *m/z* (relative intensity) 328 (M$^+$, 1), 208 (M$^+$ − MesH, 100), 193 [M$^+$ − (MesH + Me), 88], 120 (MesH, 87); ^{1}H NMR δ 1.12 (t, 3 H, CH_3CH_2O), 2.11 (s, 6 H, *p*-Me), 2.55 (s, 12 H, *o*-Me), 3.67 (q, 2 H, CH_3CH_2O), 6.77 (s, 4 H, Ar H). $Mes_2Si(OEt)CH(CH_3)_2$ (**10a**): GC/MS *m/z* (relative intensity) 311 (M$^+$ − $CHMe_2$, 100), 267 (Mes_2H, 20), 191, (MesSiOEt − H, 7); ^{1}H NMR δ 1.09 (t, 3 H, CH_3CH_2O), 1.20 (d, 6 H, CH*Me*$_2$) 2.11 (s, 6 H, *p*-Me), 2.43 (s, 12 H, *o*-Me), 3.49 (q, 2 H, CH_3CH_2O), 6.73 (s, 4 H, Ar H).

Photolysis of 2b and 2d with EtOH. The same reaction conditions were used as with **2a**; the products were identified by GC/MS analysis. For **2b**, *m/z* (relative intensity) **9**, 328 (M$^+$, 2); **10b**, 311 (M$^+$ − Et_2CH, 100), 267 (Mes_2H, 20), 191 [M$^+$ − (Et_2CH + MesH), 9]. For **2d** (relative intensity): **9**, 328 (M$^+$, 1); **10d**, 478 (M$^+$, 0.2), 311 (M$^+$ − Ph_2CH, 100), 267 (Mes_2H, 30), 147 (MesSi, 8).

Photolysis of 2a Followed by Addition of EtOH. A photolysis tube was charged with 200 mg (0.34 mmol) of **2a** and 60 mL of pentane. The solution was photolyzed at −60 °C for 4 h. The apparatus was taken into a drybox, where 2 mL of dry ethanol was added, discharging the yellow color. Removal of solvent in vacuo followed by Kugelrohr distillation (60 °C/0.01 Torr) gave 13 mg (11%) of **10a**.

Photolysis of 2a. A photolysis tube was charged with 200 mg (0.34 mmol) of **2a** and 60 mL of pentane, and the solution was photolyzed at −60 °C for 4 h. Exposure to air decolorized the solution. Preparative gel permeation chromatography was used to separate two major products from the reaction mixture after three cycles. $Mes_2(H)SiC(CH_3)=CH_2$ (**11**): 20 mg (0.064 mmol, 38%); ^{1}H NMR δ 2.00 (pseudo-t, *J* = 1.35 Hz, 3 H, CC*H*$_3$), 2.10 (s, 6 H, *p*-Me), 2.39 (s, 12 H, *o*-Me), 5.52 (dq, $^4J_{H-H}$ = 1.1 Hz, $^2J_{H-H}$ = 3.2 Hz, 1 H, =CH), 5.57 (s, 1 H, SiH), 5.69 (dq, $^4J_{H-H}$ = 1.6 Hz, $^2J_{H-H}$ = 3.2 Hz, 1 H, =CH), 6.73 (s, 4 H, Ar H); ^{29}Si NMR δ −34.5 ppm ($^1J_{Si-H}$ = 179 Hz); HRMS (EI) *m/z* M$^+$ calcd for $C_{21}H_{28}Si_2$ 308.1960, found 308.1966. $Mes_2(H)SiOMes_2SiC(CH_3)=CH_2$ (**13**): 58 mg (0.094 mmol, 55% yield); HRMS (EI), *m/z* M$^+$ calcd for $C_{39}H_{50}Si_2O$ 590.3400, found 590.3424; ^{1}H NMR δ 2.074 (s, 6 H, *p*-Me), 2.086 (s, 3 H, CC*H*$_3$), 2.100 (s, 6 H, *p*-Me), 2.375 (s, 12 H, *o*-Me), 2.406 (s, 12 H, *o*-Me), 5.67 (dq, $^4J_{H-H}$ = 1.0 Hz, $^2J_{H-H}$ = 3.2 Hz, 1 H, =CH), 5.69 (dq, $^4J_{H-H}$ = 1.6 Hz, $^2J_{H-H}$ = 3.2 Hz, 1 H, =CH), 6.179 (s, 1 H, Si–H), 6.683 (s, 8 H, Ar H); ^{29}Si NMR δ −16.5, −30.3 ppm ($^1J_{Si-H}$ = 213 Hz).

Registry No. **1**, 80785-72-4; **2a**, 84537-20-2; **2b**, 135733-82-3; **2c**, 135733-83-4; **2d**, 84537-21-3; **2e**, 135733-84-5; **2f**, 135733-85-6;

2g, 135733-86-7; **2h**, 135733-87-8; **2i**, 135733-88-9; **2j**, 135733-89-0; **4**, 933-52-8; **5**, 135733-90-3; **6**, 135733-91-4; **9**, 95599-70-5; **10a**, 135733-92-5; **10b**, 135733-93-6; **10c**, 132724-77-7; **11**, 135733-94-7; **13**, 135733-95-8; RR′C=O (R = R′ = Me), 67-64-1; RR′C=O (R = R′ = Et), 96-22-0; RR′C=O (R = R′ = *i*-Pr), 565-80-0; RR′C=O (R = R′ = Ph), 119-61-9; RR′C=O (R = Pr, R′ = H), 123-72-8; RR′C=O (R = Ph, R′ = H), 100-52-7; RR′C=O (R = CH=CH$_2$, R′ = H), 107-02-8; RR′C=O (R = CH=CH$_2$, R′ = Me), 78-94-4; RR′C=O (R = CH=CH$_2$, R′ = Et), 1629-58-9; tetraphenylcyclopentadienone, 479-33-4; methyl 2-furoate, 611-13-2.

Alkene and Alkyne Insertion Reactions of Cationic $Cp_2Zr(\eta^2$-pyridyl)(L)$^+$ Complexes. Zirconium-Mediated Functionalization of Pyridines

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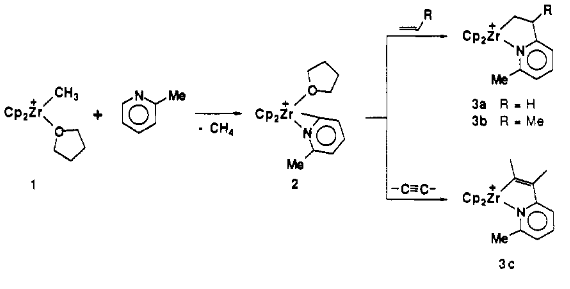
Cationic $Cp_2Zr(\eta^2$-pyridyl)(L)$^+$ complexes (L = THF, py), which are available via ortho C–H activation reactions of pyridines with $Cp_2Zr(Me)(THF)^+$, undergo insertion of alkenes and alkynes to yield new five-membered azazirconacycles. Normal 1,2-insertion leading to β-substituted azametallacycles is observed for α-olefins $H_2C=CHR$ containing electron-donating substituents (R = alkyl, CH_2SiMe_3, CH_2OR), while 2,1-insertion leading to α-substituted products is observed for styrene, 2-vinylpyridine, and vinyltrimethylsilane. The regioselectivity of these reactions is rationalized on the basis of electronic effects in the insertion transition states and products. Terminal alkynes insert regioselectively to yield α-substituted unsaturated five-membered metallacycles, but the unsymmetrical internal alkyne 2-hexyne affords a mixture of regioisomers. Steric effects appear to determine the regioselectivity in these cases. The silylacetylene $MeC\equiv CSiMe_3$ inserts selectively, yielding an α-$SiMe_3$ substituted metallacycle as a result of steric and Si electronic effects. The overall sequence of pyridine ortho C–H activation and alkene/alkyne insertion provides a powerful zirconium-mediated approach to substituted/functionalized pyridines.

Introduction

Zirconocene aryne species, e.g. Cp_2Zr(benzyne) (A, Chart I), exhibit facile insertion reactions with olefins, acetylenes, nitriles, CO_2, and other substrates,[1-3] Buchwald and coworkers have developed elegant syntheses of aromatic and heterocyclic compounds based on this chemistry.[3] We are exploring the insertion chemistry of cationic pyridyl complexes Cp_2Zr(pyridyl)(L)$^+$ (B, L = labile ligand, Chart I), which in their ligand-free form are isoelectronic with Cp_2Zr(benzyne), with the aim of developing general Zr-mediated routes to substituted pyridine-based heterocycles. The cationic zirconium(IV) alkyl complex $Cp_2Zr(CH_3)(THF)^+$ (1)[4,5] reacts selectively with a variety of pyridines, pyrazines, and related substrates via ortho C–H activation to yield new, three-membered azametallacycles, as illustrated for 2-picoline in eq 1.[6,7] The cationic pyridyl complex Cp_2Zr(6-Me-pyridyl)(THF)$^+$ (**2**) reacts readily with ethylene, propene, and 2-butyne to afford five-membered azametallacycles **3a–c** (eq 1).[8] These reactions involve initial displacement of THF by substrate, followed by insertion into the Zr–C bond. The functionalized heterocyclic ligands of **3a–c** can be removed by hydrogenolysis in a catalytic process (**3a,b**)[9] or by β-H elimina-

Chart I

A B



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