Silicon–Carbon Unsaturated Compounds. 41. Photochemical Behavior of 3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene

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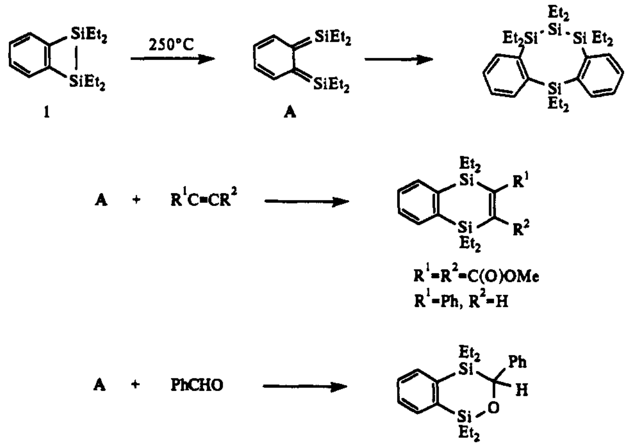
The photolysis of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene (1) with a low-pressure mercury lamp bearing a Vycor filter in hexane gave 1,2-bis[(2-diethylsilyl)phenyl]tetraethyldisilane. Irradiation of 1 in the presence of *tert*-butyl alcohol gave 1-(*tert*-butoxydiethylsilyl)-2-(diethylsilyl)benzene, while in the presence of *tert*-butyl-d_1 alcohol, compound 1 afforded 1-[*tert*-butoxy(1-deuterioethyl)ethylsilyl]-2-(diethylsilyl)benzene. The photolysis of 1 with acetone in hexane produced 2-(diethylsilyl)-1-[diethyl(isopropenyloxy)silyl]benzene. Irradiation of 1 with acetophenone gave 2-(diethylsilyl)-1-[diethyl[(1-phenylvinyl)oxy]silyl]benzene and 5,6-benzo-1,1,4,4-tetraethyl-3-methyl-3-phenyl-1,4-disila-2-oxacyclohexene (8). Similar irradiation of compound 1 with formaldehyde yielded 5,6-benzo-1,1,4,4-tetraethyl-1,4-disila-2-oxacyclohexene and 2-(diethylsilyl)-1-[ethylmethoxyvinylsilyl]benzene in 12% and 27% yields, respectively. Irradiation of 1 with benzaldehyde gave 5,6-benzo-1,1,4,4-tetraethyl-3-phenyl-1,4-disila-2-oxacyclohexene (11). The photolysis of 1 with a high-pressure mercury lamp bearing a Pyrex filter in the presence of acetophenone and benzaldehyde gave compounds 8 and 11, respectively.

Introduction

Recently, we have demonstrated that the thermolysis of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene (1) in a degassed sealed tube at 250 °C affords an *o*-quinodisilane as a reactive intermediate.[1] The *o*-quinodisilane thus formed undergoes dimerization to give 4,5,7,8-dibenzo-1,1,2,2,3,3,6,6-octaethyl-1,2,3,6-tetrasilacycloocta-4,7-diene in the absence of a trapping agent. In the presence of a trapping agent, such as dimethyl acetylenedicarboxylate, phenylacetylene, and benzaldehyde, however, the *o*-quinodisilane readily adds to the trapping agent to give [4 + 2] cycloadducts in high yields.

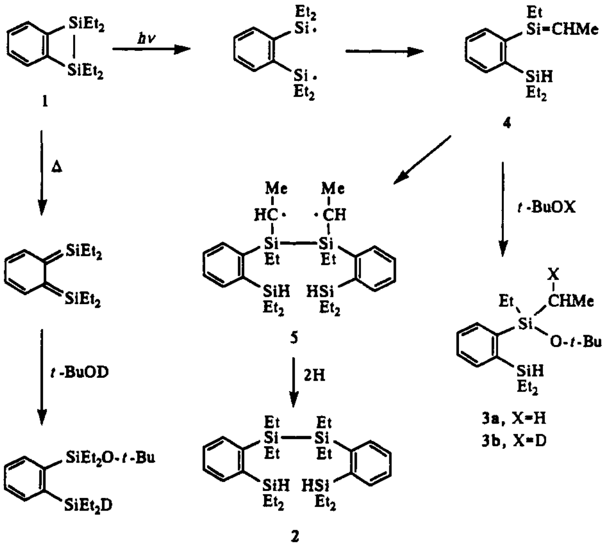


We have found that the photolysis of 1, however, gives a quite different reactive species from the *o*-quinodisilane.[2] In this paper, we report the photolysis of 1 with a low-pressure mercury lamp bearing a Vycor filter in the presence or absence of a trapping agent and with a high-pressure mercury lamp having a Pyrex filter in the presence of acetophenone and benzaldehyde.

Results and Discussion

First, we carried out the photolysis of 1 in the absence of a trapping agent. Thus, the photolysis of 1 by irradiation with a low-pressure mercury lamp bearing a Vycor filter (254 nm) in hexane for 2.5 h gave a quite unexpected product, 1,2-bis[(2-diethylsilyl)phenyl]tetraethyldisilane (2) in 64% yield, in addition to 12% of the unchanged starting compound 1 and small amounts of unidentified products (less than 9% combined yield).[3] The structure of 2 was confirmed by spectrometric analysis. The ^{13}C NMR spectrum of 2 shows the presence of two different ethylsilyl groups at δ 4.51, 7.20, 8.30, and 9.62 ppm and six resonances attributed to phenyl carbons. The IR spectrum reveals a strong absorption at 2142 cm^{-1} due to the stretching frequencies of an Si–H bond. These results are wholly consistent with the structure proposed for 2.

Scheme I



Next, we carried out the photolysis of 1 in the presence of a trapping agent. Irradiation of 1 in the presence of *tert*-butyl alcohol in hexane afforded 1-(*tert*-butoxydiethylsilyl)-2-(diethylsilyl)benzene (3a) in 68% yield, in addition to 26% of the unchanged starting 1. To our surprise, when similar photolysis was carried out in the presence of *tert*-butyl-d_1 alcohol, 1-[*tert*-butoxy(1-deuterioethyl)ethylsilyl]-2-(diethylsilyl)benzene (3b) was obtained in 79% yield, along with 18% of the starting compound 1. No Si–D bond was detected in the IR or ^2H NMR spectrum of product 3b. The IR spectrum of 3b shows absorption at 2152 cm^{-1}, attributed to the stretching

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(1) Ishikawa, M.; Sakamoto, H.; Tabuchi, T. *Organometallics* 1991, *10*, 3173.

(2) Sakamoto, H.; Ishikawa, M. *J. Organomet. Chem.*, in press.

(3) At least three products were produced in this photolysis, but all attempts to isolate these products were unsuccessful.

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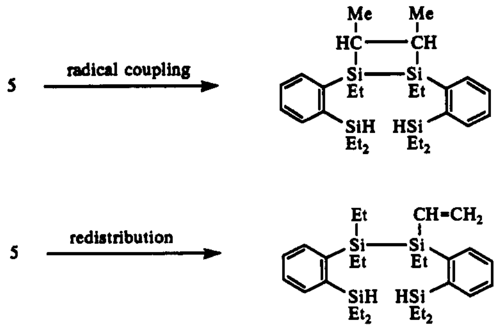
Scheme II



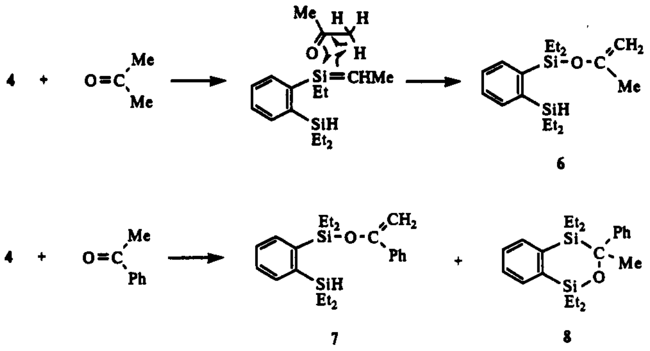
frequencies of an Si–H bond, and the ^{1}H NMR spectrum reveals a quintet signal at δ 4.61 ppm, due to a H–Si(Et)$_2$ proton. Mass and ^{2}H NMR spectra clearly indicate that the deuterium atom is incorporated on a carbon atom, but not on the silicon atom. Compound 3 is probably formed by the 1,2-addition of *tert*-butyl alcohol to silene 4, but not by the 1,4-addition to the *o*-quinodisilane intermediate (Scheme I).

As we reported recently,[2] the thermolysis of 1 in the presence of *tert*-butyl-d_1 alcohol in a sealed tube at 250 °C afforded the adduct in which a deuterium atom was attached to a silicon atom, indicating the adduct produced from the 1,4-addition of *tert*-butyl-d_1 alcohol to the *o*-quinodisilane.

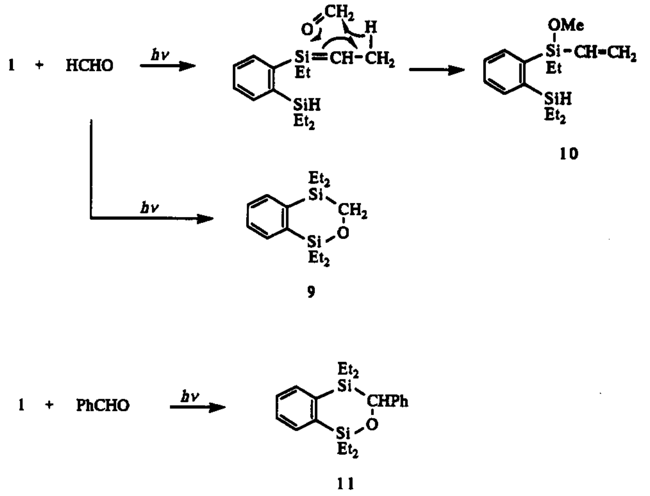
The thermolysis of 1 produces cleanly *o*-quinodisilane, but the photolysis proceeds with a quite different fashion from that of the thermolysis. In the photolysis, a diradical species is probably generated from homolytic scission of the silicon–silicon bond of 1. The resulting diradical undergoes an intramolecular disproportionation reaction to give silene 4. In the presence of *tert*-butyl alcohol, silene 4 reacts with this reagent to give compound 3, while in the absence of a trapping agent, 4 undergoes radical coupling, leading to a carbon diradical 5, which abstracts hydrogens from any available source to give product 2, as shown in Scheme I. Such photochemical behavior of 1 also differs from that observed in the photolysis of 1,1-dimethyl-2-phenyl-1-sila-2-cyclobutene[4] and 2,3-benzo-1,1-diphenyl-1-sila-2-cyclobutene,[5] which affords a 1-sila-1,3-butadiene and a *o*-silaquinone methide, respectively.

One might consider that the carbon diradical 5 was produced by intermolecular coupling of the silyl diradical species initially formed from homolytic scission of the silicon–silicon bond of 1. However, the photolysis of 1 in the presence of trapping agents affords no product derived from 5. Presumably, intramolecular disproportionation of the silyl radical leading to silene 4 is more favorable than the intermolecular coupling, followed by transformation to 5. Therefore, it seems likely that the carbon diradical 5 is produced from the dimerization of silene 4. The carbon diradical 5 thus formed would undergo radical coupling to give a disilacyclobutane or intramolecular disproportionation, leading to a vinyldisilane derivative, although these two compounds are minor products in the photolysis of 1 (Scheme II).

Scheme III



Scheme IV



One possibility to account for the production of 2 is that two radical centers in the diradical 5 are located at the anti position for steric reasons. In fact, examination of molecular models shows that the syn configuration of the two carbon radicals in 5 is sterically unfavorable. Consequently, hydrogen abstraction leading to the formation of 2 would be more favorable than radical coupling to give a four-membered cyclic system or disproportionation to produce the vinyldisilane derivative. In order to check the formation of these two products, we attempted to separate the byproducts obtained in 9% combined yield, with the use of GLC and GPC. Unfortunately, all attempts to isolate them in a pure form were unsuccessful. However, the mass spectrum of the mixture showed the parent ion at 496, corresponding to the calculated molecular weight of the dimer, $C_{28}H_{48}Si_4$. The ^{13}C NMR spectrum clearly indicates the presence of a vinyl group at δ 133.2 and 137.1 ppm and nonequivalent (Me)CHSi groups at δ 9.88 and 10.08 ppm. Therefore, both compounds might be produced in the present photolysis.

The formation of silene 4 can also be demonstrated by the photolysis of 1 in the presence of acetone. Thus, irradiation of 1 in the presence of 7 equiv of acetone in hexane afforded 1-[(isopropenyloxy)diethylsilyl]-2-(diethylsilyl)benzene (6) in 71% yield, in addition to 22% of the starting compound 1. It is well-known that the silenes generated photochemically react with enolizable ketones to give the products arising from the ene reaction,[6] analogous to 6. Similar photolysis of 1 in the presence of acetophenone produced two products, 2-(diethylsilyl)-1-[diethyl[(1-phenylvinyl)oxy]silyl]benzene (7) and 5,6-benzo-1,1,4,4-tetraethyl-3-methyl-3-phenyl-1,4-disila-2-oxacyclohexene (8) in 31% and 26% yields,[7] respectively (Scheme III).

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(4) Tzeng, D.; Fong, R. H.; Soysa, H. S. D.; Weber, W. P. *J. Organomet. Chem.* **1981**, *219*, 153.

(5) Okazaki, R.; Kang, K.-T.; Inamoto, N. *Tetrahedron Lett.* **1981**, *22*, 235.

(6) (a) Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51. (b) Ishikawa, M.; Nishimura, Y.; Sakamoto, H. *Organometallics* **1991**, *10*, 2701. (c) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

(7) The yields of compounds 7 and 8 highly depend on the amount of acetophenone used and the irradiation time. In the presence of a large excess of acetophenone, the yield of compound 8 increases. Prolonged irradiation leads to decomposition of compound 8.

Interestingly, the photolysis of 1 in the presence of formaldehyde gave again two products, 5,6-benzo-1,1,4,4-tetraethyl-1,4-disila-2-oxacyclohexene (**9**) and 2-(diethylsilyl)-1-[ethylmethoxyvinylsilyl]benzene (**10**) in 12% and 27% yields, respectively, in addition to 8% of the starting compound 1 (Scheme IV). All spectral data for compound **9** were identical with those of an authentic sample.[1] The structure of **10** was verified by mass, IR, and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopic analysis, as well as by elemental analysis. The IR spectrum reveals the strong absorptions at 2139 and 1082 cm^{-1}, due to the stretching frequencies of Si–H and Si–OMe bonds. The ^{1}H NMR spectrum of **10** shows a singlet resonance at 3.55 ppm and a quintet resonance at 4.42 ppm, due to methoxy protons and an Si–H proton, and double doublets at 5.81, 6.14, and 6.45 ppm, attributed to three vinylic protons, as well as multiple resonances at 0.79–1.00 and 7.31–7.67 ppm, due to ethylsilyl protons and phenyl ring protons. The ^{13}C and ^{29}Si NMR spectra are also consistent with the proposed structure (see Experimental Section).

Irradiation of 1 in the presence of benzaldehyde gave 5,6-benzo-1,1,4,4-tetraethyl-3-phenyl-2-oxa-1,4-disilacyclohexene (**11**) in 27% yield as the sole product, when 40% of the starting compound 1 was photolyzed.

In order to clarify the mechanism for the formation of the 5,6-benzo-2-oxa-1,4-disilacyclohexenes **8**, **9**, and **11** in the photolysis of 1 in the presence of carbonyl compounds, we investigated the photolysis of 1 using a high-pressure mercury lamp bearing a Pyrex filter. UV absorptions of 1 appear at 220 nm with a long tail at longer wavelengths. However, the photolysis of 1 with a high-pressure mercury lamp bearing a Pyrex filter in the presence of *tert*-butyl alcohol afforded no product. All of starting compound 1 was recovered unchanged. Interestingly, irradiation of 1 in the presence of acetophenone gave compound **8** as the sole product. No product arising from the ene reaction, such as compound **7**, was detected in the photolysis mixture. Similar irradiation of 1 in the presence of benzaldehyde again afforded **11** as a single product. These results clearly indicate that the 5,6-benzo-2-oxa-1,4-disilacyclohexenes may be produced by the reaction of photoexcited carbonyl compounds with compound 1. Presumably, the n,π^* excited carbonyl group was inserted into the silicon–silicon bond of the benzodisilacyclobutene 1.

In conclusion, the photolysis of 1 results in homolytic scission of a silicon–silicon bond to give diradical species, and the resulting diradical species undergoes an intramolecular disproportionation reaction to give the silene. The silene reacts with enolizable ketones to give adducts arising from the ene reaction. Photoexcited carbonyl compounds react with 1 to give 5,6-benzo-2-oxa-1,4-disilacyclohexenes.

Experimental Section

General Procedure. All photolyses were carried out under an atmosphere of dry argon. Mass spectra were determined on a Shimadzu Model GCMS-QP 1000. Infrared spectra were determined on thin liquid films for all samples using a Perkin-Elmer 1600 FT-infrared spectrometer. Gas chromatographic separations were carried out by using a column packed with 30% SE-30 silicone on Chromosorb P. Gel permeation chromatographic separation was performed with a Model LC-908 recycling preparative HPLC chromatograph (Japan Analytical Industry Co., Ltd.). ^{1}H, ^{13}C, and ^{29}Si NMR spectra were determined with a JEOL Model JNM-EX-270 spectrometer. Yields of the products were calculated on the basis of used 1 by analytical GLC, using tridecane as an internal standard.

Materials. Benzotetraethyldisilacyclobutene 1 (UV λ_{max} 220 nm) was prepared as reported previously.[1] The hexane used as a solvent for the photolysis was dried over lithium aluminum hydride and distilled before use.

Photolysis of 1 in the Absence of a Trapping Agent. A mixture of 0.3026 g (1.22 mmol) of 1 and 0.0654 g (0.355 mmol) of tridecane as an internal standard in 20 mL of hexane was photolyzed upon irradiation with a low-pressure mercury lamp for 2.5 h. The photolysis mixture was analyzed by GLC as being **2** (64% yield), unidentified products (less than 9% combined yield), and 12% starting compound 1. Product **2** was separated by preparative GPC: MS *m/e* 498 (M$^+$); IR ν_{Si-H} 2142 cm^{-1}; ^{1}H NMR (in CDCl$_3$) δ 0.75–0.99 (m, 40 H, EtSi), 4.50 (quint, 2 H, HSi, J = 3.3 Hz), 7.29–7.85 (m, 8 H, ring protons); ^{13}C NMR (in CDCl$_3$) δ 4.51, 7.20, 8.30, 9.62 (EtSi), 127.8 (2 C), 134.7, 135.5, 141.5, 144.6 (ring carbons); ^{29}Si NMR (in CDCl$_3$) δ −9.69, 0.93. Anal. Calcd for $C_{28}H_{50}Si_4$: C, 67.39; H, 10.10. Found: C, 67.59; H, 10.00.

Photolysis of 1 in the Presence of *tert*-Butyl Alcohol. A mixture of 0.2749 g (1.11 mmol) of 1, 0.3000 g (4.05 mmol) of *tert*-butyl alcohol, and 0.0875 g (0.475 mmol) of tridecane as an internal standard in 20 mL of hexane was photolyzed for 1.5 h. The photolysis mixture was analyzed by GLC as being **3a** (68% yield) and 26% starting compound 1. The solvent was evaporated and the mixture was distilled under reduced pressure to give volatile products. Product **3a** was separated by preparative GLC. All spectral data for **3a** were identical with those of an authentic sample.[1]

Photolysis of 1 in the Presence of *tert*-Butyl-d_1 Alcohol. A mixture of 0.3322 g (1.34 mmol) of 1, 0.2475 g (3.30 mmol) of *tert*-butyl-d_1 alcohol, and 0.0936 g (0.509 mmol) of tridecane as an internal standard in 20 mL of hexane was irradiated for 2 h. The mixture was analyzed by GLC as being **3b** (79% yield) and 18% starting compound 1. Pure **3b** was isolated by preparative GLC: MS *m/e* 294 (M$^+$ − Et); IR ν_{Si-H} 2144 cm^{-1}; ^{1}H NMR (in CDCl$_3$) δ 0.79–1.02 (m, 19 H, EtSi), 1.30 (s, 9 H, *t*-Bu), 4.60 (quint, 1 H, HSi, J = 3.3 Hz), 7.25–7.73 (m, 4 H, ring protons); ^{13}C NMR (in CDCl$_3$) δ 4.56, 7.10, 7.19, 8.34, 8.47 (t, J_{C-D} = 18.3 Hz), 8.84 (EtSi), 32.1 (Me$_3$C), 72.9 (CO), 127.6, 127.7, 134.8, 135.2, 142.3, 144.9 (ring carbons); ^{29}Si NMR (in CDCl$_3$) δ −9.59, 0.73; ^{2}H NMR (in C$_6$D$_6$) δ 0.96 (DC).

Photolysis of 1 in the Presence of Acetone. A mixture of 0.2448 g (0.987 mmol) of 1, 0.4132 g (7.12 mmol) of acetone, and 0.0915 g (0.497 mmol) of tridecane in 20 mL of hexane was photolyzed for 1 h. GLC analysis of the mixture showed the presence of **6** in 71% yield, in addition to 22% starting compound 1. Compound **6** was isolated by preparative GLC: MS *m/e* 277 (M$^+$ − Et); IR ν 2145, 1657, 1630, 1459, 1278 cm^{-1}; ^{1}H NMR (in CDCl$_3$) δ 0.75–1.01 (m, 20 H, EtSi), 1.84 (s, 3 H, Me), 3.94 (s, 1 H, HC=C), 4.00 (s, 1 H, HC=C), 4.47 (quint, 1 H, HSi, J = 3.3 Hz), 7.33–7.70 (m, 4 H, ring protons); ^{13}C NMR (in CDCl$_3$) δ 4.46, 6.85, 6.92, 8.28 (EtSi), 30.9 (Me), 90.8 (CH$_2$=C), 127.9, 128.2, 134.9, 135.0, 142.3, 142.9 (ring carbons), 155.9 (C=CH$_2$); ^{29}Si NMR (in CDCl$_3$) δ −8.42, 7.62. Anal. Calcd for $C_{17}H_{30}OSi_2$: C, 66.60; H, 9.86. Found: C, 66.57; H, 9.83.

Photolysis of 1 in the Presence of Acetophenone. A mixture of 0.3695 g (1.49 mmol) of 1, 0.6217 g (5.18 mmol) of acetophenone, and 0.1130 g (0.614 mmol) of tridecane in 20 mL of hexane was photolyzed for 3 h. GLC analysis of the photolysis mixture indicated the presence of **7** and **8** in 57% combined yield, in addition to 26% starting compound 1. The ratio of compounds **7** and **8** was determined by ^{1}H NMR to be 1.23:1. Compounds **7** and **8** were isolated by preparative GLC from the reaction mixture. For **7**: MS *m/e* 368 (M$^+$); ^{1}H NMR (in C$_6$D$_6$) δ 0.70–1.30 (m, 20 H, EtSi), 4.43 (d, 1 H, HC=C, J = 2.0 Hz), 4.80 (quint, 1 H, HSi, J = 3.3 Hz), 4.89 (d, 1 H, HC=C, J = 2.0 Hz), 7.33–7.70 (m, 4 H, ring protons); ^{13}C NMR (in C$_6$D$_6$) δ 4.83, 7.19, 7.31, 8.51 (EtSi), 90.8 (CH$_2$=C), 125.7, 128.5 (2 C), 128.6, 128.9, 135.3, 135.6, 138.1, 142.6, 143.2 (ring carbons), 156.1 (C=CH$_2$); ^{29}Si NMR (in C$_6$D$_6$) δ −8.26, 9.53. For **8**: see below.

Photolysis of 1 in the Presence of Formaldehyde. A mixture of 0.4335 g (1.75 mmol) of 1, formaldehyde generated thermally from 2.960 g (97.0 mmol) of paraformaldehyde, and 0.0900 g (0.493 mmol) of tridecane as an internal standard in 25 mL of hexane was photolyzed for 2.5 h. The mixture was analyzed by GLC as being **9** (12% yield) and **10** (27% yield), in addition to 8% unchanged starting compound 1. Products **9** and **10** were isolated by preparative GLC. All spectral data obtained from **9** were identical with those of the authentic sample reported previously.[1] For compound **10**: MS *m/e* 278 (M$^+$); IR ν 2139, 1446, 1411, 1082, 996 cm^{-1}; ^{1}H NMR (in $CDCl_3$) δ 0.79–1.00 (m, 15 H, EtSi), 3.55 (s, 3 H, MeO), 4.42 (quint, 1 H, HSi, J = 3.3 Hz), 5.81 (dd, 1 H, vinylic proton, J_{trans} = 20.1, J_{gem} = 3.9 Hz), 6.14 (dd, 1 H, vinylic proton, J_{cis} = 15.2, J_{gem} = 3.9 Hz), 6.45 (dd, 1 H, vinylic proton, J_{trans} = 20.1, J_{cis} = 15.2 Hz), 7.31–7.67 (m, 4 H, ring protons); ^{13}C NMR (in $CDCl_3$) δ 4.37, 6.34, 6.87, 8.36 (EtSi), 50.8 (MeO), 128.2, 128.4, 135.1, 135.6, 142.3, 142.8 (ring carbons), 134.7 ($CH_2{=}CH$), 135.3 ($CH{=}CH_2$); ^{29}Si NMR (in $CDCl_3$) δ −7.48, −2.55. Anal. Calcd for $C_{15}H_{26}OSi_2$: C, 64.68; H, 9.40. Found: C, 64.68; H, 9.39.

Photolysis of 1 in the Presence of Benzaldehyde. A mixture of 0.3456 g (1.39 mmol) of 1, 0.7498 g (7.07 mmol) of benzaldehyde, and 0.1186 g (0.645 mmol) of tridecane in 20 mL of hexane was photolyzed for 2 h. The mixture was analyzed by GLC as being compound 11 (27% yield), along with 60% starting compound 1. Compound 11 was isolated by preparative GLC: ^{1}H NMR (in $CDCl_3$) δ 0.36–1.09 (m, 20 H, EtSi), 5.18 (s, 1 H, HC), 7.30–7.55 (m, 9 H, phenyl and phenylene ring protons).[8] Other spectral data obtained from 11 were identical with those of the authentic sample.[1]

Photolysis of 1 in the Absence of a Trapping Agent with a High-Pressure Mercury Lamp Bearing a Pyrex Filter. A mixture of 0.5253 g (2.12 mmol) of 1 and 0.1169 g (0.635 mmol) of tridecane in 60 mL of hexane was photolyzed with a high-pressure mercury lamp bearing a Pyrex filter for 3 h. GLC analysis of the mixture showed that 100% of starting compound 1 was recovered unchanged.

Photolysis of 1 in the Presence of *tert*-Butyl Alcohol with a High-Pressure Mercury Lamp Bearing a Pyrex Filter. A mixture of 0.6064 g (2.45 mmol) of 1, 0.4985 g (6.74 mmol) of *tert*-butyl alcohol, and 0.1145 g (0.622 mmol) of tridecane in 60 mL of hexane was photolyzed with a high-pressure mercury lamp bearing a Pyrex filter for 3 h. GLC analysis of the mixture showed that 100% 1 was recovered unchanged.

Photolysis of 1 in the Presence of Acetophenone with a High-Pressure Mercury Lamp Bearing a Pyrex Filter. A mixture of 0.6249 g (2.52 mmol) of 1, 1.1800 g (9.83 mmol) of acetophenone, and 0.1189 g (0.646 mmol) of tridecane in 60 mL of hexane was photolyzed for 1 h. The mixture was analyzed by GLC as being 8 (79% yield), in addition to 19% starting compound 1. Compound 8 was isolated by preparative GLC: MS *m/e* 368 (M^+); IR ν 1598, 1491, 1459, 1414, 1378, 1367, 1236, 1120 cm^{-1}; ^{1}H NMR (in $CDCl_3$) δ 0.19–1.15 (m, 20 H, EtSi), 1.72 (s, 3 H, Me), 7.13–7.58 (m, 9 H, ring protons); ^{13}C NMR (in $CDCl_3$) δ 1.71, 3.85, 7.08, 7.12, 7.21, 7.78, 8.07, 8.65 (EtSi), 27.8 (Me), 72.5 (CO), 124.3, 125.1, 127.9, 128.2, 128.3, 132.9, 134.7, 141.4, 143.9, 148.2 (ring carbons); ^{29}Si NMR (in $CDCl_3$) δ −6.50, 2.48. Anal. Calcd for $C_{22}H_{32}OSi_2$: C, 71.68; H, 8.75. Found: C, 71.65; H, 8.75.

Photolysis of 1 in the Presence of Benzaldehyde with a High-Pressure Mercury Lamp Bearing a Pyrex Filter. A mixture of 0.5371 g (2.17 mmol) of 1, 1.6769 g (15.8 mmol) of benzaldehyde, and 0.1786 g (0.971 mmol) of tridecane as an internal standard in 60 mL of hexane was photolyzed for 45 min. GLC analysis of the mixture showed the presence of 11 in 67% yield, along with 23% starting compound 1. Compound 11 was isolated by preparative GLC. All spectral data obtained from 11 were identical with those of the authentic sample.

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[8] We reported the chemical shift of EtSi protons for 11 as 0.98–1.09 ppm, but this is incorrect. The correct chemical shift should be 0.36–1.09 ppm as reported here.

Synthesis, Characterization, and Properties of 16-Electron $Cp^*M(NO)(aryl)_2$ (M = Mo, W) Complexes[1]

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Treatment of $Cp^*M(NO)Cl_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$; M = Mo, W) in THF at low temperatures with equimolar amounts of diarylmagnesium reagents, $(aryl)_2Mg{\cdot}x$(dioxane), affords the diaryl complexes $Cp^*M(NO)(aryl)_2$ (aryl = Ph, *o*-tolyl, or *p*-tolyl), which are isolable in moderate yields and have been fully characterized by conventional spectroscopic methods. In addition, single-crystal X-ray crystallographic analyses have been performed on both *o*-tolyl complexes. Crystal data for $Cp^*Mo(NO)(o\text{-tolyl})_2$ (3): a = 11.570 (2) Å, b = 10.128 (3) Å, c = 18.439 (4) Å, β = 92.50 (2)°, Z = 4, space group $P2_1/a$ (No. 14), R_F = 0.030, R_{wF} = 0.033 for 3387 reflections with $I \geq 3\sigma(I)$. Crystal data for $Cp^*W(NO)(o\text{-tolyl})_2$ (6): a = 11.612 (3) Å, b = 10.168 (5) Å, c = 18.250 (3) Å, β = 91.87 (2)°, Z = 4, space group $P2_1/a$ (No. 14), R_F = 0.037, R_{wF} = 0.040 for 3019 reflections with $I \geq 3\sigma(I)$. Complexes 3 and 6 are isostructural and isomorphous and possess three-legged piano-stool molecular structures. Their intramolecular metrical parameters are comparable to those exhibited by the related dialkyl complex $CpW(NO)(CH_2SiMe_3)_2$, the most notable difference being the C_{aryl}–M–C_{aryl} angle in both 3 and 6, which is significantly greater than the C_{alkyl}–M–C_{alkyl} angle in the dialkyl species. The IR and electrochemical properties of the $Cp^*M(NO)(aryl)_2$ complexes indicate that their metal centers are more electron deficient than those in comparable $Cp'M(NO)(alkyl)_2$ (Cp' = Cp ($\eta^5\text{-}C_5H_5$), Cp*; M = Mo, W) complexes. This greater Lewis acidity is also manifested by the increased stability of the 1:1 adducts formed between the diaryl complexes and typical Lewis bases.

Introduction

Previous work in our laboratories resulted in the discovery of a family of 16-electron dialkyl complexes having the general formula $CpW(NO)R_2$ ($Cp = \eta^5\text{-}C_5H_5$; R = alkyl = CH_2SiMe_3, CH_2CMe_3, CH_2CMe_2Ph).[2] A surprising property of these formally unsaturated compounds is their thermal and oxidative stability. For example, they may be handled as solids in air for short periods of time at ambient temperatures with no deleterious effects, although

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[1] Organometallic Nitrosyl Chemistry. 53. Part 52: Reference 28.

[2] Legzdins, P.; Rettig, S. J.; Sánchez, L.; Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1985**, *107*, 1411.

0276-7333/92/2311-2583$03.00/0