ORGANOMETALLICS

Volume 16, Number 19, September 16, 1997

# Communications

## Photochemical Reactions of Oligosilanes with $C_{60}$

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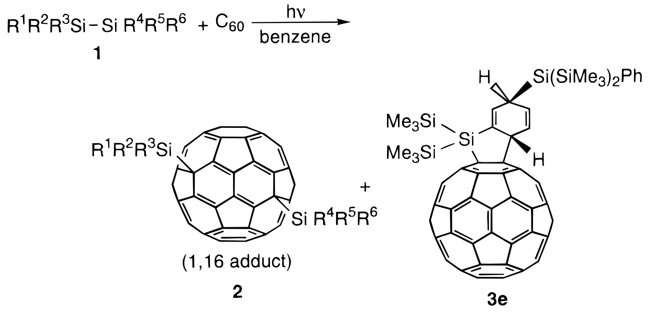
*Received April 14, 1997*[⊗]

*Summary: Photolyses of tert-butyl-substituted disilanes* ***1a*−*d*** *with $C_{60}$ result in the formation of 1,16-adducts* ***2****. The unusual products* ***3****, and* ***5*−*7****, in which the silyl and phenyl groups are attached on the 1,2-positions of $C_{60}$, also are obtained in the reactions of* ***1e*** *and* ***4*** *with $C_{60}$. A free silyl radical process is suggested for these conversions on the basis of experiments with other di- and oligosilanes.*

As part of our current studies on the reactivity of polysilanes with $C_{60}$,[1] we recently reported the isolation of 1,16 (and 1,29-)-adducts in the reactions of bulky-group-substituted silyllithiums with $C_{60}$.[1f] It has been well-established that virtually all disilanes which contain a particularly weak Si−Si bond, such as $Ph_3SiSiMe_3$ and/or those containing bulky substituents, are cleaved by 254 nm ultraviolet radiation to give silyl radicals. In this paper, we report that aryl-substituted disilanes on irradiation with 254 nm UV light in the presence of $C_{60}$ give rise to the 1,16-adducts **2** and 1,2-adducts **3** and **5**−**7** with concomitant 1,4-silyl migration.

**Scheme 1**



**a**: $R^1 = R^4 = t$-Bu, $R^2 = R^3 = R^5 = R^6 = 4$-Me-$C_6H_4$-
**b**: $R^1 = R^2 = R^4 = R^5 = t$-Bu, $R^3 = R^6 =$ Ph
**c**: $R^1 = R^4 = t$-Bu, $R^2 = R^3 = R^5 = R^6 =$ Ph
**d**: $R^1 = R^4 = t$-Bu, $R^2 = R^3 =$ Ph, $R^5 = R^6 = 4$-Me-$C_6H_4$-
**e**: $R^1 = R^2 = R^4 = R^5 = Me_3Si$, $R^3 = R^6 =$ Ph

Irradiation of a solution of 59.3 mg (111 mmol) of 1,1,2,2-tetrakis(4-methylphenyl)-1,2-di-*tert*-butyldisilane (**1a**) and 80.0 mg (111 mmol) of $C_{60}$ in 40 mL of benzene with a low-pressure mercury lamp (254 nm) for 0.5 h under an argon atmosphere, followed by purification by means of gel-permeation chromatography (Jaigel 1H and 2H columns, Japan Analytical Industry Co. Ltd.; eluent toluene), afforded 47 mg of the red-brown adduct **2a**[2] (54% yield, based on unreacted $C_{60}$; Scheme 1). The FAB mass spectrum of **2a** exhibits a peak at *m/z* 1255−1258 ($C_{96}H_{46}Si_2$, $M^+ + 1$, molecular cluster ion), as well as one for $C_{60}$ at *m/z* 720−723. The $^1H$ NMR spectrum of **2a** displays one *tert*-butyl signal,

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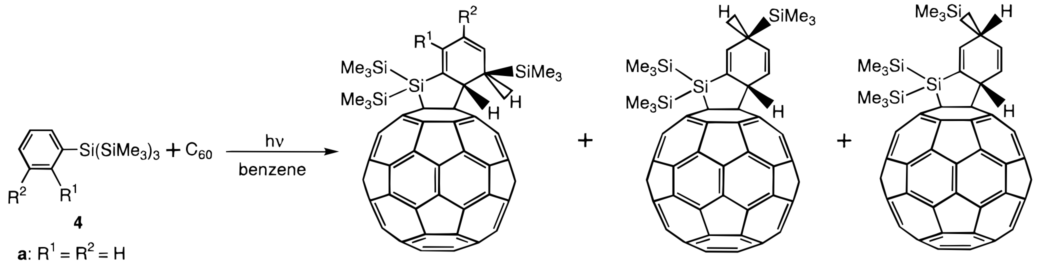
[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1997.

[1] (a) Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1993**, *115*, 1605. (b) Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1993**, *115*, 110366. (c) Akasaka, T.; Mitsuhida, E.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1994**, *116*, 2627. (d) Kusukawa, T.; Kabe, Y.; Erata, T.; Nestler, B.; Ando, W. *Organometallics* **1994**, *13*, 4186. (e) Kusukawa, T.; Kabe, Y.; Ando, W. *Organometallics* **1995**, *14*, 2142. (f) Kusukawa, T.; Ando, W. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1315. (g) Kusukawa, T.; Shike, A.; Ando, W. *Tetrahedron* **1996**, *52*, 4995. (h) Kusukawa, T.; Ohkubo, K.; Ando, W. *Organometallics* **1997**, *16*, 2746.

[2] $(C_{36}H_{46}Si_2)C_{60}$ (FAB MS, *m/z* 1255−1258): $^1H$ NMR (500 MHz, 1:1 $CDCl_3-CS_2$) $\delta$ 1.43 (s, 9H), 2.35 (s, 3H), 2.36 (s, 3H), 7.12 (d, 2H, $J = 7.7$ Hz), 7.17 (d, 2H, $J = 7.7$ Hz), 7.83 (d, 2H, $J = 7.7$ Hz), 7.89 (d, 2H, $J = 7.7$ Hz); $^{13}C$ NMR (126 MHz, 1:1 $CDCl_3-CS_2$) $\delta$ 21.61 (q), 21.63 (q), 22.32 (s), 29.12 (q), 64.99 (s, 2C), 127.61 (s), 127.67 (s), 128.26 (d), 128.35 (d), 136.52 (s, 2C), 136.74 (s, 2C), 137.40 (d), 137.51 (d), 138.68 (s, 2C), 139.59 (s, 2C), 139.72 (s), 139.76 (s), 140.55 (s, 2C), 141.30 (s, 2C), 141.47 (s, 2C), 142.07 (s, 2C), 142.14 (s, 2C), 142.34 (s, 2C), 143.36 (s, 2C), 143.80 (s, 2C), 144.29 (s, 2C), 145.44 (s, 2C), 145.86 (s, 2C), 145.88 (s, 4C), 146.01 (s, 2C), 146.06 (s, 2C), 146.40 (s, 2C), 146.81 (s, 2C), 146.93 (s, 2C), 147.00 (s, 2C), 147.74 (s, 2C), 148.55 (s, 2C), 150.22 (s, 2C), 152.90 (s, 2C), 162.39 (s, 2C), 164.07 (s, 2C); $^{29}Si$ NMR (80 MHz, 1:1 $CDCl_3-CS_2$) $\delta$ −3.71.

S0276-7333(97)00308-7 CCC: $14.00

**Scheme 2**

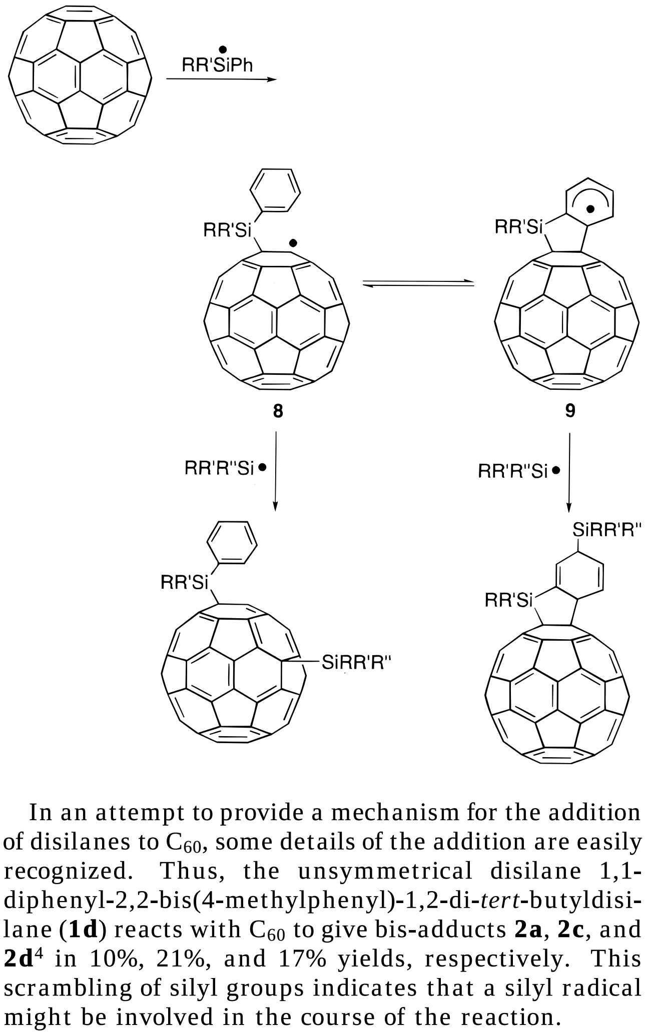


**4**
**a**: R$^1$ = R$^2$ = H
**b**: R$^1$ = R$^2$ = Me
**5**
**6a**
**7a**

two methyl signals, and two pairs of AB quartets. The $^{13}$C NMR spectrum of **2a** displays 29 signals for the $C_{60}$ carbon atoms, supporting $C_2$ symmetry for the molecule. One signal has a relative intensity of 4, and 28 signals have a relative intensity of 2; thus, the number of carbon atoms adds up to 60. Of the 29, one $C_{60}$ carbon atom resonates at 58.87 ppm. The signals of all other carbons appear in the region between 130 and 160 ppm. The $^{29}$Si NMR spectrum of **2a** shows one peak at −3.71 ppm, which is assigned to both silicon atoms of **2a**.

The reaction was attempted with the bulkier disilanes 1,1,2,2-tetraphenyl-1,2-di-*tert*-butyldisilane (**1b**) and 1,2-diphenyl-1,1,2,2-tetra-*tert*-butyldisilane (**1c**). Compounds **1b** and **1c** reacted with $C_{60}$ to give bis-adducts **2b**[3] (56% yield, based on unchanged $C_{60}$) and **2c** (62% yield, based on unreacted $C_{60}$), respectively.

**Scheme 3**



In an attempt to provide a mechanism for the addition of disilanes to $C_{60}$, some details of the addition are easily recognized. Thus, the unsymmetrical disilane 1,1-diphenyl-2,2-bis(4-methylphenyl)-1,2-di-*tert*-butyldisilane (**1d**) reacts with $C_{60}$ to give bis-adducts **2a**, **2c**, and **2d**[4] in 10%, 21%, and 17% yields, respectively. This scrambling of silyl groups indicates that a silyl radical might be involved in the course of the reaction.

Upon further investigation, we have found that photolysis of 2,3-bis(trimethylsilyl)-2,3-diphenyl-1,1,1,4,4,4-hexamethyltetrasilane (**1e**) in the presence of $C_{60}$ affords the 1,2-adduct **3e**[5] together with **2e**[6] in 43% and 24% yields (based on unreacted $C_{60}$), respectively. Interestingly, 1,2-adducts **5a**, **6**, and **7** also are obtained in 69% yield (product ratio; **5a**:**6**:**7** = 1:10:9) when a benzene solution of tris(trimethylsilyl)phenylsilane (**4a**) is photolyzed in the presence of $C_{60}$. No silylene adduct is found under these reaction conditions. Note that the (trimethylsilyl)phenylsilylene has been produced by photolysis of tris(trimethylsilyl)phenylsilane (**4a**) by Ishikawa and Kumada.[7] Furthermore, we have observed silylene addition in the photolysis of a bis(trimethylsilyl)diarylsilane with $C_{60}$.[1a] The $C_{60}$ unit of **5a**, **6**, and **7** displays the absence of any symmetry element in the $^{13}$C NMR spectrum. The $^1$H NMR

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(3) $(C_{32}H_{38}Si_2)C_{60}$ (FAB MS, *m/z* 1199−1202): $^1$H NMR (500 MHz, 1:1 $CDCl_3-CS_2$) $\delta$ 1.45 (s, 9H), 7.3−7.5 (m, 6H), 7.93 (d, 2H, $J$ = 6.8 Hz), 8.01 (d, 2H, $J$ = 6.8 Hz); $^{13}$C NMR (126 MHz, 1:1 $CDCl_3-CS_2$) $\delta$ 22.32 (s), 29.16 (q), 64.58 (s, 2C), 127.44 (d), 127.57 (d), 129.99 (d), 130.06 (d), 131.13 (s), 136.61 (s, 2C), 136.70 (s, 2C), 137.35 (d), 137.49 (d), 138.70 (s, 2C), 139.49 (s, 2C), 140.61 (s, 2C), 141.31 (s, 2C), 141.50 (s, 2C), 142.07 (s, 2C), 142.12 (s, 2C), 142.37 (s, 2C), 143.39 (s, 2C), 143.81 (s, 2C), 144.39 (s, 2C), 145.45 (s, 2C), 145.78 (s, 2C), 145.86 (s, 2C), 145.89 (s, 2C), 146.04 (s, 2C), 146.08 (s, 4C), 146.35 (s, 2C), 146.76 (s, 2C), 146.88 (s, 2C), 146.97 (s, 2C), 147.676 (s, 2C), 148.57 (s, 2C), 150.09 (s, 2C), 152.80 (s, 2C), 161.93 (s, 2C), 163.77 (s, 2C); $^{29}$Si NMR (80 MHz, 1:1 $CDCl_3-CS_2$) $\delta$ −3.99.

(4) $(C_{34}H_{42}Si_2)C_{60}$ (FAB MS, *m/z* 1227−1230): $^1$H NMR (500 MHz, 1:1 $CDCl_3-CS_2$) $\delta$ 1.42 (s, 9H), 1.45 (s, 9H), 2.34 (s, 9H), 2.36 (s, 9H), 7.12 (d, 2H, $J$ = 7.6 Hz), 7.16 (d, 2H, $J$ = 7.6 Hz), 7.3−7.5 (m, 6H), 7.82 (d, 2H, $J$ = 7.8 Hz), 7.88 (d, 2H, $J$ = 7.8 Hz), 7.94 (d, 2H, $J$ = 7.6 Hz), 8.01 (d, 2H, $J$ = 7.6 Hz); $^{13}$C NMR (126 MHz, 1:1 $CDCl_3-CS_2$) $\delta$ 21.60 (q), 21.62 (q), 22.26 (s), 22.37 (s), 29.11 (q), 29.18 (q), 64.52 (s, 1C), 65.06 (s, 1C), 127.42 (d), 127.53 (d), 127.57 (s, two carbons), 128.26 (d), 128.37 (d), 129.96 (d), 130.03 (d), 131.21 (s), 131.17 (s), 136.56 (s, 1C), 136.57 (s, 2C), 136.68 (s, 1C), 137.40 (d), 137.48 (d), 137.54 (d), 138.65 (s, 1C), 138.73 (s, 1C), 139.41 (s, 1C), 139.67 (s, 1C), 139.74 (s, 1C), 139.80 (s, 1C), 140.57 (s, 1C), 140.58 (s, 1C), 141.29 (s, 1C), 141.33 (s, 1C), 141.48 (s, 1C), 141.50 (s, 1C), 142.07 (s, 2C), 142.19 (s, 1C), 142.33 (s, 1C), 142.39 (s, 1C), 143.38 (s, 2C), 143.79 (s, 1C), 143.82 (s, 1C), 144.32 (s, 1C), 144.36 (s, 1C), 145.44 (s, 1C), 145.46 (s, 1C), 145.80 (s, 1C), 145.84 (s, 1C), 145.86 (s, 2C), 145.90 (s, 2C), 146.02 (s, 2C), 146.06 (s, 1C), 146.09 (s, 1C), 146.36 (s, 1C), 146.39 (s, 1C), 146.75 (s, 1C), 146.83 (s, 1C), 146.91 (s, 1C), 146.92 (s, 1C), 146.96 (s, 1C), 147.02 (s, 1C), 147.73 (s, 1C), 147.77 (s, 1C), 148.55 (s, 1C), 148.57 (s, 1C), 149.77 (s, 1C), 150.56 (s, 1C), 152.85 (s, 1C), 162.06 (s, 1C), 162.27 (s, 1C), 163.79 (s, 1C), 164.06 (s, 1C); $^{29}$Si NMR (80 MHz, 1:1 $CDCl_3-CS_2$) $\delta$ −3.67, −4.07.

(5) $(C_{24}H_{46}Si_6)C_{60}$ (FAB MS, *m/z* 1223−1226): $^1$H NMR (500 MHz, 1:3 $CDCl_3-CS_2$) $\delta$ 0.27 (s, 9H), 0.30 (s, 9H), 0.36 (s, 9H), 0.40 (s, 9H), 3.45 (m, 1H), 5.11 (m, 1H), 6.11 (m, 1H), 6.56 (m, 1H), 6.74 (m, 1H), 7.2−7.4 (m, 3H), 7.5−7.6 (m, 2H); $^{13}$C NMR (126 MHz, 1:3 $CDCl_3-CS_2$) $\delta$ 0.20 (q), 0.38 (q), 0.48 (q), 0.56 (q), 31.80 (d), 52.25 (d), 62.96 (s, 1C), 77.97 (s, 1C), 122.69 (d), 127.99 (d), 128.38 (d), 128.58 (d), 130.92 (s), 132.09 (s, 1C), 133.45 (s, 1C), 134.32 (s, 1C), 134.52 (s), 135.07 (d), 136.17 (s, 1C), 138.74 (s, 1C), 138.76 (d), 139.44 (s, 1C), 140.15 (s, 1C), 140.99 (s, 1C), 141.09 (s, 1C), 141.37 (s, 1C), 141.45 (s, 1C), 141.50 (s, 1C), 141.53 (s, 1C), 141.55 (s, 1C), 141.64 (s, 1C), 141.66 (s, 1C), 141.74 (s, 1C), 141.78 (s, 1C), 142.22 (s, 1C), 142.30 (s, 1C), 142.59 (s, 1C), 142.81 (s, 2C), 142.90 (s, 1C), 143.35 (s, 1C), 143.41 (s, 1C), 143.45 (s, 1C), 143.90 (s, 1C), 144.11 (s, 1C), 144.24 (s, 1C), 144.41 (s, 1C), 144.47 (s, 1C), 144.80 (s, 1C), 144.99 (s, 1C), 145.02 (s, 1C), 145.11 (s, 2C), 145.25 (s, 1C), 145.39 (s, 1C), 145.60 (s, 1C), 145.68 (s, 2C), 145.80 (s, 1C), 145.88 (s, 1C), 145.89 (s, 1C), 145.96 (s, 1C), 146.01 (s, 2C), 146.09 (s, 2C), 146.24 (s, 1C), 146.39 (s, 1C), 147.08 (s, 1C), 147.93 (s, 1C), 155.49 (s, 1C), 158.00 (s, 1C), 159.95 (s, 1C), 160.43 (s, 1C).

spectra of **5a**, **6**, and **7** show two aliphatic and three olefinic proton signals in each case. The $^{13}$C NMR spectra of **5a**, **6**, and **7** also show two aliphatic and three olefinic carbons in each case. The connectivities between these structural elements were determined by $^{13}$C−$^{1}$H COLOC (correlation spectroscopy via long-range coupling) experiments. With regard to the addition pattern of the $C_{60}$ moiety, 1,2-addition is most probable, and 1,4-addition is energetically unfavorable as determined by the AM1 semiempirical calculations.[8]

Recently, Leigh and Sluggett reported that photolysis of 1,2-di-*tert*-butyltetraphenyldisilane (**1c**)[9e] affords *tert*-butyldiphenylsilyl radicals exclusively; these were trapped quantitatively by a radical scavenger. However, pentamethylphenyldisilane behaves differently on photolysis, a major pathway being rearrangement to an intermediate written as a silene or a diradical species.[9] Sakurai and his co-worker[9c] reported ESR studies indicating the presence of radical species. One can easily anticipate that the bulkiness of the substituents on the phenyl group and the silicon atom is a key point of the process. Thus, the results are consistent with the efficient formation of 1,16-adducts **2** via silyl radicals upon photolysis. Tris(trimethylsilyl)phenylsilane (**4a**) on photolysis behaves differently, the major pathway being rearrangement of the silyl group on the phenyl ring to afford **5a**, **6a**, and **7**. Direct evidence for the formation of the rearranged products was obtained in the photolysis of **4b** with $C_{60}$. We obtained a single product, **5b**, in 79% yield.

Since $C_{60}$ is known to react efficiently with radicals, one possible course of the overall reaction may involve attack of a phenylsilyl radical on $C_{60}$ to give the radical intermediate **8**, shown in Scheme 3. There probably is a rapid equilibrium set up between this radical and the cyclohexadienyl radical **9** obtained from attack of the $C_{60}$-centered radical on the phenyl ring. The product mixture ultimately obtained now depends on which of these two radicals reacts faster with the other silicon radical produced initially. Bulky phenylalkylsilyl radicals react preferentially at the 16-position of the $C_{60}$ polycycle in the initially formed radical; trimethylsilyl and silylsilyl radicals react preferentially at the cyclohexadienyl ring of the subsequently formed radical.

**Acknowledgment.** We thank the Ministry of Education, Science and Culture of Japan for a Grand-in-Aid for Scientific Research and Shin-Etsu Chemical Co., Ltd., for a gift of chlorosilanes. We also thank one of the reviewers for useful comments during the review of this manuscript.

**Supporting Information Available:** Text giving detailed information on the experimental procedure and figures giving NMR spectra of the starting materials, **2a**−**e**, **3e**, **5a**, **6a**, **7a**, and **5b** (40 pages). Ordering information is given on any current masthead page.

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(6) $(C_{24}H_{46}Si_6)C_{60}$ (FAB MS, *m*/*z* 1223−1226): $^{1}$H NMR (500 MHz, 1:1 $CDCl_3$−$CS_2$) $\delta$ 0.41 (s, 18H), 0.42 (s, 18H), 7.2−7.4 (m, 3H), 7.74 (d, 4H, $J = 7.8$ Hz); $^{13}$C NMR (126 MHz, 1:1 $CDCl_3$−$CS_2$) $\delta$ 1.70 (q), 1.73 (q), 64.43 (s, 2C), 127.98 (d), 129.48 (d), 132.88 (s), 135.74 (s, 2C), 136.19 (s, 2C), 137.25 (d), 139.27 (s, 2C), 139.96 (s, 2C), 140.62 (s, 2C), 141.03 (s, 2C), 141.66 (s, 2C), 142.31 (s, 2C), 142.49 (s, 2C), 143.06 (s, 2C), 143.50 (s, 2C), 143.71 (s, 2C), 144.39 (s, 2C), 145.44 (s, 2C), 145.70 (s, 2C), 145.90 (s, 2C), 145.94 (s, 2C), 146.10 (s, 2C), 146.16 (s, 2C), 146.25 (s, 2C), 146.30 (s, 2C), 147.26 (s, 2C), 147.29 (s, 2C), 147.82 (s, 2C), 148.68 (s, 2C), 150.69 (s, 2C), 152.33 (s, 2C), 163.64 (s, 2C), 164.38 (s, 2C); $^{29}$Si NMR (80 MHz, 1:1 $CDCl_3$−$CS_2$) $\delta$ −12.90, −13.01, −24.36.

(7) (a) Ishikawa, M.; Nakagawa, K.; Kumada, M. *J. Organomet. Chem.* **1980**, *190*, 117. (b) Ishikawa, M.; Nakagawa, K.; Kumada, M. *J. Am. Chem. Soc.* **1981**, *103*, 4170. (c) Ishikawa, M.; Nakagawa, K.; Katayama, S.; Kumada, M. *J. Organomet. Chem.* **1981**, *216*, C48.

(8) Heats of formation (kcal mol$^{-1}$) of **5a**, **6**, and **7** are calculated by AM1 methods as follows: **5a** 1,2-form, 1067; **5a** 1,4-form, 1106; **6** 1,2-form, 1071; **6** 1,4-form, 1100; **7** 1,2-form, 1070; **7** 1,4-form, 1102.

(9) Ishikawa, M. *Pure Appl. Chem.* **1978**, *50*, 11. (b) Sakurai, H. *J. Organomet. Chem.* **1980**, *200*, 261. (c) Sakurai, H.; Nakadaira, Y.; Kira, M.; Sugiyama, H.; Yoshida, K.; Takiguchi, T. *J. Organomet. Chem.* **1980**, *184*, C36. (d) Sluggett, G. W.; Leigh, W. *Organometallics* **1992**, *11*, 3731.