groups C(4) and C(5) bend 0.04 and 0.08 Å out of this plane, respectively.

Despite the close approach of the carbene moiety, there does not appear to be any great strain on the other two ligands. The Co–S bond distance (2.175 Å) is just under the Co–S single bond value of 2.20 Å predicted from the sum of single bond radii.[23] The average Co–C(π) separation of 2.10 Å is essentially identical with the values of 2.096 (8) and 2.083 Å found for the average Co–C(cyclopentadienyl) distances in $(\eta^5\text{-}C_5H_5)_2Co$[24] and $[(\eta^5\text{-}C_5H_5)Co(PEt_3)_2]BF_4$,[21] respectively. The S–Co–C(1) bond angle of 97.8 (1)° is less than the P–Co–P angle of 101.21 (3)° observed in the more sterically demanding environment of $[(\eta^5\text{-}C_5H_5)Co(PEt_3)_2]BF_4$.[21] Smaller ligand–metal–ligand angles have been found for compounds of the type $(\eta^5\text{-}C_5Me_5)Co(CO)_2$ (CO–Co–CO = 93.7 (2)°)[25] and $(\eta^{10}$-fulvalene)$[Co(CO)_2]_2$ (CO–Co–CO = 92.7 (3)°).[26]

We are continuing to study the preparation and reactivity of other cobalt carbene complexes as well as new rhodium carbene complexes.[27]

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Supplementary Material Available: Tables of bond distances and angles, positional and thermal parameters, and observed and calculated structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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[23] Pauling, L., Ed. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; pp 255, 256.

[24] Bunder, W.; Weiss, E. *J. Organomet. Chem.* **1975**, *92*, 65.

[25] Byers, L. R.; Dahl, L. F. *Inorg. Chem.* **1980**, *19*, 277.

[26] Rogers, R. D., unpublished results.

[27] For example, $(\eta^5\text{-}C_5Me_5)Co(CO)[C(NMe)CH_2CH_2(NMe)]$ has been prepared from $(\eta^5\text{-}C_5Me_5)Co(CO)_2$ and bis(1,3-dimethylimidazolindin-2-ylidene) in boiling methylcyclohexane. Anal. Calcd for $C_{16}H_{25}CoN_2O$: C, 59.99; H, 7.87; N, 8.75. Found: C, 60.16; H, 8.01; N, 8.59. ^1H NMR (C_6D_6): 1.92 (s, 15 H), 2.47 (m, 2 H), 2.53 (m, 2 H), 3.14 (s, 6 H). $^{13}C\{^1H\}$ NMR (C_6D_6) δ 11.31, 38.08, 50.80, 90.98, 210.17, 224.02 IR (Pentane): ν_{CO} 1900 cm^{-1}. Likewise, $(\eta^5\text{-}C_5H_5)Rh(CO)[C(NMe)\text{-}CH_2CH_2(NMe)]$ was prepared in a manner similar to 1. Anal. Calcd for $C_{11}H_{15}N_2ORh$: C, 44.91, H, 5.14; N, 9.53. Found: C, 44.92; H, 5.14; N, 9.55. ^1H NMR (C_6D_6): δ 2.46 (s, 4 H), 2.98 (s, 6 H), 5.40 (s, 5 H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 39.25, 50.38, 85.60, 196.84 (d, $J_{^{103}Rh-^{13}C}$ = 92.9 Hz), 207.72 (d, $J_{^{103}Rh-^{13}C}$ = 62.9 Hz). IR (C_6D_6): ν_{CO} 1920 cm^{-1}. MS: *m/e* 294 (M$^+$).

Reaction of a Silene with a Silacyclopropane To Yield a Disilacyclopropane

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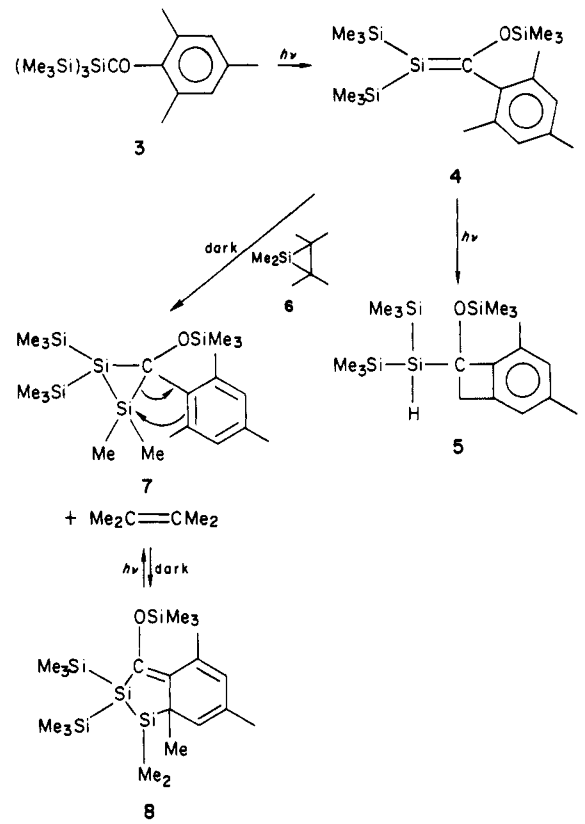
Summary: Photolysis of mesitoyltris(trimethylsilyl)silane initially yields the isomeric silene which subsequently inserts photochemically into one of the C–H bonds of an *o*-Me group to yield a substituted dihydrobenzocyclobutene. In the presence of hexamethylsilirane the silene adds Me_2Si: to yield a disilacyclopropane, the first such addition to a stable silene reported. In the dark the disilacyclopropane undergoes a 1,3-silyl carbon-to-aromatic carbon shift to give a bicyclo [4.3.0] system which photochemically isomerizes back to the disilacyclopropane.

Scheme I



As part of a program studying the behavior of relatively stable silenes, we wished to see if silylenes would add to the silicon–carbon double bond. Reasoning that the double bond of our previously made stable silenes 2, R = 1-adamantyl or CEt_3[1] would probably be too crowded (as

$$\underset{1}{(Me_3Si)_3SiCOR} \xrightarrow{h\nu} \underset{2}{(Me_3Si)_2Si{=}C(OSiMe_3)R}$$

preliminary experiments appear to confirm), we chose to investigate the behavior of the system where R = mesityl and have observed several unusual reactions including the first reported addition of a silylene to a stable silene to yield a disilacyclopropane.[2]

Photolysis of the mesitoylpolysilane 3 (see Scheme I) (prepared in the usual manner from (tris(trimethylsilyl)-silyl)lithium and mesitoyl chloride[3,4]) gave rise to the expected silene 4 as evidenced by the growth of new NMR signals, in particular a ^{13}C signal at 197.6 ppm and a ^{29}Si signal at 37.7 ppm characteristic of the sp^2-hybridized carbon and silicon atoms, respectively, of the double bond.[5,6] During extended photolysis (15 h) to isomerize

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[1] Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y. M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667.

[2] A few disilacyclopropanes have been described previously: (a) Seyferth, D.; Duncan, D. P. J. *J. Organomet. Chem.* **1976**, *111*, C21. (b) Masamune, S.; Murakami, S.; Tobita, H.; Williams, D. J. *J. Am. Chem. Soc.* **1983**, *105*, 7776. (c) Ishikawa, M.; Sugisawa, H.; Kumada, M.; Higuchi, T.; Matsui, K.; Hirotsu, K.; Iyoda, J. *Organometallics* **1983**, *2*, 174.

[3] All NMR spectra were run in C_6D_6 with H-coupled and DEPT spectra being employed as appropriate to making assignments.

[4] Properties of 3: mp 86–88 °C; IR(KBr) 1610 cm^{-1} (C═O); UV λ_{max} (ϵ) 373 (115), 387 (156), 404 (128) nm; ^1H NMR δ 0.23 (27 H, s, Me_3Si), 2.04 (3 H, s, *p*-Me), 2.15 (6 H, s, *o*-Me), 6.57 (2 H, br s, aromatic); ^{13}C NMR δ 1.66 (Me_3Si), 19.75 (*o*-Me), 20.98 (*p*-Me), 147.68, 137.56, 128.97, 131.07 (C_{ipso}, *o*, *m*, *p* of mesityl), 247.10 (C═O); ^{29}Si NMR δ −75.3 (Si), −11.4 (Me_3Si). Anal. Calcd for $C_{19}H_{38}Si_4O$: C, 57.80; H, 9.70. Found: C, 57.61; H, 9.81.

0276-7333/85/2304-1487$01.50/0

all the acylsilane, a new set of signals in addition to those of the silene **4** was observed which grew at the expense of the silene concentration such that by the end of a further 24 h photolysis all the silene had disappeared. (This reaction of the silene did not occur in the dark over several days.) The new compound was identified as the substituted dihydrobenzocyclobutene **5** based on its Si–H infrared absorption, the presence of only two Me–aryl groups, and the existence of a 2-proton AB system.[7] Formation of the dihydrobenzocyclobutene implies a photochemical insertion into a relatively unactivated C–H bond, possibly by a radical process although this is not yet proven.[8] This reaction is not an isolated example since the related (2,6-diethylbenzoyl)polysilane on photolysis gives a related dihydrobenzocyclobutene.[9]

When the mesitoylsilane **3** was photolyzed in solution with hexamethylsilirane **6**, in addition to the formation of **4** and **5** as expected, weak signals for a new compound, **7**, were observed. On standing overnight in the dark, the concentration of the silene **4** significantly diminished and considerable **7** and tetramethylethylene were formed, as well as weak signals due to a further compound, **8**. The spectroscopic properties of **7**, in particular a highly shielded silicon signal at −118 ppm as well as a less shielded silicon at −36 ppm which bore two methyl groups, are in accord with its being the disilacyclopropane **7**,[10] formed as a result of the silene reacting with the silirane in the dark and acquiring the elements of dimethylsilylene, although whether "free" dimethylsilylene is the actual reactant is not yet established. It is obvious that compound **7** is highly hindered sterically, since each methyl of the mesityl group has a separate NMR absorption.

The identity of the second new compound **8** then became a matter of some interest since on standing in the dark at room temperature over several hours **7** was cleanly converted to **8** (80% conversion in 24 h and virtually quantitative conversion in 2 days). Furthermore **8** could be rapidly reconverted to **7** by brief (20–60 min) photolysis at λ >360 nm, and cycling back and forth between **7** and **8** could be carried out repeatedly without side reactions.[11] The structure assigned to **8**[12] (or its isomer in which the groups attached to the two ring silicon atoms are interchanged) is supported by spectroscopic data and in particular the fact that the proton chemical shift of one of the three methyl groups attached to carbon moved upfield as a consequence of its attached carbon changing from sp^2 to sp^3 hybridization. The aromatic protons of **7** at 6.75 ppm moved upfield to 5.55 and 5.61 ppm as a result of the change to vinyl-type protons. In addition the absorption at −118 ppm of the highly shielded ring silicon bearing two trimethylsilyl groups moved downfield to −52 ppm as a result of the relief of steric strain: comparable shifts have been observed before as in silacyclopropanes (−49.3 ppm[13]) and silacyclobutanes (18.5 ppm[14]).

The clean, facile, reversible 1,3-isomerizations involved in the interconversions of **7** and **8** under very mild conditions, temperatures of about 25 °C and wavelengths above 360 nm, appear to constitute an exceptional situation in which ring strain energy closely balances loss of aromatic stabilization energy. We are continuing to explore this and related systems.

Acknowledgment. We are grateful to Professor Dietmar Seyferth for assistance with the hexamethylsilirane synthesis and to the Natural Science and Engineering Research Council of Canada for financial support.

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(5) Brook, A. G.; Abdesaken, F.; Gutekunst, G.; Plavac, N. *Organometallics* **1982**, *1*, 994.

(6) Properties of **4**: ^{1}H NMR δ −0.16 (18 H, s, two Me_3Si, accidental overlap), 0.29 (9 H, s, $Me_3Si(O?)$), 2.35 (9 H, s, *o*, + *p*-Me, accidental overlap), 6.70 (2 H, br s, aromatic); ^{13}C NMR δ 0.89, 1.34, 2.05 (Me_3Si), 21.25 (Me–Ar, accidental overlap), 141.75, 136.25, 128.52, 136.83 (C_{ipso}, *o*, *m*, *p* of mesityl), 197.66 (C═Si); ^{29}Si NMR δ −12.94, −11.92 (Me_3Si), 14.06 (Me_3SiO), 37.75 (Si═C).

(7) Properties of **5**: IR (neat) 2067 cm^{-1} (SiH); ^{1}H NMR δ −0.04, 0.07, 0.34 (each 9 H, s, Me_3Si), 2.13, 2.30 (each 3 H, s, Me), 3.28, 3.41 (2 H, AB system, J_{AB} = 14.5 Hz), 3.99 (1 H, s, SiH), 6.67 (2 H, br, aromatic); ^{13}C NMR (DEPT) δ 0.14, 1.05, 2.22 (each Me_3Si), 17.08, 22.14 (MeAr), 46.00 (CH_2), 75.55 ($COSiMe_3$), 121.74, 129.76 (each CH aromatic), 132.65, 138.68, 139.49, 148.61 (each C aromatic); ^{29}Si NMR δ −14.33, −16.45 (Me_3Si), 12.93 (Me_3SiO), −55.62 (SiH) ($^1J_{Si-H}$ = 164 Hz) ppm; MS, *m/e* 394 (M^+). Anal. Calcd for $C_{19}H_{38}Si_4O$: C, 57.80; H, 9.70. Found: C, 57.44; H, 9.71.

(8) A related insertion of a disilene into a mesityl CH_3 group has been described: Fink, M. J.; DeYoung, D. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 1070.

(9) These results will be described in the full paper.

(10) Properties of **7**: ^{1}H NMR δ −0.07, −0.02 (each 9 H, s, Me_3Si), 0.44 ($Me_3Si(O?)$), 0.44, 0.63 (each 3 H, s, Me_2Si), 2.11, 2.42, 2.83 (each 3 H, s, MeAr), 6.75 (2 H, br s, aromatic); ^{13}C NMR δ 1.87, 1.87, 2.63 (Me_3Si), −4.07, 0.63 (Me_2Si), 20.97, 22.43, 22.51 (MeAr), 62.02 ($COSiMe_3$), 129.50, 129.85, 136.36, 136.68, 137.73, 142.66 (aromatic); ^{29}Si NMR δ −118.5 (*Si*$(Me_3Si)_2$), −35.6 ($SiMe_2$), −11.5, −8.2 (each Me_3Si), 12.01 (Me_3SiO); MS calcd 452.2239, found 452.2245.

(11) During these interconversions the **5** present remains unchanged and hence is not involved in the interconversion of **7** and **8**.

(12) Properties of **8**: ^{1}H NMR δ 0.22, 0.23, 0.30 (each 9 H, s, Me_3Si), 0.45, 0.59 (each 3 H, s, Me_2Si), 1.40, 1.73, 2.36 (each 3 H, MeC), 5.55, 5.61 (2 H, br, HC-sp^2); ^{13}C NMR δ 1.08, 1.43, 1.96 (each Me_3Si), −0.68, 1.36 (Me_2Si), 20.95, 25.67, 33.19 (each MeC) 35.39 (sp^3-C Me), 125.19, 127.49, 131.18, 133.39, 146.06, 158.09 (C-sp^2); ^{29}Si NMR δ −52.3 (*Si*$(SiMe_3)_2$), −16.1, −14.4, −11.4 (two Me_3Si plus $SiMe_2$), 14.0 (Me_3SiO); MS calcd 452.2239, found 452.2240. Anal. Calcd for $C_{21}H_{44}Si_5O\cdot C_6D_6$: C, 60.36; H, 10.51. Found: C, 60.87; H, 10.58.

(13) Seyferth, D.; Annarelli, D. C. *J. Am. Chem. Soc.* **1975**, *97*, 2273.

(14) Seyferth, D.; Duncan, D. P.; Schmidbaur, H.; Holl, P. *J. Organomet. Chem.* **1978**, *159*, 137.

Homogeneous Catalytic Activation of Vinylic C–H Bonds. Stereoselective H–D Exchange in Neohexene

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Summary: Deuterium–hydrogen exchange between benzene-d_6 and neohexene (3,3-dimethylbutene) is catalyzed by $[(i\text{-}Pr_3P)_2IrH_5]$ at room temperature. The rate of exchange of the terminal vinyl proton trans to the *tert*-butyl group is >10 times that of the proton geminal to the *tert*-butyl group. This shows that, for certain olefins at least, activation of the vinyl C–H bond can occur more readily than addition–elimination reactions of metal hydride across the double bond.

There are numerous examples of H–D exchange reactions in arenes and alkanes, many of which are catalyzed

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