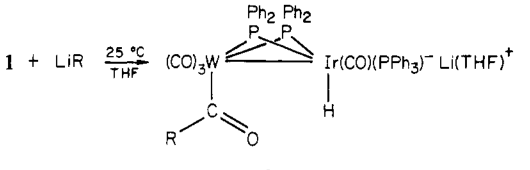
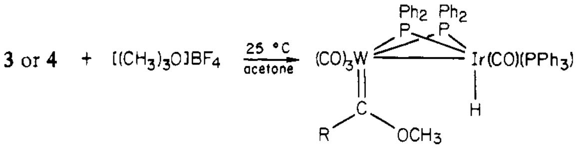


(3)

3, R = CH_3 (95%)
4, R = Ph (90%)

period to yield **1** as the only detectable organometallic product.

Treatment of **3** and **4** with $[(CH_3)_3O]BF_4$ leads smoothly to the stable binuclear carbene hydride complexes **5** and **6**, respectively (eq 4). These can be isolated as crystalline solids and have

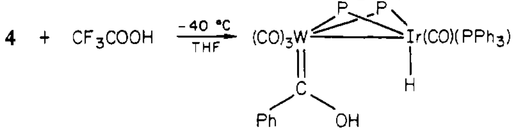


(4)

5, R = CH_3 (57%)
6, R = Ph (41%)

been spectroscopically characterized, **6** being studied more extensively.[11] These carbene hydride complexes are quite stable and show no tendency for the hydride to migrate to the carbene carbon. They can be heated to 60 °C without decomposition; prolonged heating at 90 °C induces decomposition to form **1** as the only observable organometallic product. Such behavior resembles the thermal decomposition of $Cr(CO)_5[C(OCH_3)Me]$, which yields principally $Cr(CO)_6$ upon heating.[12]

Protonation of the acyl complex **4** with CF_3COOH at -40 °C leads to the formation of a hydroxycarbene-hydride complex, **7** (eq 5). Complex **7** has been characterized spectroscopically and

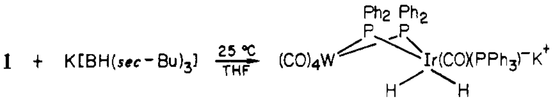


(5)

7

appears similar to the methoxycarbene complex **6**.[13] Upon warming up to 25 °C, **7** decomposes, releasing PhCHO and yielding **1** as the principal organometallic product. The latter must derive by scavenging of CO by the coordinatively saturated intermediate that is formed upon aldehyde elimination.

The preparation of a binuclear formyl hydride complex analogous to the acyl hydride complexes **3** and **4** was also attempted by reacting **1** with $K[BH(sec\text{-}Bu)_3]$, but this reaction instead led cleanly to the formation of the dihydride complex **8** (eq 6). The



(6)

8

$^{31}P\{^1H\}$ NMR resonances for the μ-PPh_2 ligands of **8** appear far upfield, implying the absence of a metal–metal bond.[14] Addition of H^- occurs at the iridium center with displacement of the W–Ir bond.

The binuclear acyl hydride and carbene hydride complexes described herein are the first reported heterobimetallic examples of such classes of compounds. Indeed, the stability of these complexes is somewhat surprising. Although facile aldehyde elimination from **3** and **4** via coupling of acyl and hydride ligands and alkyl formation from **5**–**7** by hydride migration to the carbene ligand might have been anticipated, neither of these transformations readily occur.[15] It is thus important to consider why these reactions do not take place. The most straightforward interpretation is that aldehyde elmination and alkyl formation in these complexes cannot occur by direct hydride migration from iridium to the organic ligand on tungsten but that such reactions must proceed through initial hydride migration of tungsten itself. However, the W center in these derivatives is best considered as a six-coordinate W(0) species (cf. Figure 1). It is thus coordinatively saturated with no open site to which the hydride ligand can migrate, and thus the complexes are stable as formed with the hydride remaining on iridium.

Acknowledgment. We thank the Department of Energy, Office of the Basic Energy Sciences, for support of this research and also gratefully acknowledge the assistance of the SOHIO, Union Carbide, Celanese, and Air Products and Chemicals Corporations for grants that contributed to this research program. G.L.G. acknowledges the Camille and Henry Dreyfus Foundation for a Teacher–Scholar Award (1978–1983) and the John Simon Guggenheim Memorial Foundation for a fellowship (1982).

Supplementary Material Available: Data for the X-ray diffraction study of **1**, positional and thermal parameters and their estimated standard deviations, bond distances, bond angles, and structure factors for **1** (37 pages). Ordering information is given on any current masthead page.

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[11] **6**: IR ν_{CO} (hexane) 2012 w, 1968 m, 1938 s, 1920 m cm^{-1}; $^{31}P\{^1H\}$ NMR δ 119.3 (dd, $J_{^{31}P-^{31}P}$ = 136.2, 48.4 Hz), 97.7 (dd, $J_{^{31}P-^{31}P}$ = 136.2, 2.2 Hz), 22.6 (dd, $J_{^{31}P-^{31}P}$ = 48.4, 2.2 Hz); ^1H NMR δ −13.0 (ddd, $J_{^1H-^{31}P}$ 16.4, 16.4, 17.9 Hz); MS, *m/e* (FABS) 1242 (M^+) plus fragment ions corresponding to successive loss of five CO's; satisfactory C, H analysis.

[12] Fischer, E. O.; Plabst, D. *Chem. Ber.* **1974**, *107*, 3326.

[13] **7**: $^{31}P\{^1H\}$ NMR (−10 °C, acetone-d_6) δ 113.4 (dd, $J_{^{31}P-^{31}P}$ = 128.8, 26.1 Hz), 61.5 (br d, $J_{^{31}P-^{31}P}$ = 128.8 Hz), 24.3 (br d, $J_{^{31}P-^{31}P}$ = 26.1 Hz); ^1H NMR (5 °C, acetone-d_6) δ −12.8 (ddd, $J_{^1H-^{31}P}$ = 15.3, 17.1, 18.9 Hz).

[14] **8**: $^{31}P\{^1H\}$ NMR δ 11.2 (dd, $J_{^{31}P-^{31}P}$ = 10.7, 210.5 Hz), −97.6 (dd, $J_{^{31}P-^{31}P}$ = 210.5, 48.8 Hz), −140.5 (dd, $J_{^{31}P-^{31}P}$ = 10.7, 48.8 Hz); ^1H NMR δ −7.5 m, −12.5 m.

[15] Compare the stability of **3** and **4** to the reported quantitative formation of aldehydes upon protonation of the binuclear acyl complexes $[Fe_2(\mu\text{-}PPh_2)_2(CO)_5[C(O)R]]^-$.[12]

Chemical Reactions of Tetramesityldisilene[1]

Mark J. Fink, Douglas J. DeYoung, and Robert West*

Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Josef Michl*

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

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Tetramesityldisilene, **1**, the first stable compound containing a silicon–silicon double bond, was reported early in 1981.[2] A different synthesis of **1**[3] and of a closely related molecule[4] have recently been published. We now report preliminary studies of the so-far uncharted chemical reactivity of disilenes. Except where mentioned, the reactions of **1** described below all proceed cleanly in better than 80% yield.[5]

Thermolysis. Tetramesityldisilene, a bright yellow solid at room temperature, exhibits pronounced thermochromism. On heating, it darkens to orange and then melts to a red liquid at 178 °C. This

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[1] This work was reported in part at the 16th Annual Organosilicon Symposium, Midland, MI, June 1982.

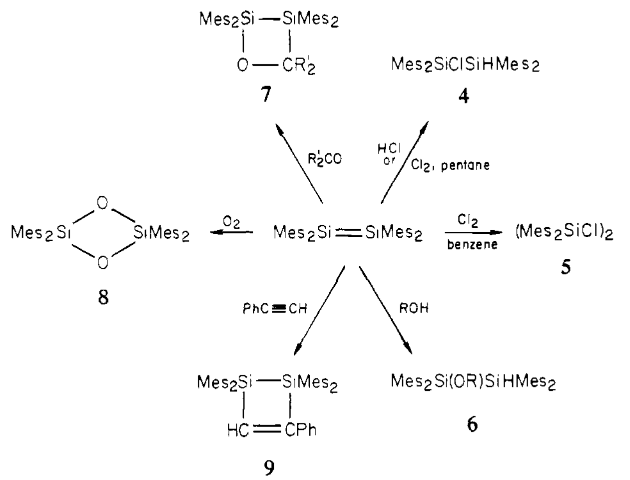
[2] West, R.; Fink, M. J.; Michl, J. 15th Organometallic Symposium, Duke University, Durham, NC, Mar 1981. West, R.; Fink, M. J.; Michl, J. 6th International Symposium on Organosilicon Chemistry, Budapest, Hungary, Aug 1981. West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* **1981**, *214*, 1343.

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

[4] Masamune, S.; Hanazawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150.

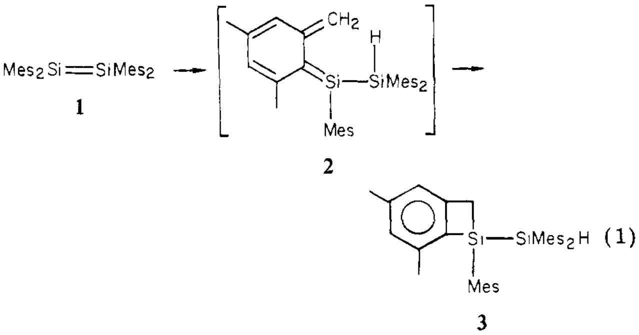
[5] All compounds described have been identified by exact molecular weight determination by high-resolution mass spectroscopy and by NMR and IR spectra consistent with the structure given.

Scheme I. Reactions of Tetramesityldisilene[a]



[a] Mes = 2,4,6-trimethylphenyl; R = H, CH_3, C_2H_5; R' = CH_3, Ph.

sequence of changes is fully reversible if the heating and cooling cycle is carried out rapidly, but if **1** is heated above 180 °C, or for a prolonged period (20 h) at 140 °C, it undergoes transformation into the benzosilacyclobutane **3**.[6] A likely pathway for this transformation is a 1,5 sigmatropic rearrangement to the sila-*o*-xylylene **2** followed by electrocyclic ring closure (eq 1, Mes = 2,4,6-trimethylphenyl), but other possible mechanisms cannot be excluded.



Photochemistry. Upon irradiation at 254 nm in pentane solution, **1** is transformed into the known dihydrodisilane $Mes_2SiHSiHMes_2$.[7] This product is that expected from abstraction of hydrogen by silyl radicals and therefore suggests radical character in the reacting electronic excited state of **1**. The reaction was not observed upon irradiation into the visible absorption band of **1**.

Addition Reactions. Some reactions of **1** are analogous to well-known addition reactions of olefins, for example, the addition of HCl to give **4** or of Cl_2 in benzene yielding **5**, portrayed in Scheme I. However, when the reaction between **1** and Cl_2 is carried out in alkanes (cyclohexane, pentane) instead of benzene, the product is the HCl adduct **4** rather than the expected **5**. In cyclohexane, chlorocyclohexane and cyclohexene are obtained as byproducts (identified by GC/MS). These results are most reasonably explained by a radical chain mechanism (eq 2–6).

$$Cl_2 + Mes_2Si{=}SiMes_2 \rightarrow Mes_2SiCl{-}\dot{S}iMes_2 + Cl\cdot \quad (2)$$

$$Cl\cdot + RH \rightarrow R\cdot + HCl \quad (3)$$

$$R\cdot + Cl_2 \rightarrow RCl + Cl\cdot \quad (4)$$

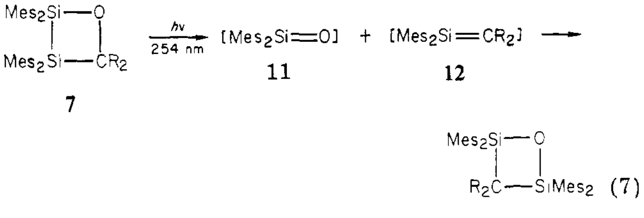
$$R\cdot + R\cdot \rightarrow \text{products} \quad (5)$$

$$HCl + Mes_2Si{=}SiMes_2 \rightarrow Mes_2SiH{-}SiClMes_2 \quad (6)$$

In many addition reactions, **1** is much more reactive than normal olefins. Thus **1** adds alcohols and water (the latter in THF as cosolvent) at 50 °C without catalysis to give the adducts **6** and adds ketones in a thermal reaction yielding the 1,2-disilaoxetanes **7**.[8,9] With oxygen, **1** is converted to the 1,3-dioxetane **8**[10] in a reaction reminiscent of ozonolysis of olefins. Compound **8** appears to be the first example of a cyclodisiloxane.

Compound **1** is unreactive toward anthracene, 2,3-dimethylbutadiene, 1,4-diphenylbutadiene, and phenyl(trimethylsilyl)acetylene, all of which are believed to serve as traps for transient, unhindered disilenes.[12,13] However, **1** does undergo cycloaddition with phenylacetylene to give the disilacyclobutene **9**, in 60% yield.[14]

Upon photolysis, the acetone adduct **7** rearranges to the 1,3-isomer **10** (eq 7). This rearrangement may take place through



10, R = Me

cleavage of **7** (R = Me) to the silanone **11** and the silene **12**, followed by ring closure in the opposite sense to form **10**. When **7** is photolyzed in methanol solution species, **11** and **12** are trapped as their methanol adducts, $Mes_2Si(OCH_3)OH$ and $Mes_2Si(OCH_3)CH(CH_3)_2$, respectively, identified by GC/MS.

In summary, many of the reactions of disilene **1** resemble those of electron-rich olefins. The differences in reactivity between **1** and olefins can be explained, at least in part, to the greater reactivity of silicon toward oxygen. Further studies of the chemistry of **1** and its addition products are under way.

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(6) ^{1}H NMR (C_6D_6) δ 2.04–2.31 (8 s, 33 H, CH_3), 2.67 (dd, 2 H, CH_2), 5.64 (s, 1 H, Si H), 6.66–6.81 (4 s, 8 H, Ar H); MS, exact mass for $C_{36}H_{44}Si_2$ calcd *m/e* 532.2970, found *m/e* 532.2981.

(7) Baxter, S. G.; Mislow, K.; Blount, J. F. *Tetrahedron* **1980**, *36*, 605.

(8) **7** (R' = Ph): ^{1}H NMR (C_6D_6) δ 7.5–7.6 (m, 4 H, Ph H), 6.8–6.9 (m, 6 H, Ph H), 6.58 (s, 8 H, Ar H), 2.59 (s, 12 H, *o*-Me), 2.27 (s, 12 H, *o*-Me), 2.04 (s, 6 H, *p*-Me), 2.02 (s, 6 H, *p*-Me). **7** (R' = Me): ^{1}H NMR (C_6D_6) δ 6.96 (s, 4 H, Ar H), 6.66 (s, 4 H, Ar H), 2.59 (s, 12 H, *o*-Me), 2.30 (s, 12 H, *o*-Me), 2.09 (s, 6 H, *p*-Me), 2.07 (s, 6 H, *p*-Me), 1.62 (s, 6 H, CMe). These compounds do not show parent ions in their mass spectrum but do show peak matches for loss of Ph_2C and Me_2C.

(9) Transient disilenes have been proposed to add similarly to carbonyl compounds; see, for example: (a) Barton, T. J.; Kilgour, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 2278; (b) **1976**, *98*, 7231.

(10) ^{1}H NMR ($CDCl_3$) δ 2.23 (s, 12 H, *p*-CH_3), 2.33 (s, 24 H, *o*-CH_3), 6.79 (s, 8 H, Ar H); IR (CCl_4) 1083 (ν_{Si-O}) cm^{-1}; MS, 564 (M^+, 5%), 444 (M – mesitylene, 85%), 325 (M – mesitylene – mesityl). Exact mass for $C_{36}H_{44}Si_2O_2$ calcd *m/e* 564.2868, found *m/e* 564.2882. This compound was first thought to have the 1,2-dioxetane structure.[2] NMR and infrared spectra are consistent with either structure, but more recent chemical and physical evidence favors structure **8**. The compound is unreactive toward iodide ion and also toward zinc/acetic acid; the latter conditions serve to reduce the hindered 1,2-dioxetane derived from bis(adamantylidene).[11] Upon reduction with $LiAlH_4$, **8** yields $Mes_2Si(OH)H$ and some Mes_2SiH_2 (the silicon–silicon bond in $(Mes_2SiH)_2$ is not attacked by $LiAlH_4$). The mass spectral cracking pattern and partial X-ray crystal structure of **8** also favor the structure now assigned. Attempts to obtain a primary product at low temperature have not been successful to date.

(11) (a) Wieringa, J. H.; Strating, J.; Wynberg, H.; Adam, W. *Tetrahedron Lett.* **1972**, 169. (b) Schuster, G. B.; Turro, N. J.; Steinmetzer, H. C.; Schaap, A. P.; Faler, G.; Adam, W.; Liu, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 7110.

(12) Heated in Decalin at 150–175 °C; higher temperatures lead to thermal decomposition of **1**.

(13) (a) Roark, D. N.; Peddle, G. J. D. *J. Am. Chem. Soc.* **1971**, *94*, 5837. (b) Sakurai, H.; Kobayashi, T.; Nakadaira, Y. *J. Organomet. Chem.* **1978**, *162*, C43. (c) Rich, J. D.; Drahnak, T. J.; West, R.; Michl, J. *J. Organomet. Chem.* **1981**, *212*, C1.

(14) **9**: ^{1}H NMR (C_6D_6) δ 8.08 (s, 1 H, vinyl H), 7.48 (m, 2 H, Ph H), 7.08 (m, 3 H, Ph H), 6.68 (s, 4 H, Ar H), 6.66 (s, 4 H, Ar H), 2.46 (s, 12 H, *o*-Me), 2.37 (s, 12 H, *o*-Me), 2.12 (s, 6 H, *p*-Me), 2.09 (s, 6 H, *p*-Me); MS, exact mass for $C_{44}H_{50}Si_2$ calcd *m/e* 634.3451, found 634.3438.