Although there is no clear explanation for the slower reaction of $Re_2(CO)_9$ with CO compared with that of $Mn_2(CO)_9$ at present, it may show a semibridging of CO also in $Re_2(Co)_9$, as in $Mn_2(CO)_9$.[8] This deserves further study by other techniques such as IR spectroscopy. The present study shows that the nonradical process (2) is important in the photolysis of $Re_2(CO)_{10}$ in hydrocarbon.

Acknowledgment. This work is partly supported by grants from the Ministry of Education, Science, and Culture, the Toray Science and Technology Foundation, and the Kurata Science Foundation to T.K. at the University of Tokyo. This work is partly supported by grants of "solar energy conversion by means of photosynthesis" given to Riken (IPCR) by the Science and Technology Agency.

Registry No. $Re_2(CO)_{10}$, 14285-68-8; $Re(CO)_5$, 53796-42-2; CO, 630-08-0; cyclohexane, 110-82-7.

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(16) Y_1/Y_2 was estimated to be 0.74 ± 15^5 on the assumption that the molar extinction coefficient of $\cdot Mn(CO)_5$ at 830 nm is equal to that of $Mn_2(CO)_9$ at 500 nm. (a) Kobayashi, T.; Ohtani, H.; Noda, H.; Teratani, S.; Yamazaki, H.; Yasufuku, K., submitted for publication in *Organometallics*.

Thermolytic Behavior of Some 1-Oxa-Substituted 1-(Trimethylsilyl)cyclopropanes

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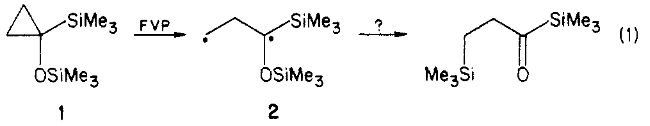
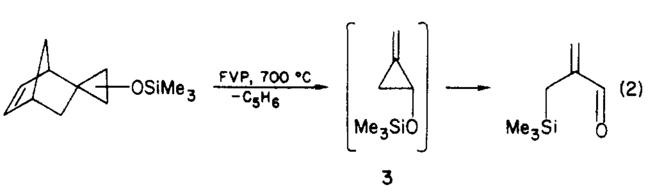
Received May 15, 1985

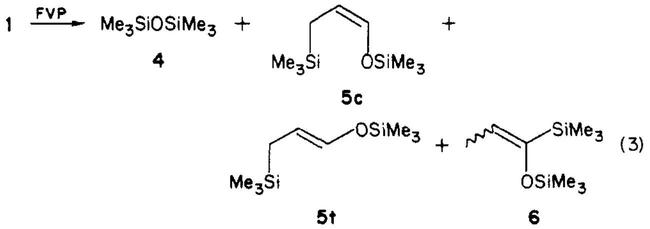
The flash vacuum pyrolysis (FVP) of 1-(trimethylsiloxy)-1-(trimethylsilyl)cyclopropane at 625 °C afforded mostly hexamethyldisiloxane and *cis*- and *trans*-1-(trimethylsiloxy)-3-(trimethylsilyl)propene. Evidence is presented supporting the intermediacy of 3-(trimethylsiloxy)-3-(trimethylsilyl)propene in this process. The thermolytic behavior of both 1-methyl-1-(trimethylsiloxy)cyclopropane and 1-ethoxy-1-(trimethylsilyl)cyclopropane shows similarities to that above, but FVP of 1-acetoxy-1-(trimethylsilyl)cyclopropane affords 3-acetoxy-2-(trimethylsilyl)propene by an alternate process.

An interest in acylsilane chemistry led us to investigate the flash vacuum pyrolysis (FVP) of 1-(trimethylsiloxy)-1-(trimethylsilyl)cyclopropane (1) as a possible route to β-silylacylsilanes (eq 1). By way of analogy, Bloch and Denis have proposed[1] that a similar O to C transfer of a silyl group occurs within a species such as **3**, where ring opening is possibly facilitated by the intermediacy of a trimethylenemethane (eq 2). Although these same authors reported that other siloxycyclopropanes were stable under these conditions, our ready access to **1**[2] and the possibility that an α-silyl group would lend additional stability[3] to the trimethylene species **2** encouraged our efforts.

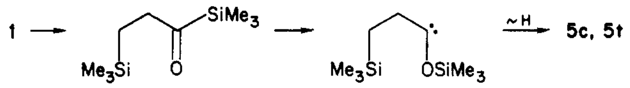




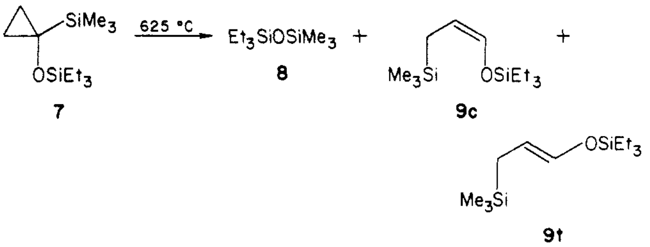
Thermolysis of **1** did indeed lead to reorganized products. Thus, FVP at 600 °C converted 90% of **1** to a mixture consisting almost entirely[4] of **4**, **5c**, **5t**, and **6** (37:45:15:4 mole ratio). At 625 °C, total conversion occurred to these same products in a 29:48:20:3 ratio (eq 3).



Scheme I



Scheme II



The formation of **4** might reasonably be attributed to a geminal elimination[5] within **1** producing cyclo-

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[1] Bloch, R.; Denis, J. M. *J. Organomet. Chem.* **1975**, *90*, C9.

[2] Cunico, R. F.; Kuan, C.-P., manuscript submitted to *J. Org. Chem.*

[3] The stability of silyl radicals is a topic of current investigation. See: Wilt, J. W.; Belmonte, F. G.; Zieske, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 5665.

[4] Trace amounts of much higher boiling materials were also present.

[5] Divalent carbon species have been produced by the geminal elimination of Si and the following. (a) OR: Atwell, W. H.; Weyenberg, D. R. *J. Am. Chem. Soc.* **1968**, *90*, 3438. Brook, A. G.; Dillon, P. J. *Can. J. Chem.* **1969**, *47*, 4347. (b) OSi: Stang, P. J.; Fox, D. P. *J. Org. Chem.* **1977**, *42*, 1667. (c) OH: Sekiguchi, A.; Ando, W. *J. Org. Chem.* **1980**, *45*, 5286.

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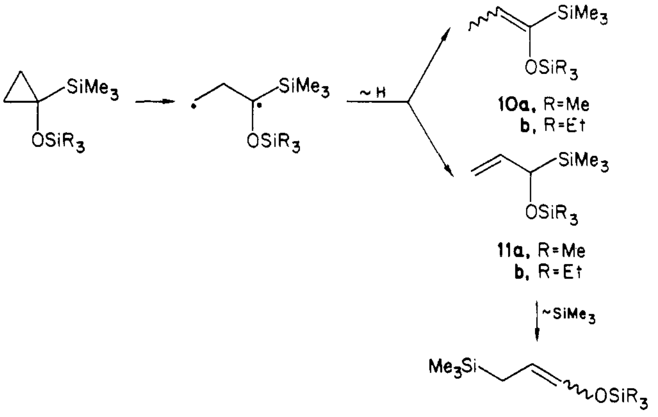
Scheme III



10a, R=Me
b, R=Et

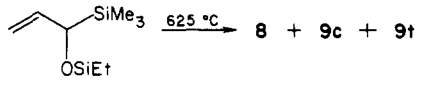
11a, R=Me
b, R=Et

5, R=Me
9, R=Et

propylidene, and ultimately allene[6] (but see below). Although acylsilanes are obviously not among the end-products of thermolysis, at least **5c** and **5t** may have arisen by way of Scheme I, in that acylsilanes are known to undergo thermolysis to siloxycarbenes which may then rearrange as shown.[7] This possibility was excluded from consideration when the thermolysis of the mixed silyl group compound **7** was carried out (Scheme II): only the products **8**, **9c**, and **9t** were observed[8] (mole ratio of 22:56:22). The absence of $Et_3SiCH_2CH{=}CHOSiMe_3$ among the products confirmed that no O to C silyl group migration had occurred and indicated that the C-bound silyl group in **1** is also C-bound in **5**.

To account for these observations, we propose the mechanism outlined in Scheme III. The pathway invokes the formation of a trimethylene intermediate which partitions between **10** and **11** by a characteristic 1,2 hydrogen shift.[9] Intuitively, the more highly substituted **10** might be expected to be a major component of any such mixture, whereas in fact it is seen (at most) in only minor amounts. That this is not an impediment to the further consideration of Scheme III was shown by the FVP behavior of independently synthesized **10a** (= **6**): at 625 °C, over 90% of **6** was converted to hexamethyldisiloxane (**4**) as the only NMR-detectable component of the pyrolysate.[10] The other postulated intermediate **11** contains an allylsilane structure and should therefore be subject to thermally induced 1,3-silatropic rearrangement[11] to the more stable isomers **5** or **9**.

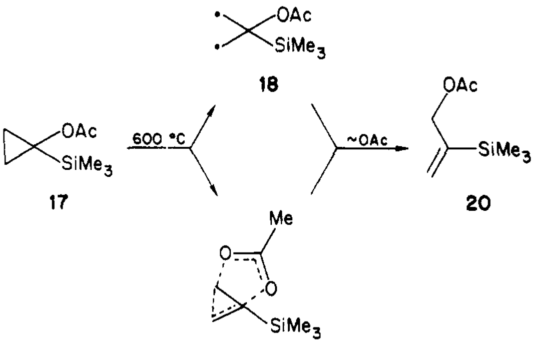
As a test of this latter hypothesis, **11b** was independently prepared and subjected to thermal rearrangement (eq 4).



(4)

Only products **8**, **9c**, and **9t** were obtained in a 70:22:8 mole ratio, a result consistent with expectations. We note as an aside that the absence of any "cross-silyl" products from either **7** or **11b** not only targets the silyl group undergoing migration but also excludes the possibility of concomitant dyotropic silyl group exchange[12] within these species.

Scheme IV



18

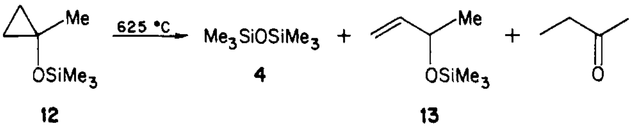
17

20

19

The high proportion of siloxane among the products obtained from **11b**, and its exclusive formation from the thermolysis of **6** suggest that these decompositions account for much of the siloxane obtained in the thermolysis of **1** and **7**, although some degree of similar elimination from the cyclopropyl compounds themselves cannot be excluded. Even at lower temperatures, siloxane remains a principal thermolysis product of **11b**. FVP of **11b** at 525 °C gave a 4:3:1 mixture of **8**, **9** (cis and trans), and unreacted **11b**, while static thermolysis (sealed tube) at 300 °C for 1 h completely converted **11b** to a 1:1 mixture of **8** and **9** (cis and trans).

A number of other 1-oxa-substituted 1-(trimethylsilyl)cyclopropanes were briefly investigated as a comparison to the behavior of **1**. Thus, at 625 °C, **12** was partially converted into a mixture containing as main components hexamethyldisiloxane (**4**), **13**, and butanone in equimolar amounts (eq 5). The presence of **13** is easily rationalized by analogy to Scheme III, since allylic methyl migration would be unlikely. The appearance of **4** and especially the (presumed) conversion of the counterpart of **10** to butanone are intriguing, but further speculation as to their origins would be premature. We note, however, that a number of silyl enol ethers have been reported to be unstable to thermolytic conditions similar to those used here.[13]



(5)

Thermolysis of **14** (eq 6) resulted in complete conversion to a complex mixture whose major components were identified as **4** and 3-(trimethylsilyl)propanal (**15**). The formation of **15** lies within the bounds of Scheme III if subsequent electrocyclic elimination occurs within the expected intermediate **16**.

FVP of 1-acetoxy-1-(trimethylsilyl)cyclopropane (**17**) at 600 °C resulted in partial conversion to **20** as the only significant product. In contrast to the previous examples presented, this result is indicative of 2,3 bond rupture accompanied by acetoxy group migration (Scheme IV).[14] Exclusive migration of the acetoxy function over silicon

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[6] Marvell, E. N. "Thermal Electrocyclic Reactions"; Academic Press: New York, 1980.

[7] Bassingdale, A. R.; Brook, A. G.; Harris, J. *J. Organomet. Chem.* **1975**, *90*, C6.

[8] The analogue of **6** (**11b**) may not survive (vide infra) because of a longer residence time in the hot zone due to its higher molecular weight.

[9] (a) Frey, H. M. and Walsh, R. *Chem. Rev.* **1969**, *69*, 103. (b) Bergman, R. In "Free Radicals"; Kochi, J., Ed.; Wiley: New York, 1973; Vol. 1.

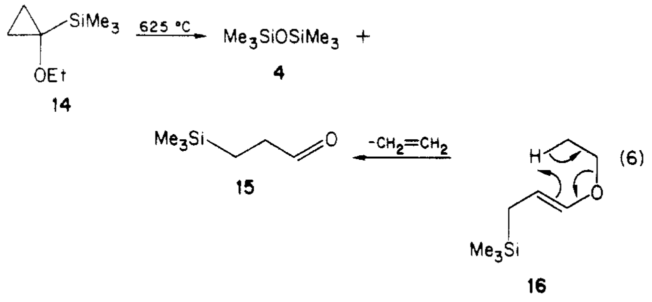
[10] Any C_3 cofragments would not have been detected under our conditions.

[11] Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, *95*, 8678.

[12] Reetz, M. T. In "Advances in Organometallic Chemistry"; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 1977; Vol. 16.

[13] Colino, C. M.; Bush, R. D.; Roark, D. N.; Sommer, L. H. *J. Organomet. Chem.* **1974**, *66*, 29.

[14] A parallel observation has been reported for acetoxycyclopropane itself: DePuy, C. H.; Zabel, D. E.; Wiedeman, W. *J. Org. Chem.* **1968**, *33*, 2198.



within a diradical intermediate (18) would be worthy of note, as the Si/H migration ratio in such species (i.e., 18, OAc = H) is known to be greater than 10^6.[15] However, the change from 1,2 to 2,3 bond cleavage accompanying exclusive acetoxy group migration in 17 suggests instead that the acetoxy group plays a participatory role in ring opening (19).

Experimental Section

Infrared spectra were determined on neat films using a Sargent-Welch 3-200 spectrophotometer; only selected strong or significant bands are quoted. ^{1}H NMR spectra were determined on $CDCl_3$ solutions ($CHCl_3$ taken as δ 7.24 as reference) using a Bruker WP 200SY FT spectrometer. VPC analyses employed a Varian Associates 1720 chromatograph and 20% SE-30 columns of various lengths (except as stated). Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI. Flash vacuum pyrolyses were carried out by vacuum-volatilizing materials through a horizontal 7 mm (o.d.) × 61 cm quartz tube heated to stipulated temperature by a Lindberg tube furnace with a 12-in. hot zone. The tube was vigreuxed throughout its length within the hot zone. Products were collected at −78 °C and allowed to attain room temperature before analysis. The pyrolysis tube was flushed with acetone and then with N_2 at temperature before each run. All other reactions were carried out under N_2. Workup, unless stated otherwise, consisted of dilution with pentane, extraction with aqueous NH_4Cl and water, drying with anhydrous $MgSO_4$, and concentration by rotary evaporator before distillation (short-path apparatus used unless otherwise indicated). Diethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl immediately prior to use. VPC quantitations are based on uncorrected peak integrals. NMR quantitations are based on comparisons of similar proton types wherever possible.

Thermolysis of 1. A sample of 1 (0.201 g) was subjected to FVP at 600 °C (0.05 mm) to give 0.186 g of condensate, of which 10% was unreacted 1. VPC and NMR analysis indicated the presence of **4**, *cis*-1-(trimethylsiloxy)-3-(trimethylsilyl)propene (**5c**), *trans*-1-(trimethylsiloxy)-1-(trimethylsilyl)propene (**5t**), and 1-(trimethylsiloxy)-1-(trimethylsilyl)propene (**6**) in the ratios indicated in the discussion.

5c: IR 1645, 1250, 1155, 1090, 840 cm^{-1}; ^{1}H NMR δ −0.03 (s, 9 H), 0.16 (s, 9 H), 1.42 (d, 2 H, J = 8 Hz), 4.46 (d of t, 1 H, J = 5 Hz, 8 Hz), 6.13 (d, 1 H, J = 5 Hz). Anal. Calcd for $C_9H_{22}OSi_2$: C, 53.41; H, 10.96. Found: C, 53.32; H, 10.89.

5t:[16] IR 1650, 1250, 1175, 1125, 840 cm^{-1}; ^{1}H NMR δ −0.03 (s, 9 H), 0.16 (s, 9 H), 1.22 (d, 2 H, J = 8 Hz), 4.97 (d of t, 1 H, J = 12 Hz, 8 Hz), 6.06 (d, 1 H, J = 12 Hz). Anal. Found: C, 53.32; H, 10.89.

6: Identified as the major isomer obtained from the literature preparation[17] by NMR spectrum superposition.

In another run, FVP of 1 at 625 °C totally converted 1 to a mixture of **4**, **5c**, **5t**, and **6** as stated in the discussion.

Synthesis and Thermolysis of 1-(Triethylsiloxy)-1-(trimethylsilyl)cyclopropane (7). A solution of 0.40 g (0.0020 mol) of 1 in 4 mL of 1,2-dimethoxyethane was treated with 1.5 mL of 1.56 N methyllithium in ether (0.0023 mol) by syringe. After 2.5 h at 25 °C, 0.30 g (0.0020 mol) of chlorotriethylsilane was added to the yellow-orange suspension and the mixture refluxed 3 h. After the mixture was left standing overnight at 25 °C, workup followed by Kugelrohr distillation gave 0.22 g of material, bp 25 °C (1 mm), and 0.25 g of distillate with a boiling point of 80 °C (1 mm). The former was mostly 1-(trimethylsilyl)cyclopropanol, while the latter was mostly **7**. VPC collection (5 ft PMPE column) gave analytically pure material: IR 1245, 1200, 1040, 1000, 840, 730 cm^{-1}; ^{1}H NMR δ −0.01 (s, 9 H), 0.41 (m, 2 H), 0.55 (q, 6 H, J = 8 Hz), 0.66 (m, 2 H), 0.92 (t, 9 H, J = 8 Hz).

Anal. Calcd for $C_{12}H_{28}OSi_2$: C, 58.95; H, 11.54. Found: C, 58.73; H, 11.68.

A VPC-collected sample of **7** was subjected to FVP at 625 °C (0.05 mm) using an air bath at 80–100 °C to hasten evaporation. A mixture of **8**, **9c**, and **9t** was obtained as indicated in the discussion, as adjudged from ^{1}H NMR and VPC analysis (5-ft PMPE column, 140 °C).

Preparation and Thermolysis of 6. The *S*-phenyl ester of propionic acid was employed in the preparation of **6**.[17] The final distillate contained **6** (9:1 isomer ratio), (phenylthio)trimethylsilane, and what was believed to be bis(trimethylsilyl) sulfide (^{1}H NMR δ 0.34). The first two compounds eluted together from a 10-ft SE-30 column (140 °C), while the last two eluted simultaneously from a 5-ft PMPE column (140 °C). Sequential collection from these columns afforded pure **6** which was then subjected to FVP at 625 °C (0.1 mm). Over 90% conversion occurred, and NMR and VPC analysis of the pyrolysate showed hexamethyldisiloxane as the only other significant component of this mixture.

Preparation and Thermolysis of 3-(Triethylsiloxy)-3-(trimethylsilyl)propene (11b).[18] The procedure of Lau and Chan[18b] was followed, but in our hands gave rise to mixtures of O- and C-triethylsilylated products. Thus a mixture of 1.95 g (0.015 mol) of (allyloxy)trimethylsilane and 25 mL of THF at −78 °C was treated dropwise with 7.4 mL of 2.3 N *tert*-butyllithium (0.017 mol) in pentane. After 1.5 h at −78 °C, 2.4 mL (0.014 mol) of chlorotriethylsilane was added and the mixture stirred 0.5 h at −78 °C and added to NH_4Cl solution. After workup, Kugelrohr distillation gave 2.73 g (75%) of material with a boiling point of 80 °C (1 mm). VPC (2 ft SE-30, 140 °C) showed this to be an 85:15 mixture, in order of elution, of **11b** and *cis*-3-(triethylsilyl)-1-(trimethylsiloxy)propene. The latter showed the following spectral data: IR 1645, 1250, 1155, 1090, 1000, 875, 840, 725 cm^{-1}; ^{1}H NMR δ 0.15 (s, 9 H), 0.49 (q, 6 H, J = 8 Hz), 0.92 (t, 9 H, J = 8 Hz), 1.45 (d of d, 2 H, J = 8 Hz, 1.5 Hz), 4.34 (d of t, 1 H, J = 8 Hz, 6 Hz), 6.09 (d of t, 1 H, J = 6 Hz, 1.5 Hz).

Anal. Calcd for $C_{12}H_{28}OSi_2$: C, 58.95; H, 11.54. Found: C, 59.47; H, 11.56.

11b: IR 1625, 1245, 1145, 1105, 1050, 1010, 900, 840, 810, 740 cm^{-1}; ^{1}H NMR δ −0.02 (s, 9 H), 0.55 (q, 6 H, J = 8 Hz), 0.93 (t, 9 H, J = 8 Hz), 3.96 (d of t, 1 H, J = 6 Hz, 2 Hz), 4.88 (d of t, 1 H, J = 11 Hz, 2 Hz), 5.00 (d of t, 1 H, J = 17 Hz, 2 Hz), 5.87 (four d, 1 H, J = 17 Hz, 11 Hz, 6 Hz).

A VPC-collected sample of **11b** was subjected to FVP (625 °C, 0.05 mm) with air-bath assistance (80–100 °C). This gave a mixture of **8**, *cis*-1-(triethylsiloxy)-3-(trimethylsilyl)propene (**9c**), and trans isomer **9t** as described in the discussion. A static thermolysis of **11b** (sealed capillary tube) at 200 °C (4.5 h) effected no change, but after 1 h at 300 °C, total conversion occurred to an approximately equimolar mixture of **8** and **9** (cis and trans).

9c:[18b] ^{1}H NMR δ −0.03 (s, 9 H), 0.63 (q, 6 H, J = 8 Hz), 0.96 (t, 9 H, J = 8 Hz), 1.42 (d of d, 2 H, J = 8 Hz, 1 Hz), 4.39 (d of t, 1 H, J = 6 Hz, 8 Hz), 6.17 (d of t, 1 H, J = 6 Hz, 1 Hz).

9t: ^{1}H NMR δ −0.04 (s, 9 H), 0.63 (q, 6 H, J = 8 Hz), 0.96 (t, 9 H, J = 8 Hz), 1.20 (d of d, 2 H, J = 8 Hz, 1 Hz), 4.96 (d of t, 1 H, J = 12 Hz, 8 Hz), 6.10 (d of t, 1 H, J = 12 Hz, 1 Hz).

Preparation and Thermolysis of 1-Methyl-1-(trimethylsiloxy)cyclopropane (12). Cyclopropanation of 2-(trimethylsiloxy)propene was carried out by slowly adding (1 h) 9.05 g (0.034 mol) of CH_2I_2 to a refluxing mixture of 2.0 g (0.015 mol) of the silyl enol ether, 2.94 g (0.045 mol) of Zn powder, and 2.86 g (0.045

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[15] (a) Ashe, A. J. *J. Am. Chem. Soc.* **1973**, *95*, 818. (b) Mironov, V. F.; Sheherbinen, V. V.; Viktorov, N. A.; Sheludyakov, V. D. *Dokl. Akad. Nauk SSSR* **1975**, *222*, 364.

[16] Picard, J. P.; Ekouya, A.; Dunogues, J.; Duffaut, N.; Calas, R. *J. Organomet. Chem.* **1975**, *93*, 51.

[17] Kuwajima, I.; Mori, A.; Kato, M. *Bull Chem. Soc. Jpn.* **1980**, *53*, 2634.

[18] (a) Hosomi, A.; Hashimoto, H.; Sakurai, H. *J. Org. Chem.* **1978**, *43*, 2551. (b) Lau, P. W. K.; Chan, T. H. *J. Organomet. Chem.* **1979**, *179*, C24.

mol) of CuCl in 40 mL of dioxane. After an additional 1.5-h reflux, the reaction mixture was diluted with pentane and filtered through Celite, the solids were reextracted with pentane, and the combined filtrates were washed with NH_4Cl solution and water (3×). Workup gave 1.30 g (68%) of **12**: bp 58–70 °C (130 mm); IR 1270, 1255, 1045, 870, 845, 755 cm^{-1}; ^{1}H NMR δ 0.11 (s, 9 H), 0.37 (m, 2 H), 0.71 (m, 2 H), 1.37 (s, 3 H).

Anal. Calcd for $C_7H_{16}OSi$: C, 58.28; H, 11.18. Found: C, 58.16; H, 11.20.

FVP of **12** at 625 °C (10 mm) gave partial conversion to a mixture of products. NMR analysis indicated the major components of this mixture to be **4**, 3-(trimethylsiloxy)-1-butene (**13**), and butanone in approximately equimolar amounts.

Preparation and Thermolysis of 1-Ethoxy-1-(trimethylsilyl)cyclopropane (14). A 6.4-g (0.044-mol) sample of 1-ethoxy-1-(trimethylsilyl)ethene[2] was cyclopropanated as in the preparation of **1**[2] to give 5.3 g (76%) of **14**: bp 63–65 °C (40 mm); IR 1250, 1195, 1125, 1070, 1020, 900, 840, 755 cm^{-1}; ^{1}H NMR δ 0.04 (s, 9 H), 0.39 (m, 2 H), 0.69 (m, 2 H), 1.08 (t, 3 H, J = 7 Hz), 3.33 (q, 2 H, J = 7 Hz).

Anal. Calcd for $C_8H_{18}OSi$: C, 60.70; H, 11.46. Found: C, 60.68; H, 11.30.

FVP of 0.206 g of **14** led to complete conversion to 0.120 g of water-white condensate which VPC showed consisted of many components. The largest of these with retention time just lower than that of **14** was collected and identified as 3-(trimethylsilyl)propanal:[16] ^{1}H NMR δ 0.00 (s, 9 H), 0.74 (m, 2 H), 2.37 (m, 2 H), 9.74 (t, 1 H, J = 2 Hz).

Preparation and Thermolysis of 1-Acetoxy-1-(trimethylsilyl)cyclopropane (17).[2] A solution of 0.96 g (0.0074 mol) of 1-(trimethylsilyl)cyclopropanol,[2] 1.51 g (0.0148 mol) of acetic anhydride, and a trace of 4-(dimethylamino)pyridine in 30 mL of ether was allowed to stand at 25 °C for 30 h. After the solution was washed with dilute HCl, $NaHCO_3$ solution, and water, workup gave 1.16 g (91%) of **17**, bp 60–72 °C (20 mm).

FVP of **17** at 600 °C (2 mm) led to recovery of some **17** and the formation of 3-acetoxy-2-(trimethylsilyl)propene (**20**) as the only significant product.[19] VPC collection gave pure **20**: IR 1743, 1250, 1231, 1032, 840 cm^{-1}; ^{1}H NMR δ 0.11 (s, 9 H), 2.07 (s, 3 H), 4.67 (m, 2 H), 5.44 (m, 1 H), 5.75 (m, 1 H).

Anal. Calcd for $C_8H_{16}O_2Si$: C, 55.77; H, 9.36. Found: C, 55.90; H, 9.47.

For comparison purposes, an authentic sample of **20** was prepared as follows. A solution of 1.89 g (0.010 mol) of 1-bromo-1-(trimethylsilyl)ethene in 25 mL of THF at −78 °C was treated dropwise with 9.5 mL of 2.3 N *tert*-butyllithium in pentane (0.022 mol). After 25 min at −78 °C, 0.64 g (0.21 mol) of dry paraformaldehyde was added at once and the cooling bath removed. The reaction mixture eventually reached 40–45 °C spontaneously. Five minutes later, the water-white solution was poured into NH_4Cl solution and worked up. Distillation gave 0.92 g (71%) of 2-(trimethylsilyl)-2-propen-1-ol: bp 60–72 °C (20 mm); IR 3320 (br), 1245, 1025, 835 cm^{-1}; ^{1}H NMR δ 0.10 (s, 9 H), 1.35 (t, 1 H), 4.45 (m, 2 H), 5.39 (m, 1 H), 7.69 (m, 1 H).

Anal. Calcd for $C_6H_{14}OSi$: C, 55.31; H, 10.83. Found: C, 55.41; H, 10.95.

A mixture of 0.26 g (0.020 mol) of the above alcohol, 0.22 g (0.022 mol) of acetic anhydride, and 0.20 g (0.020 mol) of triethylamine in 5 mL of ether gave, upon standing several days at 25 °C, a sample of **20** identical with that obtained above.

Registry No. **1**, 98720-91-3; **4**, 107-46-0; **5c**, 98720-92-4; **5t**, 56919-88-1; **6**, 64299-50-9; **7**, 98720-93-5; **8**, 2652-41-7; **9c**, 98720-94-6; **9t**, 98720-95-7; **11b**, 66662-18-8; **12**, 98720-97-9; **13**, 18269-41-5; **14**, 98720-98-0; **17**, 98720-99-1; **20**, 98721-01-8; CH_2I_2, 75-11-6; chlorotriethylsilane, 994-30-9; (allyloxy)trimethylsilane, 18146-00-4; *cis*-3-(triethylsilyl)-1-(trimethylsiloxy)propene, 98720-96-8; 2-(trimethylsiloxy)propene, 1833-53-0; 2-butanone, 78-93-3; 1-ethoxy-1-(trimethylsilyl)ethene, 81177-92-6; 1-(trimethylsilyl)cyclopropanol, 98721-00-7; 1-bromo-1-(trimethylsilyl)ethene, 13683-41-5; paraformaldehyde, 30525-89-4; 2-(trimethylsilyl)-2-propen-1-ol, 55287-89-3; 3-(trimethylsilyl)propanol, 2917-47-7.

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(19) The author thanks Mr. C. P. Kuan for carrying out this experiment.

Formation of Carboalkoxyiridium Complexes by Carbonylation of Alkoxyiridium Complexes and the Crystal Structure of *trans*-PhOIr(CO)$(PPh_3)_2$

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Received April 5, 1985

The preparation of iridium alkoxide complexes *trans*-ROIr(CO)$(PPh_3)_2$ and their carbonylation to carboalkoxy complexes ROC(O)Ir$(CO)_2(PPh_3)_2$ are described for R = Me, *n*-Pr, *t*-Bu, and Ph. The preparations involve metathetical reactions between *trans*-Ir(CO)$(PPh_3)_2$Cl and NaOR. In the carbonylation an intermediate can be identified by infrared and conductivity studies as $[Ir(CO)_3(PPh_3)_2^+][OR^-]$. Thus a mechanism involving alkoxide displacement by CO and subsequent nucleophilic attack of alkoxide on a CO of the cation is indicated. The complex *trans*-PhOIr(CO)$(PPh_3)_2$ crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (no. 14) with a = 15.790 (3) Å, b = 11.461 (3), c = 19.986 (5) Å, β = 100.326 (18)°, V = 3558 (2) Å^3, and Z = 4. Diffraction data (Mo Kα, 2θ = 5–55°) were collected with a Syntex P2$_1$ automated four-circle diffractometer, and the structure was solved and refined to R_F = 6.2% and R_{wF} = 4.6% for all 8220 reflections (R_F = 3.8% and R_{wF} = 4.1% for those 5981 reflections with $|F_0| > 6\sigma(|F_0|)$). The iridium atom has the expected square-planar geometry with Ir–P(1) = 2.328 (1) Å, Ir–P(2) = 2.344 (1) Å, Ir–CO = 1.795 (5) Å, and Ir–OPh = 2.049 (4) Å. The phenoxide ligand is "bent" with ⟨Ir–O–C(ipso) = 126.5 (3)°.

Alkoxy compounds have formed a part of inorganic chemistry for a number of years.[1-3] Alkoxy complexes of low oxidation state metals are not common, although a number of important reactions in methanol may involve alkoxy compounds. Among the important reactions are those that involve the use of palladium catalysts to effect the conversion of alkenes, CO, and methanol to esters, the

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