I as a model for CH_4 chemisorbed on a trimetal site.[4] The ferraborane II, then, constitutes a possible model for chemisorbed CH_2 in the act of being dehydrogenated to CH on a trimetal site. Further studies on these and related compounds are in progress.

Acknowledgment. The support of the National Science Foundation under Grant CHE 81-09503 is gratefully acknowledged. The NMR facility was purchased with the support of the National Institutes of Health (Grant No. CM 25845-02S1).

Kinetics and Mechanism of Pyrolysis of Hydridosilacyclobutanes

I. M. T. Davidson,* A. Fenton, S. Ijadi-Maghsoodi, and R. J. Scampton

Department of Chemistry, The University
Leicester, LE1 7RH8 England

N. Auner and J. Grobe

Anorganisch-Chemisches Institut
University of Munster, FRG

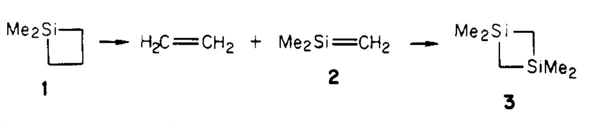
N. Tillman and T. J. Barton*

Department of Chemistry, Iowa State University
Ames, Iowa 50011

Received March 27, 1984

Summary: The thermal decomposition of hydridosilacyclobutanes was examined kinetically by low-pressure pyrolysis and stirred-flow reactor techniques, independent generation of proposed intermediates, and deuterium labeling. It was concluded that RSiH and propene arise from an initial rearrangement to *n*-propylsilylenes and not from the previously assumed sequence of homolytic cleavages.

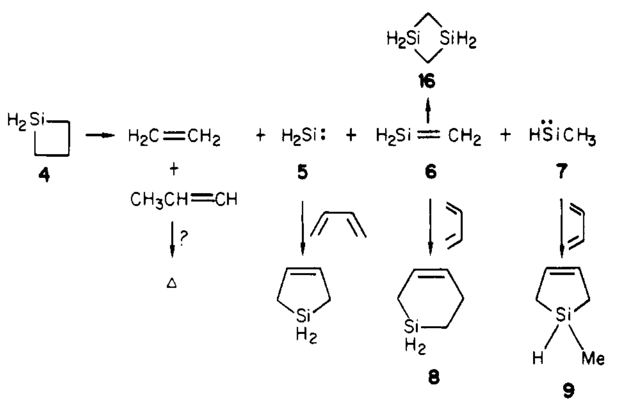
Pyrolysis of 1,1-dimethyl-1-silacyclobutane (1) is a clean, unimolecular reaction giving ethene and dimethylsilene (2) that can either be trapped or allowed to dimerize to 1,3-disilacyclobutane 3.[1]



However, gas-phase pyrolysis of the parent system 4 is far more complex as considerable formation of H_2 and propene is observed.[2] Conlin[3] has elegantly demonstrated through butadiene trapping that three silicon-reactive intermediates are formed in this pyrolysis: silylene (5), silene (6), and methylsilylene (7) (Scheme I).

Although the formation of methylsilylene (7) is easily rationalized by isomerization of silene (6) via 1,2-hydrogen migration,[4] it could also be accounted for[5] by a sequence of C-C bond homolysis in 4, 1,2-H migration to form either the 1,3 diradical 11 or silacyclopropane 12, and extrusion of :SiHMe as shown in Scheme II.

Scheme I



Scheme II

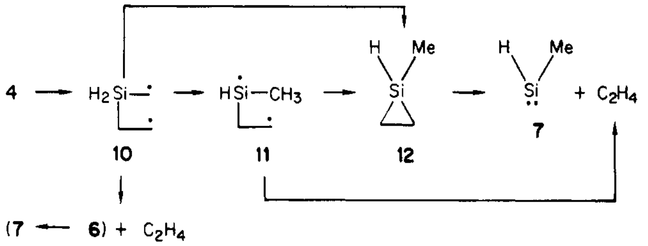
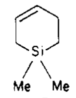
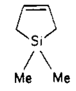
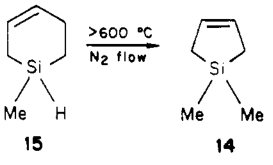


Table I. Arrhenius Parameters and Rate Constants for Decomposition of Silacycloalkenes

compd	log *A*, s^{-1}	E_a, kJ mol^{-1}	$k_{900\ K}$, s^{-1}
 13	14.1 ± 0.5	252 ± 8	0.298
 14	13.5 ± 0.6	255 ± 11	0.050

To distinguish between these two pathways, Conlin[3] noted that the process with the lowest activation entropy is the isomerization of 10 to 11 (as opposed to fragmentation of 10 to ethene and 6). Thus, if the multistep diradical process were operative, increasing temperature should favor formation of 6 over 7. His experiments indicated the opposite, as increasing temperature *increased* the 9/8 ratio. Therefore, it was reasonably concluded that only 5 and 6 are primary products from 4, and 7 must be derived from isomerization of 6.

This conclusion, while quite possibly correct, cannot be made from these data since silacyclohexenes are not thermally stable under the conditions required for decomposition of 4. For example (Table I), dimethylsilacyclohexene 13 decomposes six times more readily than dimethylsilacyclopentene 14 at 900 K. Indeed, both we and Conlin[6] have independently found that above 600 °C (vertical N_2 flow) hydridosilacyclohexene 15 begins to isomerize to silacyclopentene 16. Thus, the observed increasing 9/8 ratio is to be expected regardless of the mechanism of silacyclobutane decomposition.



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[1] Flowers, M. C.; Gusel'nikov, L. E. *J. Chem. Soc. B* 1968, 428, 1396.
[2] Maltsev, A. K.; Khabasheku, V. N.; Nefedov, O. M. Dokl. *Akad. Nauk SSSR* 1979, *247*, 383.
[3] Conlin, R. T.; Gill, R. S. *J. Am. Chem. Soc.* 1983, *105*, 618.
[4] Yoshioka, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* 1981, *103*, 7366.
[5] Barton, T. J.; Burns, S. A.; Burns, G. T. *Organometallics* 1982, *1*, 210.
[6] Conlin, R. T.; Kwak, Y.-W. *Organometallics* 1984, *3*, 918.

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Table II. Arrhenius Parameters and Rate Constants for Pyrolysis of Silacyclobutanes by SFR

process	compd	log A, s^{-1}	E_a, kJ mol^{-1}	$k_{800\ K}$, s^{-1}	K_{rel}
C_2H_4 formn	1^a	15.6 ± 0.3	262 ± 3	0.037	1
	4	15.8 ± 0.6	260 ± 8	0.067	1.8
	17^b	16.4 ± 0.3	264 ± 4	0.145	3.9
C_3H_6 formn	4	13.4 ± 0.6	243 ± 8	0.004	1
	17	14.4 ± 0.2	242 ± 3	0.040	10
total decomp	1^a	15.6	262	0.37	1
	4	14.4^c	233^c	0.143	3.9
	17	14.0^c	220^c	0.431	11.6

[a] From ref 1. [b] 17 = MeHSiCH$_2$CH$_2$CH$_2$. [c] These values are approximate as curved Arrhenius plots were obtained due to secondary, induced decomposition.

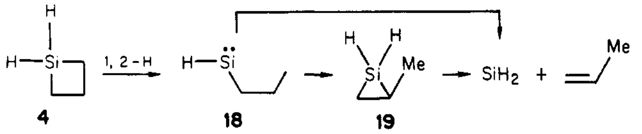
With regard to the other reactive intermediate generated from 4, silylene (5), it was concluded[3] that this did not arise from a concerted extrusion of SiH_2 but rather from a stepwise process initiated by two sequential Si–C bond homolyses. It was noted that at lower pyrolysis temperatures (556 °C) cyclopropane was formed, which at the higher temperatures was converted to propene. In our experiments, even at conditions of very low conversion of 4, we observe only propene and *no* cyclopropane. Thus, mechanisms should be sought that would exclusively afford propene in the formation of SiH_2.

In view of the questions of general interest raised by the pyrolysis of 4 and of 1-methylsilacyclobutane (17), which is reported[7] to decompose in an analogous fashion, we have undertaken kinetic studies of both systems by low-pressure pyrolysis (LPP)[8] with continuous analysis by mass spectroscopy and by pyrolysis in a stirred-flow reactor (SFR)[9] in a stream of nitrogen with analysis by gas chromatography (Table II).

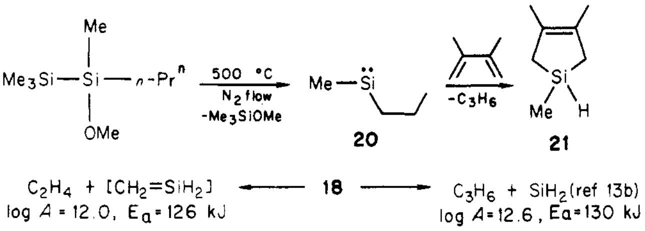
In the LPP apparatus, pyrolysis of 4 with added butadiene afforded the expected adducts (Scheme I), although it was not possible to distinguish between 8 and 9. In the absence of trapping agents, ethene and propene were observed in a ratio of ca. 3:1, propene formation having the lower activation energy. Also formed are dihydrogen and an apparent dimer of 6 or 7, presumably 16 (Scheme I). Since there is no doubt that initial unimolecular decomposition steps for 4 would be well into the fall-off region under LPP conditions (<0.1 torr), there was no point in pursuing detailed kinetic studies by this technique; however, it was established that 4 decomposed ca. 3 times faster than 1 without consideration of fall-off effects, and that the E_a for decomposition of 4 decreased as the pressure was increased from 0.1 to 15 torr. Both of these features point to extensive secondary reactions in the pyrolysis of 4, in sharp contrast to 1.

Kinetic data for the formation of C_2H_4 and C_3H_6 were obtained between 707 and 816 K in the SFR in a N_2 stream of 2.5 atm. Formation of both olefins was first order, with the Arrhenius parameters given in Table II.[10] In the pyrolyses of 4 and 17, ethene formation had the same E_a as found for 1, but both had slightly higher Arrhenius A factors. The simplest explanation is that the primary process forming ethene in each case is the same but that there may be secondary reactions of low activation energies forming more ethene from 4 and 17. Since (a) the Si–C bond in a silacyclobutane ring is stronger than a C–C bond,[11] (b) pyrolysis of dimethylsilacyclobutane (1) does not produce propene, and (c) substituents on silyl radicals play virtually no role in stabilization,[11] it is not obvious that propene formation must be the proposed direct result of an initial Si–C bond rupture. Thus, we suggest an alternative explanation that is consistent with the observed Arrhenius parameters and dependent upon silicon being substituted by hydrogen. This mechanism (Scheme III) is initiated by a 1,2-hydrogen shift in 4 to form *n*-propylsilylene (18) that eliminates SiH_2, possibly via the intermediacy of silarane 19. Alkane extrusion from alkylsilanes was first reported[12] as a minor reaction in the pyrolysis of CH_3SiH_3. A better analogy for 4 is elimination of methane from dimethylsilane with Arrhenius parameters of log A = 15 and E_a = 301 kJ mol^{-1}, recently measured by Ring, O'Neal, and co-workers.[13b] Since the ring strain in 4 (ca. 70 kJ mol^{-1})[14] will be to some degree released in the first step of the decomposition, the reduction in E_a from 301 to 243 kJ mol^{-1} is not unexpected. The second step, β-elimination of an alkylsilylene to form an olefin and a new silylene, is well precedented.[13]

Scheme III



Support for this mechanism comes from our observation that when methylpropylsilylene (20) is generated in a N_2-flow system at 500 °C in the presence of 2,3-dimethylbutadiene, the major product of this clean reaction is the adduct of methylsilylene, 21. Most recently, Ring and O'Neal[13b] have produced *n*-propylsilylene (18) in the shock-induced pyrolysis of *n*-propylsilane and found 18 to rapidly decompose to propene and ethene.[15]



Thus, since there are other pathways for decomposition of 18 (including bimolecular), log A would be somewhat greater than our observed value of 14.4 for propene formation, in agreement with the value of 15 found for the model reaction of $Me_2SiH_2 \rightarrow CH_4 + MeHSi$.

The view of the decomposition of 4 as proceeding through radical fragmentation to ethylene, and silylene decomposition to propene (Scheme III) is reinforced by our preliminary observations on the flash vacuum pyrolysis (FVP) of 1,1-dideuterio-1-silacyclobutane (22). While the ethylene is almost solely C_2H_4 (<10% C_2H_3D), the majority of the propene produced contains one deuterium. Thus,

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(7) Conlin, R. T.; Wood, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 1843.

(8) Davidson, I. M. T.; Ostah, N. A.; Seyferth, D.; Duncan, D. P. *J. Organomet. Chem.* **1980**, *187*, 297.

(9) Baldwin, A. C.; Davidson, I. M. T.; Howard, A. V. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 972.

(10) Under SFR conditions, a new product, CH_3SiH_3, was observed, presumably arising from an addition–elimination sequence between 7 and 4.

(11) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

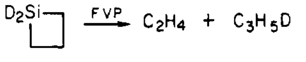
(12) Davidson, I. M. T.; Ring, M. A. *J. Chem. Soc., Faraday Trans. 1* **1980**, *786*, 1520.

(13) (a) Barton, T. J.; Burns, G. T. *Organometallics* **1983**, *2*, 1. (b) Ring, M. A.; O'Neal, H. E.; Rickborn, S. F.; Sawrey, B. A. *Organometallics* **1983**, *2*, 1891.

(14) O'Neal, H. E.; Ring, M. A. *J. Organomet. Chem.* **1981**, *213*, 419.

(15) (a) Barton, T. J.; Burns, G. T. *Organometallics* **1983** *2*, 1. (b) Gusel'nikov, L. E.; Lopatnikova, E.; Polyakov, Yu. P.; Nametkin, N. S. *Dokl. Akad. Nauk SSSR* **1980**, *253* (6), 1387.

migration of H (D) in 4 (22) is demanded in the formation of propene.



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At this time we are at a loss to explain the formation of ethylene observed by Ring[13b] in the decomposition of propylsilylene (18). The derived rates of ethylene formation make it impossible for 4 to enter the kinetic scheme. Furthermore, we can find neither ethylene nor silacyclobutane 17 in the products from 20. Thus, further study is clearly warranted (and is in progress) before the complete picture of the deceptively simple decomposition of hydridosilacyclobutanes can be viewed.

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Registry No. 4, 287-29-6; 17, 765-33-3.

Coordination and Scission of Alkynes on a Ditungsten–Diiridium Framework. The Crystal Structure of $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_6(\mu_3\text{-}CPh)(\mu_3\text{-}\eta^3\text{-}C_3Ph)$

John R. Shapley* and Colin H. McAteer

Department of Chemistry and
Materials Research Laboratory
University of Illinois, Urbana, Illinois 61801

Melvyn Rowen Churchill* and Linda Vollaro Biondi

Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

Received June 1, 1984

Summary: The reaction between $Cp_2W_2Ir_2(CO)_{10}$ and C_2Ph_2 produces $Cp_2W_2Ir_2(CO)_8(C_2Ph_2)$ (by cleavage of a W–W bond) and $Cp_2W_2Ir_2(CO)_6(\mu_3\text{-}CPh)(\mu_3\text{-}\eta^3\text{-}C_3Ph_3)$ (by cleavage of a W–Ir bond); these processes apparently operate independently and appear to be general for disubstituted acetylenes. The species $Cp_2W_2Ir_2(CO)_6(\mu_3\text{-}CPh)(\mu_3\text{-}\eta^3\text{-}C_3Ph_3)$, studied by X-ray diffraction, crystallizes in the monoclinic space group $P2_1/c$ with a = 14.253 (9) Å, b = 15.629 (4) Å, c = 18.731 (4) Å, β = 96.86 (4)°, V = 4143 (3) Å^3, and Z = 4. Convergence was achieved with R_F = 8.5% for all 4887 data and R_F = 5.8% for those 3395 data greater than 3σ. The metal core defines a fused triangulated rhombus with a dihedral angle of 170.33° about the common Ir(1)–W(1) edge. The μ_3-CPh ligand lies above the Ir(1)–W(1)–W(2) triangle. A $\mu_3\text{-}C_3Ph_3$ ligand lies above the Ir(1)–W(1)–Ir(2) triangle (i.e., on the same side of the cluster as the μ_3-CPh ligand); it participates in a η^3-allyl linkage to Ir(2) and is σ bonded to Ir(1) and W(1).

Previously we reported the syntheses and structures of $CpWIr_3(CO)_{11}$ and $Cp_2W_2Ir_2(CO)_{10}$ together with the use of these compounds as precursors to alumina-supported bimetallic particles.[1] In order to develop an understanding of the way in which the compounds might interact with the support, we have explored aspects of their reactivity in solution. Herein we report the results of treating $Cp_2W_2Ir_2(CO)_{10}$ with alkynes, including the crystal structure of one product that provides evidence for C≡C bond scission and redistribution of alkylidyne units.

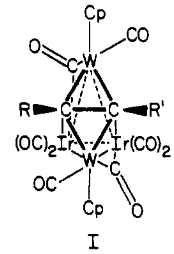
Table I. Yields (%) of Products from Reaction of $Cp_2W_2Ir_2(CO)_{10}$ with Alkynes

alkyne	$Cp_2W_2Ir_2(CO)_8$-(alkyne)	$Cp_2W_2Ir_2(CO)_6$-(alkyne)$_2$
C_2Ph_2	34	16
$C_2(p\text{-tol})_2$	55	trace
$C_2(CF_3)_2$	92	trace
$C_2Ph(CO_2Et)$	29	trace
$C_2(CO_2Et)_2$	58	none observed[a]
C_2PhMe	48	none observed[a]

[a] In these cases minor amounts of brown compounds containing *seven* carbonyl groups (MS) are obtained. These products have not been structurally characterized.

$Cp_2W_2Ir_2(CO)_{10}$ and C_2Ph_2 were heated in refluxing CH_2Cl_2 until all starting material was consumed (3 h). After preparative TLC and crystallization, green $Cp_2W_2Ir_2(CO)_8(C_2Ph_2)$ and dark green "$Cp_2W_2Ir_2(CO)_6(C_2Ph_2)_2$" were isolated in 34% and 16% yields, respectively. The formulas of the products were determined by FAB mass spectroscopy and confirmed by additional spectroscopic and physical data.[2] Treatment of isolated $Cp_2W_2Ir_2(CO)_8(C_2Ph_2)$ with C_2Ph_2 in refluxing CH_2Cl_2 did not form any of the minor product. Similar treatment of $Cp_2W_2Ir_2(CO)_{10}$ with other alkynes gave generally analogous results, with $Cp_2W_2Ir_2(CO)_8$(alkyne) the dominant product in all cases (see Table I).

The ^1H and ^{13}C NMR data show that the general structure of $Cp_2W_2Ir_2(CO)_8(C_2RR')$ is a "butterfly" complex, a closo octahedron derived from inserting the alkyne into a W–W bond of the W_2Ir_2 framework (see I). Rapid terminal-to-bridging and bridging-to-terminal rearrangement of the carbonyls bound to tungsten is indicated by the observation of only one averaged ^{13}C NMR signal for these carbonyls in $Cp_2W_2Ir_2(CO)_8(C_2Ph_2)$ even at −70 °C. In the case of an unsymmetrical alkyne, however, operation of this process does not fully average the carbonyl environments; two averaged W–CO signals and four averaged Ir–CO signals are seen for $Cp_2W_2Ir_2(CO)_8(C_2PhMe)$ even



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(1) (a) Shapley, J. R.; Hardwick, S. J.; Foose, D. S.; Stucky, G. D.; Churchill, M. R.; Bueno, C.; Hutchinson, J. P. *J. Am. Soc.* **1981**, *103*, 7383. (b) Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1981**, *20*, 4112. (c) Churchill, M. R.; Bueno, C.; Hutchinson, J. P. *Inorg. Chem.* **1982**, *21*, 1359.

(2) $Cp_2W_2Ir_2(CO)_8(C_2Ph_2)$: ^1H NMR ($CDCl_3$) δ 6.9 (10 H, m, Ph), 4.60 (10 H, s, Cp); ^{13}C NMR (CD_2Cl_2, −70 °C) δ 225.4 (4 C, J_{WC} = 171 Hz), 173.2 (2 C), 173.0 (2 C); IR (CCl_4, ν_{CO}) 2104 (w), 2074 (s), 2047 (s), 2023 (w), 2007 (m), 1821 (m, br), 1769 cm^{-1} (w, br); MS (FAB), m/z 1284 (M^+), 1284 − 28X, X = 1–8. Anal. Calcd for $C_{32}H_{20}O_8W_2Ir_2$: C, 29.92; H, 1.57. Found: C, 29.91; H, 1.57. $Cp_2W_2Ir_2(CO)_6(C_2Ph_2)_2$: ^1H NMR ($CDCl_3$) δ 6.8–6.3 (20 H, m, br, Ph), 5.22 (5 H, s, Cp), 5.16 (5 H, s, Cp); ^{13}C NMR (CD_2Cl_2, −30 °C) δ 243.4, 239.4, 214.1, 205.3, 169.2, 167.6; IR (CCl_4, ν_{CO}) 2055 (vs), 2031 (w), 2011 (s), 1989 (m), 1929 (m), 1801 cm^{-1} (m, br); MS (FAB), m/z 1406 (M^+), 1406 − 28X, X = 1–6.

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