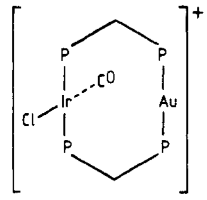
(OC)Ir(μ-dppm)$_2$Au]Cl (**4**), whereas neutral complexes are formed with [AgCl(PPh$_3$)]$_4$ or CuCl, **5a** or **5b**, respectively. Treatment of the iridium–silver complex **5a** with [Rh$_2$Cl$_2$(CO)$_4$] in CDCl$_3$ rapidly gave a mixture of two iridium–rhodium species, with no dirhodium or diiridium species being formed. Moreover, [Ir(dppm)$_2$(CO)]Cl and [Rh$_2$Cl$_2$(CO)$_4$] in dichloromethane at ca. 20 °C react together to give the same two iridium–rhodium species but more slowly than by using **5a**; the mole ratio of the two species in the mixture was ca. 5:1. Treatment of a solution of the mixture with CO rapidly gave the major component exclusively. We assign structure **6a** to this major species (chloride salt) on the basis of microanalytical, IR, and $^{31}P\{^1H\}$ NMR data and by comparison of these IR and NMR data with those reported for the known dirhodium (**6b**) and diiridium (**6c**) analogues.[13] The minor species is presumably formed by loss of CO from **6a** and may possibly have the "A frame" structure **7**. Facile loss or gain of CO is a common feature of dirhodium- and diiridium-bis(diphenylphosphino)methane chemistry.[13,14] Treatment of the iridium–silver complex **5a** with [IrCl(CO)$_2$(p-toluidine)] immediately displaces silver chloride to give a single species, almost certainly [Ir$_2$(CO)$_2$(μ-CO)(μ-Cl)(μ-dppm)$_2$]$^+$ as evidenced by the ^{31}P chemical shift which was the same as that previously reported for this ion, made by a different method.[13] There have been many studies on dirhodium- and diiridium-bis(diphenylphosphino)methane complexes,[15] but ours are the first examples of mixed rhodium–iridium complexes.



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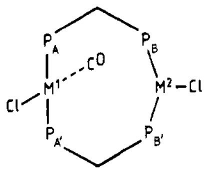
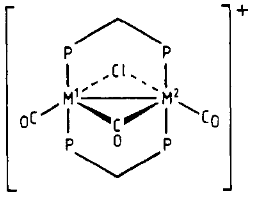
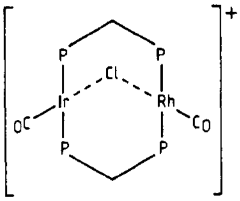


5a M¹ = Ir, M² = Ag
5b M¹ = Ir, M² = Cu
5c M¹ = Rh, M² = Ag



6a M¹ = Ir, M² = Rh
6b M¹ = M² = Rh
6c M¹ = M² = Ir



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We also find that [Rh(dppm)$_2$CO]Cl reacts with [(Ph$_3$P)AgCl]$_4$ in dichloromethane at ambient temperature to give the mixed rhodium–silver complex [Cl(OC)Rh(μ-dppm)$_2$AgCl] (**5c**) in 88% yield. This complex shows a particularly well-defined $^{31}P\{^1H\}$ NMR spectrum at −50 °C: $\delta(P_A)$ +29.9 ($^1J(RhP_A)$ = 122 Hz), $\delta(P_B)$ −7.7 ($^1J(^{109}AgP)$ = 449 Hz, $^1J(^{107}AgP)$ = 391 Hz, N = 103 Hz). At +21 °C the spectrum was broad due to rapid phosphine exchange at silver.[16]

Preliminary results show that many of the above described complexes undergo oxidative addition and other reactions, which we are investigating.

Acknowledgment. We thank Johnson Matthey Limited, the University of Leeds, and the SERC for generous support.

Registry No. **1a**, 87482-43-7; **1b**, 87482-44-8; **1c**, 87482-45-9; **1d**, 87482-46-0; **2a**, 87482-47-1; **2b**, 87482-49-3; **3**, 87482-51-7; **4**, 87482-52-8; **5a**, 87482-53-9; **5b**, 87482-54-0; **5c**, 87482-55-1; **6a**, 87482-56-2; **7**, 87482-57-3.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths and angles, and observed and calculated structure factor amplitudes (33 pages). Ordering information is given on any current masthead page.

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[13] Mague, J. T.; Sanger, A. R. *Inorg. Chem.* **1979**, *18*, 2060.

[14] Cowie, M. *Inorg. Chem.* **1979**, *18*, 286. Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Ibid.* **1980**, *19*, 2733.

[15] Mague, J. T.; Mitchener, J. P. *Inorg. Chem.* **1969**, *8*, 119. Kubiak, C. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1977**, *99*, 6129. Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1982**, *21*, 2119 and references therein. Balch, A. L.; Labadie, J. W.; Delker, G. *Ibid.* **1979**, *18*, 1224 and references therein. Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1981**, 228. Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2500 and references therein. Cowie, M.; Southern, T. G. *Ibid.* **1982**, *21*, 246 and references therein. Mague, J. T.; DeVries, S. H. *Ibid.* **1982**, *21*, 1632 and references therein. Mague, J. T. *Ibid.* **1983**, *22*, 45. Mague, J. T. *Ibid.* **1983**, *22*, 1158. Hoffman, D. M.; Hoffman, R. *Ibid.* **1981**, *20*, 3543 and references therein.

[16] Muetterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.* **1972**, *94*, 6386.

Kinetics of the High-Temperature Thermal Decomposition of Silanes and Alkylsilanes

M. A. Ring,* H. E. O'Neal,* S. F. Rickborn, and B. A. Sawrey

Department of Chemistry, San Diego State University
San Diego, California 92182

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Summary: The homogeneous decomposition kinetics of ViSiH$_3$, EtSiH$_3$, PrSiH$_3$, Me$_2$SiH$_2$, Me$_3$SiH, and Et(Me)$_2$SiH were examined under shock tube conditions. Primary process Arrhenius parameters were obtained for the first three when excess 1,3-butadiene was present to quench short silylene chains. Under our reaction conditions, neither toluene nor 1,3-butadiene could quench free radical and silylene chains in the di- and trialkyl-substituted silane decompositions.

We have examined the homogeneous gas-phase thermal decomposition of a series of hydrosilanes. A single pulse shock tube reactor was employed in the studies as other standard kinetic methods (e.g., static and flow reactors) are complicated by heterogeneous processes that can be strongly catalytic. Reaction temperatures were high, ranging from 950 (disilane) to 1300 K (monosilanes), and reaction times were short (~300 ± 20 μs). The systems studied to data can conveniently be placed in three groups: group I, silane,[1] methylsilane,[2] and disilane;[3] group II, vinylsilane, ethylsilane, and n-propylsilane, group III, dimethylsilane, trimethylsilane, and ethyldimethylsilane. The rationale for this grouping is based on kinetic behavior under our reaction conditions.

The silanes of group I are well-behaved kinetically (i.e., their reactant loss kinetics can be equated directly with

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[1] C. G. Newman, H. E. O'Neal, M. A. Ring, F. Leska, and N. Shipley, *Int. J. Chem. Kinet.*, 11, 1167 (1979).

[2] B. A. Sawrey, H. E. O'Neal, M. A. Ring, and D. Coffey, *Int. J. Chem. Kinet.*, in press.

[3] J. Dzarnoski, S. F. Rickborn, H. E. O'Neal, and M. A. Ring *Organometallics*, 1, 1217 (1982).

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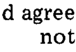
Table I. Hydrosilane Primary Process Arrhenius Parameters

Group I

reaction	log *A*	*E*, kcal	ref
$CH_3SiH_3 \longrightarrow CH_3SiH + H_2$	15.2	64.8[d]	2
$\longrightarrow CH_4 + SiH_2$	14.7	66.7[d]	2
$\longrightarrow CH_2{=}SiH_2 + H_2$	14.2	64.8	2
overall experimental[a]	14.3	60.7	2
$SiH_4 \longrightarrow SiH_2 + H_2$	15.5	59.6	1
experimental[b]	13.3	52.7	1
$Si_2H_6 \longrightarrow SiH_2 + SiH_4$	14.4	48.8[d]	3
$\longrightarrow Si_2H_4 + H_2$	15.3	55.3	3
overall experimental[c]	12.9	42.8	3

Group II

reaction	primary process[e]		overall decomp[f]	
	log *A*	*E*, kcal	log *A*	*E*, kcal
$CH_2{=}CHSiH_3$[g] $\longrightarrow CH_2{=}CHSiH + H_2$	14.9[h]	63.3	(13.4	54.0)
$\longrightarrow C_2H_4 + SiH_2$	14.1[h]	63.3		
$C_2H_5SiH_3$[i] $\longrightarrow C_2H_5SiH + H_2$	15.2	65.0	12.6	50.1
$C_3H_7SiH_3$[j] $\longrightarrow C_3H_7SiH + H_2$	15.3	65.3	14.6	60.2

[a] Pressure dependent reaction at T = 1125–1250 K and $P_T \cong$ 4700 torr (96.7% Ar). [b] Pressure dependent reaction at T = 1035–1184 K and $P_T \cong$ 4000 torr (96% Ar). [c] Pressure dependent reaction at T = 850–1000 K and $P_T \cong$ 2500 torr (96.8% Ar). [d] These parameters are in good agreement with previous results for CH_3SiH_3[4,5] and Si_2H_6.[6] [e] Decomposition in the presence of a SiH_2 trap  not pressure dependent. [f] Decomposition without a SiH_2 trap. Considerable convex curvature in Arrhenius plots. [g] T = 1100–1260 K and $P_T \simeq$ 3100 torr (96.5% Ar). [h] This is with $\phi_{C_2H_4}$ = 0.14. [i] T = 1100–1250 K and $P_T \simeq$ 3100 torr (96.5% Ar). [j] T = 1100–1240 K and $P_T \simeq$ 3100 torr (96.5% Ar).

the kinetics of their primary dissociation reactions). The primary processes generate silylene intermediates that are stable to further decomposition and that do not induce the decomposition of reactant through subsequent reactions. Termination of the silylene intermediates is by dimerization followed by hydrogen elimination, and the dehydrogenated silicon products thus formed are apparently lost to the walls.

$$2SiH_2 \underset{-1}{\overset{1}{\rightleftharpoons}} Si_2H_4 \xrightarrow{2} Si_2H_2 + H_2$$

$$2CH_3SiH \underset{-3}{\overset{3}{\rightleftharpoons}} CH_3SiH{=}SiHCH_3 \rightarrow CH_3Si{\equiv}SiCH_3 + H_2$$

For further comparison, the primary process Arrhenius parameters for the group I silanes are listed in Table I.

In this communication we report primary process Arrhenius parameters for the group II silanes (see Table I). These parameters were obtained from decompositions in the presence of a good silylene trap, 1,3-butadiene (in excess). Without 1,3-butadiene present, the group II silanes have overall decomposition rates that are significantly faster than their primary process rates (see Table I), and Arrhenius plots from these data had considerable curvature. Toluene (a free radical scavenger) was unable to inhibit the enhanced decomposition rates. Thus it appears that the enhanced group II silane decomposition rates are due to short silylene chain reactions.

Silylene Chains. In the group II silanes, the induced decompositions involve asymmetric disilane intermediates that can decompose by more than one reaction channel to generate products. Our evidence for the silylene chain processes is from the detection of the expected products of the intermediate disilanes and from our ability to match the observed reaction rates in computer-modeling studies using Arrhenius parameters either known or obtained by analogy to known reactions. For example, in the ethylsilane and *n*-propylsilane decomposition, the chain reactions are shown in reactions 5–10 (illustrating for ethylsilane). Note that the above is a *branching* chain reaction

$$CH_3CH_2\ddot{Si}H \xrightarrow{5} C_2H_4 + SiH_2 \quad E_{act} \simeq 31 \pm 2 \text{ kcal/mol}$$

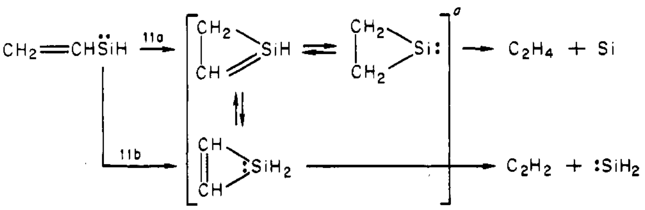
$$\ddot{Si}H_2 + C_2H_5SiH_3 \underset{-6}{\overset{6}{\rightleftharpoons}} [C_2H_5SiH_2SiH_3] \xrightarrow{7} C_2H_5\ddot{Si}H + SiH_4$$

$$\xrightarrow{8} C_2H_5SiH_2\ddot{Si}H + H_2$$

$$[C_2H_5SiH_2\ddot{Si}H \rightleftharpoons C_2H_5SiH{=}SiH_2] \underset{-9}{\overset{9}{\rightleftharpoons}} C_2H_5\ddot{Si}H + \ddot{Si}H_2$$

$$\xrightarrow{10} C_2H_5Si{\equiv}SiH + H_2$$

if the disilane eliminates hydrogen faster than it eliminates silane. This appears to be the case with $k_8 > 3k_7$. The same kind of reactions occur in the vinylsilane decomposition (reactions 11–15 where $ViSiH_3$ is vinylsilane).



$$:SiH_2 + ViSiH_3 \underset{-12}{\overset{12}{\rightleftharpoons}} [ViSiH_2SiH_3] \xrightarrow{13} ViSiH_2\ddot{Si}H + H_2$$

$$\xrightarrow[14]{} SiH_4 + ViSiH$$

$$ViSiH_2\ddot{Si}H \xrightarrow{15} Vi\ddot{Si}H + :SiH_2$$

Here we depict the pathway via a mechanism proposed and substantiated in part by Barton.[7] Silylene chains are possible in both of these group II systems because of two conditions: (1) the original silylenes decompose readily at our reaction temperatures (i.e., reactions 5 and 11a,b are fast or at least competitive with the dimerization–decomposition sink reactions, like reactions 1–4); (2) the asymmetric disilanes produced after silylene insertion into Si–H bonds of the reactant can react to new products. The hydrogen eliminations of the alkyldisilanes (reactions 8 and

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(4) P. S. Neudorfl and O. P. Strausz, *J. Phys. Chem.*, **82**, 241 (1978).

(5) I. M. T. Davidson and M. A. Ring, *J. Chem. Soc., Faraday Trans. 1*, **76**, 1520 (1980).

(6) M. Bowery and J. H. Purnell, *Proc. R. Soc. London, Ser. A*, **321**, 341 (1971).

(7) T. J. Barton, and G. T. Burns, *Tetrahedron Lett.*, **24**, 159 (1983).

Table II. Hydrosilane Decomposition Kinetics of Group III Silanes

	primary process		overall decomp[a]	
reaction	log *A*	*E*, kcal	log *A*	*E*, kcal
$(CH_3)_2SiH_2 \longrightarrow (CH_3)_2Si + H_2$[b]	14.3	68.0		
$\longrightarrow CH_3SiH + CH_4$[c]	15.0	72.0	(13.3	58.0)
$\longrightarrow CH_3SiH_2 + \cdot CH_3$[d]	17.3	88.6		
$(CH_3)_3SiH \longrightarrow (CH_3)_2Si + CH_4$[d]	14.9	73.0	(11.9	51.7)
$\longrightarrow (CH_3)_3Si + \cdot CH_3$[d]	17.5	88.6		
$C_2H_5Si(CH_3)_2H \longrightarrow C_2H_5SiCH_3 + CH_4$[c]	14.7	73.0		
$\longrightarrow (CH_3)_2SiH\cdot + \cdot C_2H_5$[d]	17.0	85.6	(10.8	43)
$\longrightarrow C_2H_5Si(CH_3)H\cdot + \cdot CH_3$[d]	17.3	88.6		

[a] Arrhenius parameters are uncertain due to considerable curvature in Arrhenius plots. [b] From ref 4. [c] Estimated from CH_3SiH_3 decomposition data. [d] Calculated from thermodynamic estimates.[8]

13), by analogy with the 1,1-H_2 elimination reaction observed for disilane itself, are estimated to be 2–5 times faster than the competing 1,2-H shift reactions (reactions 7 and 14) at shock tube temperatures. Since the decompositions of vinylsilylene to acetylene and ethylene have fairly high activation energies (e.g., $k_{11b} \simeq 10^{14.9} \times e^{-49.6/RT}$ s^{-1}), we can predict that if the vinylsilane reaction could be studied homogeneously at lower temperatures ($T \leq 1000$ K), there would be no induced reaction and the overall kinetics would be identifiable with the primary process reactions. On the other hand, ethyl- and *n*-propylsilanes should involve silylene chain reactions even at static system temperatures ($T \approx 700$ K) since their respective silylene decompositions are low activation energy processes. Also, major products should be H_2, SiH_4, and the respective olefins (i.e., 1,2-H shift decompositions of the disilane intermediates like reactions 7 and 14 should dominate). These predictions have been confirmed by a brief 700 K static system investigation of *n*-propylsilane: products were those expected and chain lengths (a significant amount of the induced reaction is probably heterogeneous in origin) of about 80 were observed.

Intramolecular Silylene Insertion into (C–H) Bonds. Propylene and ethylene, in the ratio of about 3/1, respectively, with no apparent temperature variation over a 90 °C range were the major olefin products of the *n*-propylsilane decomposition. Both products arise from the decomposition of *n*-propylsilylene (reactions 16 and 17).

$$n\text{-Pr}\ddot{\text{Si}}\text{H} \xrightarrow{16} CH_3CH{=}CH_2 + \ddot{\text{Si}}H_2 \quad \Delta H^\circ_{16} \simeq 29.6 \text{ kcal}^{8}$$

$$n\text{-Pr}\ddot{\text{Si}}\text{H} \xrightarrow{17} C_2H_4 + CH_2{=}SiH_2 \quad \Delta H^\circ_{17} \simeq 17.4 \text{ kcal}$$

The mechanisms of these decompositions are not yet resolved, but it is possible that both involve intramolecular insertions of the silylene group into C-H bonds of the *n*-propyl group. Since an excess of 1,3-butadiene (i.e., [butadiene]/[*n*-propylsilane] = 15/1) had no effect on the yields of propylene (effect on ethylene yield is not known since some ethylene is generated directly from butadiene), one can estimate an upper limit for the activation energies of the above reactions of 30 ± 3 kcal. A lower limit is provided by the thermochemistry of reaction 16. Hence it follows that $E_{16} \simeq E_{17} \simeq 31 \pm 2$ kcal.[2] Silylene insertion into the C–H of methane has an activation energy of 19 kcal.[2] Therefore, if reactions 16 and 17 do proceed via intramolecular C–H insertions of the silylene groups, only about 12 kcal of cyclic intermediate strain energy is carried over into their transition states.

Free Radical Chains. We also wish to report results obtained on the decomposition of the group III silanes whose decomposition gave unexpected products such as ethylene and acetylene and whose decomposition kinetics were found to be extraordinarily complex under our reaction conditions. Both silylenes and free radicals are produced in their primary dissociation reactions. The subsequent induced decompositions of the reactant are the result of chain reactions carried by these intermediates. Additions of the usual types of free radical and silylene trapping agents (e.g., toluene and olefins for the former or butadiene and acetylene for the latter), while reducing reaction rates slightly, do not significantly effect overall reaction rates. This is probably because the silylene trapping products and the free radical trapping agents are both thermally unstable at the group III silane reaction temperatures. Our preliminary modeling studies appear to support the above assertions.

Because 1,1-hydrogen elimination activation energies increase with alkyl substitution, one finds that Si–C bond fission begins to be competitive for dimethylsilane (see Table II). Also, because (Si–C) bond energies are basically unchanged by alkyl substitution, free radical generation by Si–C bond fission occurs in all alkyl silanes at very similar rates. Thus it is not surprising that the overall decomposition kinetics of di-, tri-, and tetrasubstituted alkylsilanes are very similar and that silane thermal stabilities follow the sequence: $SiH_4 < MeSiH_3 < Me_2SiH_2 \simeq Me_3SiH \simeq Me_4Si$. Free radical induced decomposition of the higher alkyl-substituted silanes undoubtedly follows a Rice–Herzfeld type chain sequence. Thus, illustrating for Me_2SiH_2, one can write reactions 18–25.

Chain Steps

$$CH_3\cdot + Me_2SiH_2 \xrightarrow{18} Me_2\dot{\text{Si}}H + CH_4$$

$$\xrightarrow{19} \cdot CH_2(Me)SiH_2 + CH_4$$

$$Me_2\dot{\text{Si}}H \xrightarrow{20} Me\ddot{\text{Si}}H + CH_3\cdot$$

$$\cdot CH_2(Me)SiH_2 \xrightarrow{21} CH_2{=}SiH_2 + CH_3\cdot$$

$$CH_2{=}SiH_2 \underset{-22}{\overset{22}{\rightleftharpoons}} Me\ddot{\text{Si}}H$$

Terminations

$$CH_3\cdot + CH_3\cdot \xrightarrow{23} C_2H_6$$

$$CH_3\cdot + Me_2\dot{\text{Si}}H \xrightarrow{24} Me_3SiH$$

$$CH_3\cdot + \cdot CH_2(Me)SiH_2 \xrightarrow{25} CH_3CH_2SiH_2(Me)$$

The free radical chains generate silylenes as products; silylenes are also generated in the primary dissociation reactions of group III silanes. Thus silylene chains also contribute significantly to the highly substituted alkylsilane decompositions. In dimethylsilane the formation

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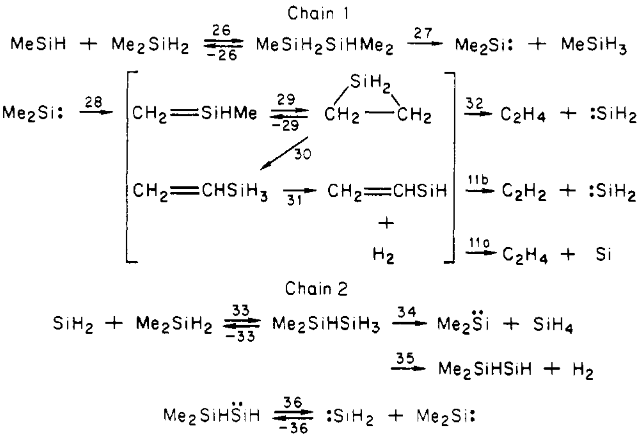
(8) H. E. O'Neal and M. A. Ring, *J. Organomet. Chem.*, **213**, 419 (1981).

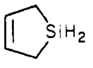
Table III. Kinetics of Some Silylene Reactions

reaction	log A, s^{-1}	E, kcal	how obtained
$CH_2{=}CH\ddot{Si}H \longrightarrow C_2H_2 + SiH_2$	15.0	49.6	modeling studies (VS)
$\longrightarrow C_2H_4 + Si$	15.0	50.6	modeling studies (VS)
$SiH_2 + \ddot{Si}H_2 \longrightarrow Si_2H_4$	11.9	0	kinetic molecular theory
$Si_2H_4 \longrightarrow 2SiH_2$	15.3	58.0	thermochemistry (DS, MS)
$Si_2H_4 \longrightarrow Si_2H_2 + H_2$	14.5	53.0	modeling studies (DS)
$ViSiH_2SiH_3 \longrightarrow ViSiH_2\ddot{Si}H + H_2$	15.45	55.3	modeling studies (VS)
n-$PrSiH \longrightarrow C_3H_6 + \ddot{Si}H_2$	12.6	31 ± 5	see text
$\longrightarrow C_2H_4 + CH_2{=}SiH_2$	12.0	30.4 ± 5	see text
$SiH_2 + C_2H_4 \longrightarrow CH_2{=}CHSiH_3$	10.1	14.0	modeling studies (MS); thermochemistry (VS)

Scheme I



of silane, methylsilane, ethylene, and acetylene as products suggest the occurrence of the two coupled silylene chains shown in Scheme I. Subsequent decompositions of $MeSiH_3$ and SiH_4 promote chain branching in the system. As stated earlier the radical and silylene chains are not appreciably quenched by additions of trapping agents. This is undoubtedly a consequence of the high temperatures needed to investigate these reactions by our experimental technique (SPST, T(K) $\simeq$ 1150→1300 K). For example, we have found that the 1,3-butadiene–SiH_2



product decomposes fairly rapidly at temperatures around 1200 K. Further, the use of toluene as a free radical trap is relatively inefficient at these temperatures because toluene decomposes to H and benzyl radicals at rates that are *faster* than the primary processes of the reactant under our reaction conditions (30 toluene/1 reactant, $T > 1200$ K). Also, benzyl radicals, produced by trapping of more active radicals, can initiate chain decomposition of the reactant through hydridic H abstraction at these temperatures. Toluene should, therefore, not be used as a free radical trapping agent at temperatures much above 1200 K even in a shock tube.

In Table II we have summarized our observations on the overall decomposition kinetics for the group III silanes (various conditions). These kinetic parameters should be compared with those measured or estimated for the primary dissociation processes alone.

In Table III we summarize other kinetic data relative to secondary reactions of silylenes that we have been able to establish either completely or in part through our kinetic studies.

In conclusion, we would like to emphasize a point frequently overlooked. The kinetics of silane and silylene systems, like all kinetic systems, will vary significantly from one temperature and pressure regime to another. Full knowledge of the pertinent kinetics is therefore essential to even a qualitative understanding of these systems. Hopefully the kinetic data reported here will prove to be useful in this regard.

Acknowledgment. We are indebted to the Department of Energy for financial support of this work from Grant DE-FG02-80CS-83103.

Registry No. $CH_2{=}CHSiH_3$, 7291-09-0; C_2H_4, 74-85-1; $C_2H_5SiH_3$, 2814-79-1; $C_3H_7\ddot{Si}H$, 87640-43-5; $C_3H_7SiH_3$, 13154-66-0; $(CH_3)_2SiH_2$, 1111-74-6; CH_4, 74-82-8; $(CH_3)_3SiH$, 993-07-7; $C_2H_5Si(CH_3)_2H$, 758-21-4; C_3H_6, 115-07-1; $CH_2{=}CH\ddot{Si}H$, 78442-50-9; $\ddot{Si}H_2$, 13825-90-6; $C_2H_5\ddot{Si}H$, 81875-16-3; $CH_3\ddot{Si}H$, 55544-30-4; $CH_3SiH_2\cdot$, 24669-75-8; $\cdot CH_3$, 2229-07-4; $(CH_3)_2\ddot{Si}$, 6376-86-9; $(CH_3)_3Si\cdot$, 16571-41-8; $C_2H_5\ddot{Si}CH_3$, 87640-44-6; $(CH_3)_2SiH\cdot$, 24669-76-9; $\cdot C_2H_5$, 2025-56-1; $C_2H_5Si(CH_3)H\cdot$, 87640-45-7; Si_2H_4, 15435-77-5; silacyclopent-3-ene, 7049-25-4.

Preparation and Structure of (η-$C_5H_5)_2Ti(SC_6H_5)(SSSC_6H_5)$: The Product of a Sulfur Catenation Reaction

Alan Shaver[*1a] **and James M. McCall**
Department of Chemistry, McGill University
Montreal, Quebec, Canada H3A 2K6

Peter H. Bird[*1b] **and Nasrin Ansari**
Department of Chemistry, Concordia University
Montreal, Quebec, Canada H3G 1M8

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Summary: The complex $Cp_2Ti(SH)_2$ was treated with 2 equiv of RS–imide, where imide = phthalimide and R = $CHMe_2$ and p-$C_6H_4CH_3$ and imide = succinimide and R = C_6H_5, to give the symmetrical disulfane $Cp_2Ti(SSR)_2$ when R = $CHMe_2$ and the unsymmetrical trisulfanes $Cp_2Ti(SR)(SSSR)$ when R = C_6H_5 and p-$C_6H_4CH_3$. The structure of the compound where R = C_6H_5 was determined and the TiSSSR linkage characterized.

Complexes containing cyclic polysulfane chelating ligands often have strongly preferred ring sizes.[2,3] For the complexes Cp_2MS_5, where M = Ti, Zr, and Hf, the ring size is six despite careful attempts to prepare smaller rings.[2] Thus, $Cp_2Ti(SH)_2$ reacts with sulfur-transfer reagents of the type imide–S_x–imide, where imide = phthalimide and

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[1] (a) To whom correspondence concerning the preparations should be sent. (b) To whom correspondence concerning the X-ray structural determination should be sent.

[2] McCall, J. M.; Shaver, A. *J. Organomet. Chem.* **1980**, *193*, C37–C39.

[3] Bird, P. H.; McCall, J. M.; Shaver, A.; Siriwardane, U. *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 384–385.