Organometallics **1992,** *11,* 983–985

showed a 60:40 mixture of diastereomers, which was then purified on alumina(I) as before to afford orange crystalline acyl **5** (7 mg, 41%). After preparative TLC (SiO_2) as before, the more polar acyl diastereomer (*S,R*)-(+)-**5b** was isolated and characterized as follows: mp 186 °C; ^1H NMR (400 MHz, C_6D_6) δ 8.04 (d, J = 8.5 Hz, 1 H), 7.94 (d, J = 8.5 Hz, 1 H), 7.71 (m, 9 H), 7.32 (m, 4 H), 6.97 (m, 12 H), 4.12 (s, 1 H), 4.08 (s, 1 H), 3.89 (d, J = 13.0 Hz, 1 H), 3.80 (m, 1 H), 3.42 (d, J = 15 Hz, 1 H), 3.26 (m, 2 H), 2.60 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 278.20 (d, J = 21.0 Hz, acyl carbon), 219.81 (d, J = 39.0 Hz, CO), 136.65, 136.23, 135.72, 134.80, 134.46, 133.40–133.30, 132.68, 132.40, 132.28, 132.14, 132.03, 131.93, 130.32, 129.61, 128.95, 128.86, 128.54, 128.46, 128.29–127.70, 126.90, 126.79, 126.52, 126.26, 125.87, 125.30, 100.26, 96.68, 94.17, 84.31, 82.48, 52.81 (d, J = 5.5 Hz, acyl CH_3), 33.42, 33.00; IR (neat film) 3055, 2963, 2924, 1910, 1593, 1434, 1261, 1092, 1023, 865, 800, 696 cm^{-1}; $[\alpha]^{23}_D$ +6° (c 0.20, C_6D_6); MS, m/z (CI, NH_3, relative intensity) 749 ($M^+ + NH_3$, 0.05%), 733 ($M^+ + 1$, 0.15), 732 (M^+, 0.29), 470 (0.69), 454 (100), 344 (2), 263 (56).

Configurational Stability of *rac*-[2,3-(1,1′-Binaphthyl-2,2′-diyldimethylene)cyclopenta-1,3-dienyl]carbonyl(triphenylphosphine)acetyliron (5a) under Oxidative Conditions. Acyliron **5a** (9 mg, 0.012 mmol) was dissolved in CH_3CN (900 μL), and the solution was cooled to −40 °C and excluded from light. A solution of $(NH_4)_2Ce(NO_3)_6$ (7.4 mg, 0.014 mmol) in CH_3CN (600 μL) was then added via syringe, causing a consecutive color change from yellow starting material to brown to red to dark green over a period of 10 min. A solution of $C_{10}H_8Na$ (0.234 M in THF, 58 μL, 0.014 mmol) was then added via syringe at −40 °C, which caused an immediate color change from green to orange. The reaction mixture was allowed to stir at −40 °C for 10 min after which it was quenched in a separatory funnel with CH_2Cl_2 and water. After workup, the crude ^1H NMR spectrum revealed the presence of **5a** with no detection of **5b**. Likewise acyliron diastereomer **5b** was subjected to these reaction conditions, producing the same series of color changes with recovery of **5b** and no detectable trace of diastereomer **5a**. When oxidation of **5a** was performed at 23 °C (15 min), there was no detection of the characteristic green 17-electron acyl cation. Subsequent addition of $C_{10}H_8Na$ at 0 °C (15 min) resulted in no presence of either isomer.

Configurational Stability of *rac*-[5a]$^+$ in the Presence of PPh_3. Acyliron **5a** (13 mg, 0.018 mmol) was dissolved in CH_3CN (1.0 mL), and the solution was cooled to −40 °C and excluded from light. A solution of $(NH_4)_2Ce(NO_3)_6$ (10.7 mg, 0.020 mmol) in CH_3CN (600 μL) was then added via syringe and stirred for 30 min and then warmed to −20 °C (15 min) and 0 °C for 15 min. The green reaction mixture was cooled to −10 °C, and a solution of PPh_3 (9.8 mg, 0.037 mmol) in CH_3CN (600 μL) was added and stirred for 20 min. The green reaction mixture was then cooled further to −40 °C, and a solution of $C_{10}H_8Na$ (0.234 M in THF, 84 μL, 0.020 mmol) was added via syringe, causing an immediate color change from green to orange. The reaction mixture was allowed to stir at −40 °C for 10 min, after which it was quenched and worked up. The crude ^1H NMR spectrum revealed the presence of **5a** with no detection of **5b**. Likewise acyliron diastereomer **5b** was subjected to the same reaction conditions recovering **5b** with no detectable trace of diastereomer **5a**. Conducting this reaction isothermally at 0 °C (15 min each step, 8 mM in CH_3CN) with addition of a homogeneous solution of PPh_3 (36 mg, 0.137 mmol) to **5a** (10 mg, 0.014 mmol) preceding reduction resulted in the recovery of **5a** and the absence of **5b**.

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Registry No. (*S*)-(+)-**2**, 138259-99-1; (*S,S*)-(+)-**5a**, 138259-98-0; *rac*-**5a**, 138332-60-2; (*S,R*)-(+)-**5b**, 138332-59-9.

Supplementary Material Available: Tables of bond lengths and angles, crystallographic data, and thermal and positional parameters for **5a** (9 pages); listings of h,k,l, F_o, F_c, and $\sigma(F_o)$ values for **5a** (16 pages). Ordering information is given on any current masthead page.

Decomposition Kinetics of Methyl- and *n*-Propyldisilane

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Summary: The thermal decomposition kinetics of methyl- and *n*-propyldisilane (MDS and PrDS, respectively) under static reaction conditions are reported. These kinetics, extrapolated via transition-state theory to 298 K, are combined with kinetic data on the reverse reactions to obtain heats of formation of the reactant disilanes and the product silylenes. Thus $\Delta H_f°$(MDS) = 4.7 kcal/mol, $\Delta H_f°$(PrDS) = −2.0 kcal/mol, $\Delta H_f°$(MeSiH) = 49.6 kcal/mol, and $\Delta H_f°$(nPrSiH) = 41.6 kcal/mol.

The only important primary dissociation reactions in the thermal decompositions of disilanes having at least one Si–H bond are 1,2-H shifts[1] forming a monosilane and a silylene as products. For example there are just two primary dissociation channels in the thermal decomposition of methyldisilane (reactions 1 and 2). In neat systems,

$$MeSi_2H_5 \rightarrow MeSiH_3 + SiH_2 \tag{1}$$

$$MeSi_2H_5 \rightarrow MeSiH + SiH_4 \tag{2}$$

primary process silylenes react further to form trisilanes which, being somewhat more reactive than the reactant,[2] decompose to produce additional silane products and other potentially reactive silylenes, as in reactions 3–5. Under

$$SiH_2 + MeSi_2H_5 \rightarrow MeSi_3H_7 \tag{3}$$

$$MeSi_3H_7 \rightarrow SiH_4 + MeSi_2H_3 \tag{4}$$

$$MeSi_3H_7 \rightarrow MeSiH_3 + SiH_3SiH \tag{5}$$

such chain-enhanced conditions, identification of the formation kinetics of any monosilane product with the kinetics of its corresponding primary process reaction could be erroneous, particularly in studies carried to high reactant conversions. Nevertheless, such identifications were routine in most early disilane kinetic studies.[3] We have been concerned in recent years with establishing the thermochemistry of key organosilanes and silylenes, the ultimate objective being the generation of a Benson type group additivity scheme for polysilanes and organosilanes.

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Table I. Decomposition Kinetic Results for Methyldisilane

system	reaction[a]	log *A*, s^{-1}	*E*, kcal	ref
neat[b]	1	15.28 ± 0.15	50.75 ± 0.36	3
neat	2	14.14 ± 0.14	49.89 ± 0.35	3
BD/MDS = 19[c]	1 + 2	15.48 ± 0.30	51.20 ± 0.85	this work
	1	15.58 ± 0.22	51.64 ± 0.62	this work
	2	14.16 ± 0.20	50.22 ± 0.57	this work
BD/MDS = 79[c]	1 + 2	15.35 ± 0.40	50.90 ± 1.3	this work
	1	15.53 ± 0.28	51.53 ± 0.65	this work
	2	13.96 ± 0.28	49.65 ± 0.75	this work

[a] Reaction 1 + 2 = overall MDS loss kinetics. Reaction 1 = MDS → SiH_2 + $MeSiH_3$. Reaction 2 = MDS → MeSiH + SiH_4. [b] Temperature range = 540–570 K. [c] Temperature range = 580–628 K.

In particular, we have focused on a kinetic approach for determining the thermochemistry of methylated disilanes and silylenes. Thus by combining kinetic measurements of the 1,2-H shift primary dissociation reactions of methylated disilanes with kinetic data on their reverse silylene insertions, one obtains reaction thermochemical information (enthalpies and entropies) which, via Hess' law analyses and existing thermochemical data on silane, disilane, and the methylsilanes, yield heats of formation of the reactant disilanes and their product silylenes. Results of this kinetic-based bootstrap procedure have been reported,[4] but some of the kinetic data used in that analysis were from early decomposition studies of the neat reactants and could be in error. Just how much in error was the question central to the reinvestigation of the methyldisilane decomposition kinetics reported here. This decomposition is critical to the kinetic determinations of the heats of formation of 1,*x*-methylated disilanes (*x* = 0–3) and of methylsilylene. To evaluate the primary process Arrhenius parameters reported in the earlier study,[3] the methyldisilane (MDS) gas-phase decomposition was studied both in the neat form and under conditions of maximum inhibition. 1,3-Butadiene was used as the silylene-trapping agent. The decomposition kinetics of *n*-propyldisilane (PrDS), the first alkyldisilane with an R group larger than methyl, were also studied and are here reported.

Results and Discussion

Methyldisilane. The decomposition of neat MDS and of MDS in the presence of excess butadiene (1,3-BD/MDS = 19/1 and 79/1) was studied between 580 and 628 K and at total pressures of 112 ± 12 Torr. Reactant conversions ranged from 30 to 70%, and good first-order kinetics for MDS loss, based either on reactant loss or on monosilane product formations, were obtained over the entire conversion range. Besides the usual diene trapping products, silane and methylsilane were the only products observed. Their yield ratios at any given temperature were conversion and BD concentration independent. Arrhenius parameters derived for MDS loss and for the individual primary dissociation reaction channels are shown in Table I. The nearly identical reactant loss and product formation Arrhenius parameters found for two reactant mixtures (inhibition ratios of BD/DMS = 19/1 and 79/1) indicates complete silylene scavenging for both systems. Further, the good agreements with the former results[3] indicate negligible decomposition of the trisilane products at the low conversions (<6%) of that study. These results, coupled with unpublished time-resolved kinetics of the MeSiH + SiH_4 back-reaction,[5] provide the data required for a reliable kinetic method calculation of the heats of formation of methyldisilane and of methylsilylene. Thus a transition-state theory extrapolation of the reaction 1 Arrhenius parameters to 298 K gives an activation entropy and enthalpy of $\Delta S_1^{\ddagger} = 4.45$ cal/deg and $\Delta H_1^{\ddagger} = 49.3$ kcal and a decomposition rate constant of $k_1 = 1.18 \times 10^{-22}\ s^{-1}$. With $k_{-1,298} = 2.33 \times 10^9\ atm^{-1}\ s^{-1}$,[6] this gives an equilibrium constant of $K_{1,-1} = 5.05 \times 10^{-32}$ atm. The reaction entropy at 298 K is $\Delta S_{1,2}^{\circ} = 31.6$ eu,[7] therefore $\Delta H_{1,-1}^{\circ} = 52.1$ kcal. With $\Delta H_f^{\circ}(MeSiH_3) = -7.2$ kcal/mol[8] and $\Delta H_f^{\circ}(SiH_2) - \Delta H_f^{\circ}(MDS) = 59.3$ kcal/mol and under the assumption that $\Delta H_f^{\circ}(SiH_2) = 64 \pm 2$ kcal/mol,[4] one obtains $\Delta H_f^{\circ}(MDS) = 4.7 \pm 1.4$ kcal/mol. This can be compared to our earlier estimate of 5.0 kcal/mol.[4] Both values are in reasonably good agreement with the MM2 value[4] of 3.4, our revised EECBA value[4] of 4.0, and a recent BAC-MP4(SDTQ)[9] value of 5.1, all in kcal/mol. A similar transition-state theory extrapolation to 298 K of the reaction 2 Arrhenius parameters gives $\Delta S_2^{\ddagger} = 0.28$ eu, $\Delta H_2^{\ddagger} = 48.4$ kcal, and $k_2 = 4.26 \times 10^{-23}\ s^{-1}$, and an extrapolation to 298 K of the latest time-resolved laser absorption results of Walsh[5] for the MeSiH + SiH_4 reaction between 361 and 544 K, gives $k_{-2} = 2.00 \times 10^9\ atm^{-1}\ s^{-1}$; hence $K_{2,-2} = 2.13 \times 10^{-32}$ atm. This order of magnitude smaller value than our prior estimate[4] is due mainly to the higher rate constant of the back-reaction and not to any significant change in the MDS decomposition kinetics (see Table I). With $\Delta S_{2,-2}^{\circ} = 33.4$ eu,[7] one then obtained $\Delta H_{2,-2}^{\circ} = 53.1$ kcal and $\Delta H_f^{\circ}(MeSiH) - \Delta H_f^{\circ}(MDS) = 44.9$ kcal/mol, all at 298 K. Finally, using the derived heat of formation of 4.7 kcal/mol for MDS, one calculates $\Delta H_f^{\circ}(MeSiH) = 49.6$ kcal/mol. Our prior deduced methylsilylene value was 48.7;[4] isodesmic calculations[10] (corrected for a $\Delta H_f^{\circ}(MeSiH_3) = 7.2$ kcal/mol) give 47.8 and the BAC-MP4(SDTQ)[9] value is 48.4, all in kcal/mol. It appears, then, that a methylsilylene heat of formation of $\Delta H_f^{\circ}(MeSiH) = 49 \pm 1$ kcal/mol satisfies all the most recent results for this species.

***n*-Propyldisilane.** The decomposition of *n*-propyldisilane (PrDS) was studied statically between 593 and 643 K at total pressures of 150 Torr in the presence of excess 1,3-dienes. Both 1,3-butadiene and 2,3-dimethyl-1,3-butadiene at respective BD/PrDS inhibition ratios of 40/1 and 60/1 were used. Reactant conversions ranged from 30 to 70%, and the only products, other than diene trapping products, were silane (S) and propylsilane (PS), as expected from the primary dissociation reactions 6 and 7.

$$nPrSiH_2SiH_3 \rightarrow nPrSiH_3 + SiH_2 \qquad (6)$$

$$nPrSiH_2SiH_3 \rightarrow SiH_4 + nPrSiH \qquad (7)$$

Again, good first-order kinetics were obtained for PrDS loss and for the propylsilane and silane product formations. Product ratios PS/S were constant at any given reaction temperature and were conversion independent (see Table II). Arrhenius parameters for PrDS loss and for the individual primary dissociation reaction channels (based on the monosilane formation kinetics) are shown in Table II. Transition-state theory kinetic analyses of reactions 6 and 7 lead to the thermochemical and kinetic values of Table

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Table II. *n*-Propyldisilane Kinetics and Observations[a]

system	$nPrSiH_3/SiH_4$ product yield ratios			
	613 K	623 K	633 K	643 K
DMBD/PrDS = 40	5.35 ± 0.28	5.63 ± 0.19	5.90 ± 0.22	6.32 ± 0.06
DMDS/PrDS = 60	5.31 ± 0.81	6.8 ± 1.8	7.85 ± 0.83	6.03 ± 0.81

system	reaction[b]	log *A*, s^{-1}	*E*, kcal	ref
BD/PrDS = 40	6 + 7	15.19 ± 0.22	50.44 ± 0.63	this work
	6	15.26 ± 0.18	50.83 ± 0.52	this work
	7	13.66 ± 0.52	48.44 ± 1.58	this work

[a] Temperature range of the study was 593–643 K. [b] Reaction 6 = PrDS → SiH_2 + $nPrSiH_3$. Reaction 7 = PrDS → nPrSiH + SiH_4. Reactions 6 + 7 overall loss kinetics of PrDS.

Table III. Kinetic and Thermochemical Results Summary (298 K)

reaction[k]	log k_f,[a] s^{-1}	log k_b,[b] $atm^{-1}\ s^{-1}$	log K_{eq},[c] atm	ΔS,[d] cal/deg	ΔH,[e] kcal	$\Delta H_f°$(X),[f] kcal/mol
1	−21.95	9.37	−31.32	31.6	52.1	4.7[g]
2	−22.42	9.30	−31.72	33.4	53.2	49.7[h]
6	−21.68	8.99	−30.67	31.6	51.2	−2.0[i]
7	−21.80	8.92	−30.72	33.4	51.8	41.6[j]

[a] Decomposition rate constants. [b] Back-reaction rate constants. [c] Equilibrium constants. [d] Decomposition reaction entropy. [e] Decomposition reaction enthalpy. [f] Heats of formation of X as obtained from reactins 1, 2, 6, and 7. See below. [g] X = methyldisilane (MDS); based on $\Delta H_f°(SiH_2)$ = 64 kcal/mol. [h] X = methylsilylene (MeSiH). [i] X = *n*-propyldisilane (PrDS). [j] X = *n*-propylsilylene (nPrSiH). [k] Reactions ($\Delta H_f°$ in kcal/mol reported under equations):

$$\underset{X,\ 4.7}{MeSi_2H_5} \rightarrow \underset{-7.2}{MeSiH_3} + \underset{64}{SiH_2} \qquad \Delta H_{298}° = 52.1\ \text{kcal} \qquad (1)$$

$$\underset{4.7}{MeSi_2H_5} \rightarrow \underset{8.2}{SiH_4} + \underset{X,\ 49.7}{MeSiH} \qquad \Delta H_{298}° = 53.1\ \text{kcal} \qquad (2)$$

$$\underset{X,\ -2.0}{nPrSi_2H_5} \rightarrow \underset{-14.8}{nPrSiH_3} + \underset{64}{SiH_2} \qquad \Delta H_{298}° = 51.2\ \text{kcal} \qquad (6)$$

$$\underset{-2.0}{nPrSi_2H_5} \rightarrow \underset{8.2}{SiH_4} + \underset{X,\ 41.6}{nPrSiH} \qquad \Delta H_{298}° = 51.8\ \text{kcal} \qquad (7)$$

By group additivity

$$\underset{-14.8}{\Delta H_f°(nPrSiH_3)} = \underset{-7.2}{\Delta H_f°(MeSiH_3)} + \underset{-4.93}{\Delta H_f°[C\text{–}(C)(Si)(H)_2]} + \underset{-2.63}{\Delta H_f°[C\text{–}(C)_2(H)_2]}$$

III. The analysis assumes an *n*-propylsilane heat of formation of −14.8 kcal/mol (derived as a best value from the Allen scheme,[11] from EECBA calculations,[12] and from group additivity and the methyldisilane heat of formation), a $\Delta H_f°(SiH_2)$ = 64 ± 2 kcal/mol, and a small 1.5/*C* steric factor decrease[13] in the back-reaction rate constants relative to those in the MDS system. Thus at 298 K, $k_{-6} = 10^{8.99}$ and $k_{-7} = 10^{8.92}$ in units of $atm^{-1}\ s^{-1}$. The most important values deduced from the PrDS studies are the *n*-propyldisilane and *n*-propylsilylene heats of formation, i.e., $\Delta H_f°$(PrDS) = −2.0 and $\Delta H_f°$(PrSiH) = 41.6, in kcal/mol. Our analysis of calculated and experimental organosilane[11] heats of formation gives a group additivity value of $\Delta H_f°[C\text{–}(H)_2(C)(Si)] = -2.63 \pm 0.2$ kcal/mol, and by additivity, the following relations should be valid:

$$PrDS = MDS + [C\text{–}(H_2)(C)_2] + [C\text{–}(H)_2(C)(Si)] = -2.9\ \text{kcal/mol}$$

$$PrSiH = MeSiH + [C\text{–}(H_2)(C)_2] + [C\text{–}(H)_2(C)(Si)] = 42.0\ \text{kcal/mol}$$

These estimates are easily within 1 kcal/mol of the directly derived values (see Table III).

Experimental Section

MDS and PrDS were prepared by a slow flow pyrolysis of Si_2H_6 in the presence of excess $MeSiH_3$ and $PrSiH_3$,[14] respectively. MDS was isolated by distillation through U-traps cooled by standard low-temperature slush baths in a high-vacuum system. The final distillation (separation from Si_3H_8) was carried out in a low-temperature vacuum distillation column cooled by air passed through liquid N_2. MDS was identified by MS and IR spectrophotometry,[14] and its purity, determined by gas chromatography, was greater than 98%. Identification of PrDS was based on its mass spectrum: major peaks were at *m/e* 104 (parent), 103, 102, 101, 100, and 99 (loss of the five Si–H), 74, 73, and 72 (loss of SiH_2, SiH_3, and SiH_4, respectively), and 61–56 (loss of C_3H_7 and H atoms). The infrared spectrum showed absorption in the C–H stretching region at 2968, 2937, and 2885 cm^{-1} and in the Si–H stretching and bending region at 2148 cm^{-1} and 941, 885, 829, and 786 cm^{-1}. The very strong 700-cm^{-1} absorption of Si_3H_8, the major expected contaminant, was absent. Purification of PrDS, carried out by procedures similar to those used in the MDS preparation, produced *n*-propyldisilane in a purity in excess of 99%. That only SiH_4 and $nPrSiH_3$ were obtained from the thermal decomposition of PrDS supports the latter's identification and purity.

Kinetic studies were carried out in a static system by methods previously described.[3] Chromatographic analyses were made on a Varian 1400 thermal conductivity chromatograph using a 4 ft. × 1/8 in. stainless steel Poropak N column in the MDS studies and a 4 ft. × 1/8 in. stainless steel Poropak Q column in the PrDS studies.

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Registry No. MDS, 13498-43-6; PrDS, 120287-21-0; MeSiH, 55544-30-4; nPrSiH, 87640-43-5.

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