P(OPh)$_3$), 4.62 (m, 2 H, 2-H, 3-H), 4.01 (m, 4 H, 2 C*H*$_2$OAc), 2.83 (m, 1 H, 1-H), 2.50 (br t, $J = 4.3$ Hz, 1 H, 4-H), 2.01 (obscured m, 1 H, 5-H), 2.02 (s, 6 H, 2 OAc), 1.77 (m, 3 H), 1.18 (br d, $J_{\text{gem}} = 12.8$ Hz, 1 H, endo-6-H), 0.84 (qd, $J = 12.8$, 4.1 Hz, 1 H, exo-6-H); FD MS *m/z* (relative intensity) 675 [M$^+$ + 1, 32], 674 [M$^+$, 100]. Anal. Calcd for $C_{34}H_{35}FeO_9P$: C, 60.55; H, 5.23. Found: C, 60.94; H, 5.47.

Dicarbonyl[1–4-η-5-(1,3-diacetoxy-2-propyl)-7-methylcyclohepta-1,3-diene](triphenyl phosphite)iron (19e). Reaction of **16b** (0.072 g, 0.095 mmol) with Me$_2$CuLi gave the product **19e** as a pale yellow oil (0.048 g, 74%) after purification by PLC (50% EtOAc/hexane): IR (ν_{max}, CCl$_4$) 1997, 1945, 1745 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.29 (m, 15 H, P(OPh)$_3$), 4.59 (m, 2 H, 2-H, 3-H), 4.08 (m, 4 H, 2 C*H*$_2$OAc), 2.61 (t, 1 H, $J = 6.7$ Hz, 4-H), 2.48 (m, 1 H, 1-H), 2.14 (m, 1 H, 5-H), 2.03 (s, 3 H), 2.02 (s, 3 H), 1.85 (m, 2 H), 1.09 (br d, $J_{\text{gem}} = 12.6$ Hz, 1 H, endo-6-H), 0.9 (d, $J = 7$ Hz, 3 H, CH$_3$), 0.47 (q, $J = 12.6$ Hz, 1 H, exo-6-H); FD MS, *m/z* (relative intensity) 689 [M$^+$ + 1, 36], 688 [M$^+$, 100].

Dicarbonyl[dimethyl (2–5-η-6-(1,3-diacetoxy-2-propyl)-cyclohepta-2,4-dienyl)malonate](triphenyl phosphite)iron (19f). Reaction of **16b** (0.066 g, 0.089 mmol) with NaCH(CO$_2$CH$_3$)$_2$ gave the complex **19f**, after purification by PLC (50% EtOAc/hexane) as a pale yellow oil (0.057 g, 82%): IR (ν_{max}, CCl$_4$) 2001, 1949, 1745 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.27 (m, 15 H, P(OPh)$_3$), 4.63 (m, 2 H, 3-H, 4-H), 3.98 (m, 4 H, 2 C*H*$_2$OAc), 3.69 (s, 6 H, 2 CO$_2$CH$_3$), 3.16 (d, $J = 6.5$ Hz, 1 H, malonate CH), 2.58 (m, 3 H, 2-H, 5-H, 6-H), 2.15 (m, 1 H), 2.03 (s, 3 H), 2.02 (s, 3 H), 1.84 (m, 1 H), 1.12 (br d, $J_{\text{gem}} = 12.6$ Hz, 1 H, endo-7-H), 0.78 (q, $J = 12.6$ Hz, 1 H, exo-7-H); FD MS, *m/z* (relative intensity) 805 [M$^+$ + 1, 7], 804 [M$^+$, 50], 674 [36], 310 [100]. Anal. Calcd for $C_{39}H_{41}FeO_{13}P$: C, 58.22; H, 5.14. Found: C, 58.57; H, 5.25.

Dicarbonyl[methyl (2–5-η-6-(1,3-diacetoxy-2-propyl)-cyclohepta-2,4-dienyl)acetoacetate](triphenyl phosphite)-iron (19g). Reaction of **16b** (0.056 g, 0.074 mmol) with NaCH(CO$_2$CH$_3$)(COCH$_3$) gave the 1:1 mixture of diastereomers **19g** (0.031 g, 53%) as a pale yellow oil after purification by preparation TLC: IR (ν_{max} CCl$_4$) 2001, 1949, 1748, 1424 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.29 (m, 15 H, P(OPh)$_3$), 4.62 (m, 2 H, 3-H, 4-H), 3.89 (m, 4 H, 2 C*H*$_2$OAc), 3.69 and 3.67 (2 s, 3 H, CO$_2$CH$_3$ diastereomers), 3.19 and 3.15 (2 d, 1 H, $J = 6$ Hz, acetoacetate CH), 2.57 (m, 3 H), 2.19 and 2.16 (2 s, 3 H, COCH$_3$ diastereomers), 2.02 (m, 1 H), 2.03 (s, 3 H), 2.02 (s, 3 H), 1.83 (m, 1 H), 1.07 (br d, $J_{\text{gem}} = 12.3$ Hz, 1 H, endo-7-H), 0.69 (q, $J = 12.3$ Hz, 1 H, exo-7-H); FD MS, *m/z* (relative intensity) 788 [M$^+$, 50], 674 [78], 310, [100].

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Registry No. **3a**, 12307-12-9; **3b**, 51508-59-9; **3c**, 42535-11-5; **4a**, 103816-77-9; **4b**, 81857-48-9; **4c**, 87420-57-3; **5a**, 103834-73-7; **5b**, 103816-78-0; **6a**, 103816-79-1; **6b**, 103816-80-4; **7a**, 103816-82-6; **7b**, 103816-84-8; **10a** (isomer 1), 103816-85-9; **10a** (isomer 2), 103882-97-9; **10b** (isomer 1), 103816-86-0; **10b** (isomer 2), 103882-31-1; **11a**, 103834-74-8; **11b**, 103816-87-1; **12**, 103816-88-2; **13**, 103817-02-3; **15a**, 85939-52-2; **15b**, 85939-56-6; **15c**, 103816-89-3; **15d**, 103816-90-6; **15e**, 103816-91-7; **15f**, 103816-92-8; **15g**, 103834-75-9; **16a**$^+$BF$_4^-$, 103816-94-0; **16a**$^+$PF$_6^-$, 103882-32-2; **16b**, 103834-77-1; **17**, 103816-95-1; **18a**, 103816-96-2; **18b**, 103816-97-3; **19a**, 103816-98-4; **19b**, 103816-99-5; **19c** (isomer 1), 103817-00-1; **19c** (isomer 2), 103882-33-3; **19d** (isomer 1), 103817-01-2; **19d** (isomer 2), 103882-34-4; **19e**, 103834-78-2; **19f**, 103834-79-3; **19g** (isomer 1), 103834-80-6; **19g** (isomer 2), 103882-98-0; NaCH(CO$_2$CH$_3$)(COCH$_3$), 34284-28-1; NaCH(CO$_2$CH$_3$)$_2$, 18424-76-5; methyl acetate, 79-20-9; diisobutylaluminum hydride, 1191-15-7; methyl (phenylsulfonyl)acetate, 34097-60-4; methyl (phenylsulfonyl)sodioacetate, 60729-65-9; dimethyl malonate, 108-59-8.

Catalytic Methods for the Synthesis of Oligosilazanes

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We have previously reported on the use of homogeneous catalysts [e.g., Ru$_3$(CO)$_{12}$ and Rh$_6$(CO)$_{16}$] for the ring-opening oligomerization of octamethylcyclotetrasilazane. We now find that a variety of homogeneous and heterogeneous catalysts promote this reaction. We also observe that low pressures of hydrogen (1 atm) enhance transition-metal-catalyzed ring-opening oligomerization by up to 2 orders of magnitude. Furthermore, metal hydrides, which form under the reaction conditions, are equally active as catalysts in the absence of hydrogen. These results suggest that oligomerization catalysis proceeds via hydrogenation of Si–N bonds followed by reaction of an –NH$_2$ group with a metal-activated Si–H bond. To test this hypothesis, we have reacted a simple silazane, HSiMe$_2$NHSiMe$_2$H, with NH$_3$ using Ru$_3$(CO)$_{12}$ as a catalyst. We observe extremely rapid oligomerization, even at temperatures as low as 35 °C, with concomitant evolution of hydrogen. This reaction represents a new synthetic method for the oligomerization of silazane monomers, which does not require Si–N bond cleavage to precede Si–N bond formation, a fatal flaw in our original oligomerization process.

Introduction

The current search for silicon-containing polymers that can serve as precursors for the pyrolytic generation of silicon carbide (SiC)[1,2] and silicon nitride (Si$_3$N$_4$)[3,4] based ceramics has renewed interest in developing synthetic routes to silicon-based polymers. Present efforts center

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on developing synthetic methods that permit one to control not only oligomer pyrolysis properties vis â vis the yields and quality of the ceramic product but also the tractability of the precursor polymer.[5] The latter property can be defined as a measure of the polymer's ability to be transformed into coatings, binders (for ceramic powders), fibers, or three-dimensional shapes prior to pyrolysis.

The ability to combine all these properties into a single polymer is not trivial. For example, oligosilazanes (silicon nitride precursors), the subject of this paper, that give high ceramic yields are readily available if one synthesizes highly cross-linked precursors. Unfortunately, these precursors are often brittle and intractable[3e] (insoluble, and unmeltable); although see ref 4. Furthermore, the ceramic product varies greatly in composition depending on the starting silazane. More often than not, the ceramic product consists of mixtures of Si_3N_4, SiC, carbon, and/or silicon.[3c,d,4] Alternately, highly soluble, readily manipulable linear oligosilazanes can be prepared that give extremely low yields of Si_3N_4 (see below).

The objective of the work reported here is to develop catalytic routes to oligo- and polysilazanes that will not suffer the above described drawbacks.

Background

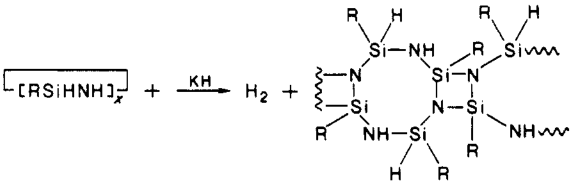
Synthetic routes to oligosilazanes, based on the ammonolysis of dichlorosilanes (eq 1), were first described more

$$R_2SiCl_2 + NH_3 \longrightarrow [R_2SiNH]_x + 2NH_4Cl \quad (1)$$

than 60 years ago.[6] Since then, a number of workers have explored ammonolysis of silyl chlorides as a route to polysilazanes.[3b,5b,7] In most instances, the reported products were low molecular weight linear oligomers (x = 4–5) mixed with tri- and tetrasilazane cyclomers.

In an effort to surmount this problem a number of investigators have attempted to convert both the oligomers and cyclomers to branched and cross-linked polymers by using either acidic (NH_4Br,[8] $AlCl_3$,[9] $TiCl_4$,[9] H_2SO_4[9]) or basic (KOH[10]) catalysts. While some improvements in molecular weight were observed, especially with cross-linking, these methods are not useful for preparing true manipulable polysilazanes nor have they proved valuable as routes to ceramic precursors as discussed in a recent review by Wynne and Rice.[5] In general, the oligomer precursors produced suffer from the typical problems discussed above; that is, the ceramic yields are low or the ceramic product is a mixture of silicon nitride, silicon carbide, carbon, and/or silicon.

Most recently, Seyferth and Wiseman have described[3] (and patented[3c]) a novel polymerization method,[4] based on the work of Fink,[11] in which low molecular weight oligomers containing an Si–H moiety adjacent to an NH moiety, i.e., $-[RSiHNH]_x-$, react with catalytic amounts of an alkali metal;[3c,e] alkali-metal hydride or base (e.g., K, KH, Na, $NaNH_2$, NaH) to give sheet oligomers as illustrated in reaction 2.



(2)

The Seyferth–Wiseman approach provides soluble oligomers with molecular weights of ~800–2000 that give extremely high (~85%) ceramic yields on pyrolysis. The ceramic product ratios of a typical pyrolysis were found to be 0.88:1.27:0.75 for Si_3N_4:SiC:carbon.

Our own efforts in this area originated with the discovery that a variety of metal catalysts could cleave and reform the silicon–nitrogen bonds in octamethylcyclotetrasilazane (**1**) in the presence of hexamethyldisilazane (**2**). The reaction, as exemplified by reaction 3, gives an envelope of oligomers whose number average molecular weight is dependent on the concentration of hexamethyldisilazane, the capping agent.[12]

$$\underset{\mathbf{1}}{[Me_2SiNH]_4} + \underset{\mathbf{2}}{(Me_3Si)_2NH} \xrightarrow{Ru_3(CO)_{12}/135\ °C} Me_3SiNH\text{-}[Me_2SiNH]_xSiMe_3 \quad (3)$$

$$x = 1\text{-}12$$

To our knowledge, this represents the first example of transition-metal-catalyzed oligomerization of silazanes, although, Curtis has described a somewhat related oligomerization or redistribution reaction with siloxanes (eq 4).[13]

$$HSiR_2OSiR_2H \xrightarrow{cat.} HSiR_2[OSiR_2]_xH + R_2SiH_2 \quad (4)$$

We have now explored the effects of varying both the reaction conditions and types of catalysts on oligomerization efficiencies and product selectivities for reaction 3. We describe here our general observations concerning these oligomerization studies and the discovery of yet another and more effective way of forming both oligosilazanes and polysilazanes.

Results and Discussion

Catalyst Activities. Because the reaction rates in our preliminary studies were quite slow, we evaluated a variety of both homogeneous and heterogeneous catalysts for their efficacy for promoting reaction 3 under a standard set of conditions (time variable). In addition, we also evaluated two of the well-known acidic catalysts H_2SO_4 and $AlCl_3$. The results of this survey are recorded in Table I. Table I compares catalyst reactivity as a function of the disappearance of the tetracyclomer with time at specific temperatures.

The salient observations that can be made regarding the results are as follows: (1) there is an apparent upper conversion limit of ~80%; (2) improved reaction rates are obtained in the presence of added H_2; and (3) the same relative conversions are obtained by using H_2SO_4, the metal hydride, $H_2Os_3(CO)_{10}$, or Pt/C as catalyst.

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Table I. The Conversion of 1 in Reaction 3 with Different Catalysts

run	cat.	temp, °C	time,[b] h	convn,[c] %	decompn[d]
1	$Ru_3(CO)_{12}$	135	6	22	S
2	$Ru_3(CO)_{12}$	180	15	80	M
3	$Ru_3(CO)_{12}/H_2$	135	1	78	
4	$H_4Ru_4(CO)_{12}$	135	1	77	S
5	$Ru_3(CO)_{12}/Fe(CO)_5$	135	6	26	S
6	$Ru_3(CO)_{12}/Fe_3(CO)_{12}$	135	3	80	S
7	$Fe_3(CO)_{12}$	135			
8	$Fe_3(CO)_{12}/H_2$	135	3	80	F
9	$Os_3(CO)_{12}$	135			
10	$Os_3(CO)_{12}$	180	20	78	
11	$Os_3(CO)_{12}/H_2$	135	6	73	
12	$H_2Os_3(CO)_{10}$	135	3	78	
13	$Rh_6(CO)_{16}$	135	20	55	g
14	$Rh_6(CO)_{16}/H_2$	135	3	78	g
15	$Ir_4(CO)_{12}$	135			M
16	$Ir_4(CO)_{12}$	180	15	70	F
17	$Ir_4(CO)_{12}/H_2$	135	3	76	F
18	Pt/C[e]	135	3	75	
19	PtO_2	180	15	25	
20	Pd/C[e]	135	3	78	
21	$AlCl_3$	135	3	23	
22	H_2SO_4	135	6	65	
23	H_2SO_4	135	23	69	
24	H_2SO_4[f]	80	6	76	

[a] Reaction conditions: The molar ratio between 1, 2, and catalyst was 250:84:1. The reaction was carried out under N_2 or H_2 (as noted), and Bu_2O was used as an internal standard for GC analysis. [b] The time indicates the shortest time in which there was no further conversion of 1. [c] The percent conversion of 1. [d] Decomposition of the catalyst: S, slow; M, moderate; F, fast. [e] 200 mg of 5% Pt/C and 150 mg of 5% Pd/C were used; the catalysts were activated under H_2. [f] $[H_2SO_4]$ was 5 times the amount according to *a*. [g] It was not clear whether the $Rh_6(CO)_{16}$ reacted homogeneously or decomposed.

Table II. Yield of Volatile and Nonvolatile Oligomers in Reaction 3

run	cat.	$(Me_3Si)_2NH$	1 convn,[a] %	oligomeric yield (% weight)[c]		no. av[d] M_r
				volatile	nonvolatile	
1	H_2SO_4	–	46	33	10	727
2	H_2SO_4	+	45	21	32	582
3	$Ru_3(CO)_{12}/H_2$	–	74	54	18	990
4	$Ru_3(CO)_{12}/H_2$	+	68	28	44	684
5	Pt/C	–	62	23	35	1080
6	Pt/C	+	71	28	45	736

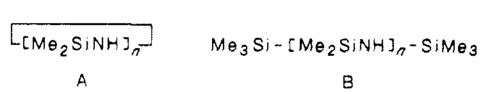
[a] The same conditions as shown in Table I at 135 °C; with added **2** (+); without **2** (–); the reactions were carried without internal standard, and the analyses were made following distillation of the product solutions at 180 °C (0.5 mm). [b] The conversion is based on the amount of 1 remaining after completion. [c] Yield is weight percentage of the total reactant weight. The volatile, oligomer fraction contains unreacted disilazane 2. [d] Average molecular weight was found by VPO analysis in toluene.

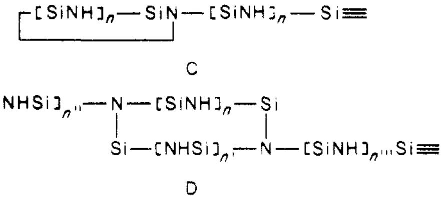
The apparent upper limit to conversion of the tetracyclomer to other presumably linear products (see below) is not unreasonable in view of the fact that tetracyclomer conversion requires catalytic cleavage of Si–N bonds. Because the same catalyst that cleaves Si–N bonds in the tetracyclomer can also cleave the Si–N bonds in the oligomeric products to reform cyclomers such as 1, the reaction must reach an equilibrium. The overall reaction conditions will determine the final equilibrium concentrations of the various products. Under the conditions employed in the Table I studies, this equilibrium lies at about 80% conversion of the tetracyclomer. This observation highlights the flaw in using reaction 3 as a means of producing polysilazanes. *The fact that all the catalysts exhibit almost as much ability to cleave Si–N bonds in the oligomeric products as they do in the tetracyclomer fatally limits its applicability for polymer synthesis.* Fortunately, other results point to an alternate synthetic method.

Product Selectivities. In Table II, we attempt to develop a relative measure of the product quality, for each type of catalyst, as determined by the number average molecular weight, $\bar{M}_n$, of the nonvolatile oligomers remaining following distillation of the original product mixture at 180 °C and 300 μm. Table II also presents comparative data for reaction 3 run in the absence of capping agent **2**. Two valuable observations can be gleaned from the Table II results. The observation of lesser importance is that the $Ru_3(CO)_{12}$-catalyzed reaction run with hexamethyldisilazane, in the presence of H_2, gives high yields of nonvolatile oligomer. The more important observation is that the yield of nonvolatile polymers diminishes in the absence of hexamethyldisilazane. However, the product quality, as measured by the molecular weight, is far superior to that obtained with hexamethyldisilazane, especially in the $Ru_3(CO)_{12}$- and Pt/C-catalyzed reactions. In effect, there appears to be a tradeoff between conversion and average molecular weight.

We have tentatively identified the product envelopes produced in the reactions run both in the presence and absence of capping agent based on mass spectral (MS) fragmentation patterns of the nonvolatile products. Unfortunately, our GC–MS analytical capabilities extend only to masses of approximately 1000 daltons; thus, we cannot be sure that the higher molecular weight products follow the same compositional patterns observed for the various product envelopes observed below mass 1000.

In runs 3 and 4 (Table II), we have identified two major





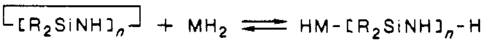
NHSi = NHSiMe$_2$; Si≡ = SiMe$_3$

fractions, A and B. In run 4, B (n = 1–8) is the major product and A (n = 3–7) is observed in small quantities. Two additional oligomer families, C and D, are observed in still smaller quantities. Mass spectral fragmentation patterns suggest that C contains one chain attached to a cyclic fragment ($n + n'$ = 2–7) and that D consists of two chains attached to a cyclic fragment ($n + n' + n'' + n'''$ = 2–6). Run 6 gives results parallel to those observed with $Ru_3(CO)_{12}$ but with greater quantities of C and D. By comparison the Pt/C system, when used in the absence of hexamethyldisilazane (run 5 Table II), produces oligomer family A as the major product, but with small quantities of still a third set of families that are the bi- and tricyclic oligomeric species E ($n + n' + n''$ = 5–8) and F ($n + n' + n'' + n'''$ = 8, 9).

The oligomers produced in the H_2SO_4 catalyst system consist of families A (n = 5, 6) and B (n = 2–8) as major products and small quantities of the C family of oligomers. Oxygenated species are also observed as a consequence of the water present in the concentrated acid.

The Effects of Added Hydrogen. The catalytic rate enhancements (as much as 2 orders of magnitude), obtained at low hydrogen pressures (normally 1 atm), warrant further comment. The effect of added hydrogen can be ascribed either to its ability to promote formation of the active catalyst species or/and because it changes the nature of the silazane intermediates. Because many metal carbonyls react with H_2 to form metal hydrides, it seems likely that these species could serve as the active catalyst intermediates in reaction 3. Indeed, in the $Ru_3(CO)_{12}/H_2$ catalyst system we can recover 90% of the ruthenium as $H_4Ru_4(CO)_{12}$. Further support for the intermediacy of metal hydrides in catalysis comes from the observation that both $H_4Ru_4(CO)_{12}$ and $H_2Os_3(CO)_{10}$ are quite effective catalysts for (3) even in the absence of hydrogen. This suggests that these metal hydrides are directly responsible for the generation of the active species or are rapidly [by comparison with $Ru_3(CO)_{12}$] transformed into the active catalyst, perhaps by loss of H_2. Because H_2SO_4 is also a reasonably active catalyst for (3) and given the fact that metal hydrides are known to be quite acidic under some instances,[14] one could argue that the metal catalyst systems function only as novel acid catalysts. However, our observation that the Pt/C catalysts (activated initially under H_2) are as effective as the metal hydride catalysts suggests that this argument is at least partially incorrect. Further evidence counter to the acid catalyst concept is presented below. A final point concerning the metal/H_2 systems is that in all cases, if we start with a metal hydride derivative, the presence of H_2 is not required to promote catalysis. Thus, metal hydrides appear to be the true catalytic species.

Given this information, we can speculate on how the catalyst might function. We propose that the metal hydride acts to promote Si–N bond scission through hydrogenation of the Si–N bond and that oligomerization proceeds by nucleophilic attack by NH_2 on a metal-activated Si–H bond. The oligomerization mechanism, based on these concepts, that best explains all our observations to date, including the formation of products C–F, is presented in reactions 5–7; although reasonable alternatives are available.

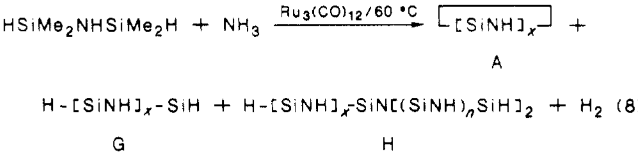


$$[R_2SiNH]_n + MH_2 \rightleftharpoons HM\text{-}[R_2SiNH]_n\text{-}H \quad (5)$$

$$HM\text{-}[R_2SiNH]_n\text{-}H \rightleftarrows H\text{-}[R_2SiNH]_n\text{-}H + M \quad (6)$$

$$HM\text{-}[R_2SiNH]_n\text{-}H + H\text{-}[R_2SiNH]_n\text{-}H \rightarrow H\text{-}[R_2SiNH]_{2n}\text{-}H + MH_2 \quad (7)$$

If a hydrogen capped oligomer is in fact produced in a reaction such as (6) and reacts in a manner similar to reaction 7, then reaction 8, with the commerically available, tetramethyldisilazane (TMDS) would be a simple test of reaction 7. Our initial evaluation of reaction 8, using either the homogeneous ruthenium catalyst or activated Pt/C, gives cyclomers A (x = 3–7), linear oligomers G (x = 2–11), and very small amounts of branched oligomers H ($x + n$ = 1–7; < 5%) as evidenced by the GC–MS analyses. On the basis of our experimental procedures, we would expect to see considerable quantities of NH_2-capped oligomeric products as well. However, we have been unable to detect them by GC–MS or NMR despite the fact that we can establish oligomer composition by NMR studies that include integration of NH protons (see experimental) and can observe terminal $-NH_2$ groups in oligomers of the type $H\text{-}[Et_2SiNH]_x\text{-}H$.[15]



$$HSiMe_2NHSiMe_2H + NH_3 \xrightarrow{Ru_3(CO)_{12}/60\ °C} [SiNH]_x + H\text{-}[SiNH]_x\text{-}SiH + H\text{-}[SiNH]_x\text{-}SiN[(SiNH)_nSiH]_2 + H_2 \quad (8)$$

We find that reaction 8 is fast by comparison with reaction 3 and can be run effectively at temperatures as low as 35 °C. Of primary importance is the fact that in reaction 3 no Si–N bond cleavage occurs below 90 °C, yet Si–N bond formation does occur in reaction 8. This suggests that there may be some conditions in which Si–N bonds can be formed in the absence of Si–N bond cleavage, which could permit the development of catalytic routes to polysilazanes. These conditions are not met in reaction 8 given that we see significant amounts of oligomers with odd numbers of silazane units, implying the possibility of Si–N bond cleavage in linear structures at lower temperature.

We have examined, in a cursory fashion, the effects of changing the reaction conditions in reaction 8, on product selectivity. Our objective was to optimize the yields of nonvolatile/high $\bar{M}_n$ oligomers. We have found conditions that provide nonvolatile oligomeric yields of 68% (see experimental section). The results of these studies are presented in Table III. One important observation is that high NH_3 pressures favor the formation of volatile cyclomers with the tricyclomer being the major cyclic compound formed under all conditions. Surprisingly, the yield

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Table III. The Effects of Temperature and Ammonia Pressure on Product Selectivity in the Reaction of TMDS with NH_3 in the Presence of $Ru_3(CO)_{12}$[a]

				turnover[c] freq		yield of cyclomers in the volatile fraction,[d] %			
run[a]	NH_3[a]	temp, °C	time,[b] hours	TDMS convn	Si–H disappearance	total	tricyclomer	nonvolatile oligomer yield, %	av M_r ($\bar{M}_n$)
1	1	60	66	640	1000	39	25	19	1297
2	1	90	60	720	1160	34	18	21	1006
3	13	60	12	1220	1300	88	69	19	2024
4	13	90	8	1960	3438	91	70	5	1425

[a] See Experimental Section. [b] At these reaction times, the catalyst is still active but the rate of reaction is considerably reduced because of the low Si–H bond concentration. [c] TF (mol of substate/mol of cat./h) based on initial rates, determined by GC (TDMS conversion) and NMR integration (Si–H signal disappearance) referenced to the CH_3Si signals. [d] Based on GC area integration of the volatile fraction (products recovered by distillation at 60–80 °C (300 μm). The tricyclomer is the principle cyclomer. The percentages are calculated on the basis of experimental measurements, with known compounds, that show linearity between the number of dimethylsilazane units $-[Me_2SiNH]_x-$ and the FID detector integration for different oligosilazanes. Therefore, we can assume that the total integration area represents 100% of all silazane units. This allows us to calculate the weighted amount of a given oligomer (e.g., the tricyclomer) in the reaction mixture as identified by GC–MS.

Table IV

type	EI[a]	CI[a,b]	NCI[a,b]
A	59, 73, 130, 132, 158, 171, 187, 204; M − (15, 30, 48)	M + 1; M − 15	219; M − 1
B	73, 130, 132, 146, 147, 187, 189, 203, 243, 244, 261, 276, 292; M − (15, 32, 104, 177, 234)	73, 90, 147, 219, 275, 292, M + 1; M − (88, 161, 234)	218, 234, 290, 307; M − (1, 17, 73, 146)
C	73, 130, 147, 203, 243, 261, 301, 318, 333; M − (15, 32, 104, 177)	73, 90, 247, 203, 220, 244, 292, 333; M + 1; M − 16	218; M − (1, 220)
D	73, 130, 187, 203, 243, 245, 261, 275, 301, 316, 333; M − (15, 32, 104)	73, 86, 119, 163, 203, 219, 275, 292, 333, 349; M + 1	290; M − 1

[a] In *m/e*. A general fragment index: 58 ≡ Me_2Si; 73 ≡ Me_3Si/Me_2SiNH; 88 ≡ $Me_3SiNH/Me_2Si(NH)_2$; 131 ≡ $Me_2SiNHSiMe_2$; 146 ≡ $Me_3SiNHSiMe_3/[Me_2SiNH]_2$; 161 ≡ $Me–[Me_2SiNH]_2/HN[Me_2SiNH]_2$; 188 ≡ $(Me_2Si)_3N$; 204 ≡ $Me_2Si[NHSiMe_2]_2$; 219 ≡ $[Me_2SiNH]_3/Me_3Si[NHSiMe_2]_2$; 234 ≡ $Me_3SiNH[Me_2SiNH]_2/HN[Me_2SiNH]_3$; 277 ≡ $[Me_2SiNH]_3SiMe_2$; 292 ≡ $[Me_2SiNH]_4/Me_3Si[NHSiMe_2]_3$; 307 ≡ $Me_3SiNH[Me_2SiNH]_3$ M − 104 ≡ − (88 + 16); M − 177 ≡ (M − 104) − 73. [b] The ionizing gas is NH_3 (pressures used are 0.2 atm).

of nonvolatile oligomers is similar at both low and high NH_3 pressures. Another surprising result is that high NH_3 pressures give a greater $\bar{M}_n$ for the nonvolatile fraction. Improved yields of nonvolatiles can be obtained by recycling the recovered volatiles as discussed in the Experimental Section.

NMR (proton and silicon), $\bar{M}_n$, and elemental analysis (C, H, and N), when used to estimate the yields of branched or cross-linked oligomers (except when it is extensive), give the same values, within experimental error, as those obtained by GC–MS (see Experimental Section).

We hope to provide explanations for these novel results through detailed kinetic studies currently underway in these laboratories.

Sommer et al.[16] have described reactions similar to (8) wherein they observe the catalytic formation of monosilazanes with the concomitant evolution of H_2 from reactions of silanes with primary or secondary amines. However, in no instance do they report the catalytic formation of disilazanes. A number of researchers including Sommer have also observed related reactions between alcohols and silanes[17] (reaction 9),

$$ROH + R'_3SiH \xrightarrow{\text{cat.}} R'_3Si\text{–}OR + H_2 \qquad (9)$$

Reaction 8 serves as the basis for a number of novel oligomerization and *polymerization reactions* which we will describe in future publications.[15]

Experimental Section

General Methods. All the silazanes were purchased from Petrarch Systems Inc. Hexamethyldisilazane and tetramethyldisilazane were purified by distillation over CaH_2. Most of the commercial catalysts were purchased from Strem and were used without further purification. $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $H_2Os_3(CO)_{10}$, and $H_4Ru_4(CO)_{12}$ were synthesized by known methods.[18] Pt/C and Pd/C were activated first by heating under hydrogen.

Analytical Procedures. Product analyses for all reactions studied were performed on a Hewlett-Packard 5880A reporting GC equipped with a flame ionization detector using a 5 m × 0.325 cm column packed with a OV17 on Chromosorb Q. GC mass spectral analyses were performed by using an LKB 9000 or Ribermag R10 10 C spectrometers. Average molecular weights of polymers were measured by vapor-phase osmometry (VPO) in toluene at 65 °C using a Microlab 301 osmometer. Proton NMR spectra were performed on a JEOL FX-90Q (90 MHz) in $CDCl_3$ referenced to $CHCl_3$ at 7.24 ppm. Silicon-29 NMR spectra were obtained on a JEOL FX-90Q at 17.76 MHz in $CDCl_3$ in the presence of tetramethylsilane as a reference and approximately 300 mol of $Cr(acac)_3$ as a relaxation reagent.

General Reaction Procedures. (a) Catalytic Reactions between Octamethylcyclotetrasilazane and Hexamethyldisilazane. To a 6.5 mmol (1.90 g) of octamethyltetrasilazane and 2.1 mmol (0.50 mL) of hexamethyldisilazane is added 0.025 mmol of catalyst. Di-*n*-butyl ether (0.25 g) is added as internal standard. The mixture is heated at the reaction temperature, under N_2 or H_2 in a magnetically stirred 45-mL stainless-steel Parr reactor. The results are shown in Table I.

(b) Measurements of Actual Conversions to Oligomers and Polymers. Octamethyltetrasilazane (4.10 g, 14.0 mmol) and 0.056 mmol of catalyst are heated at 135 °C with or without hexamethylsilazane (1.10 mL, 4.6 mmol) as in method a. After 6 h the solution is distilled under reduced pressure (160–180 °C, 500 μm). The distillate includes remaining reactants and the volatile oligomeric fraction. The remaining material, the nonvolatile oligomers, is then subjected to VPO analysis. Heterogeneous catalysts were removed by dissolving the initial reaction products in CH_2Cl_2 followed by filtration rotary evaporation and distillation. The results are shown in Table II.

GC. GC–Mass Spectral Analyses. The conversion of starting materials to the equilibrium mixture was followed by GC. The

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distribution pattern was established by GC–MS analyses using electron-impact (EI), chemical-ionization (CI), and negative CI (NCI) techniques.

Table IV shows the typical fragmentation patterns for A–D as determined by the three mass spectral methods. The fragments noted are found in the fragmentation pattern of each member of a specific family.

Conversion of $Ru_3(CO)_{12}$) to $H_4Ru_4(CO)_{12}$. $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol) in 2 mL of hexamethyldisilazane is heated at 135 °C under 1 atm of H_2. After 10 min, the solution color turns red and then back to orange and a yellow-orange precipitate (165 mg) is formed. After 0.5 h the solution is cooled and the precipitate is washed with petroleum ether and identified as $H_4Ru_4(CO)_{12}$ with traces of $H_2Ru_4(CO)_{13}$. (Identified by IR and NMR in comparison with authentic samples.) In the absence of an H_2 atmosphere, $Ru_3(CO)_{12}$ is recovered as the major product even after an 8-h reaction time, although a significant amount of decomposition occurs during the heating period.

Polymerization of Tetramethyldisilazane in the Presence of Ammonia. (a) To 100.0 mmol of tetramethyldisilazane (TDMS, 13.3 g) is added 50.0 μmol of $Ru_3(CO)_{12}$ (32.0 mg), and the solution is heated under ammonia under various reaction conditions as noted in Table III. The volatile oligomers were separated from the solution by vacuum distillation (up to 180 °C (300 μm)). The residue is the nonvolatile fraction. ^{1}H NMR ($CDCl_3$, δ, reference $CHCl_3$): TDMS, Si–H, 4.46 (m); N–H, 0.50 (br); Si–CH_3, 0.14 (d); Nonvolatile products (for run 3, Table III), Si–H (not evident); N–H 0.52 (br); Si–CH_3, 0.12 (s, 5%), 0.08 (s, 95%). ^{29}Si NMR ($CDCl_3$, δ, reference Me_4Si): −13.99 ppm. We can use the NMR data in conjunction with $\bar{M}_n$ to calculate polymer composition (linear vs. branched species) for simple mixtures. Given (for run 3, Table III) M_n 2024, a completely linear polymer will be H-$[Me_2SiNH]_{27}$–Me_2SiH (M_r 2033) and we can calculate a chemical composition for $Si_{28}C_{56}H_{195}N_{27}$: C, 33.07; H, 9.66; N, 18.60; Si, 38.66; O, 0.00. We find: C, 32.92; H, 8.67; N, 17.65; Si, 40.42; O, 0.40. For a DP of 27, capped at both ends by Me_2SiH groups, we should see two methyl carbon signals in the ratio of 2:26 or 7% vs. 93%. In fact, the ratio of the two signals we observed, δ 0.12 and 0.08, is found to be 5% vs. 95% (TMDS methyl protons are at δ 0.14). The error limits are probably ±2%, and the NMR sensitivity is too low to show SiNH.

We conclude that branching in this oligomer product must be less than 2 per 30 monomer units. The chemical analysis is high for silicon and low for nitrogen. The low nitrogen can be explained by the 0.40% oxygen impurity. The high silicon could result from the formation of some $Me_2SiN(SiMe_2H)$ branches; in fact the GC–MS results for oligomers with a DP of <12 do show approximately 2–3% branching where the branches are of the type $Me_2SiN(SiMe_2H)$. Note that this suggests oligomer uniformity for all the species even for those species we cannot see by GC–MS.

NH_3 pressures: 1 atm is obtained by quickly pressurizing and depressurizing the reactor once before sealing. Repeating this cycle until no more ammonia will dissolve provides 12 atm of pressure at temperature.

(b) To 20.0 mmol of TMDS (2.66 g) is added 23 μmol of $Ru_3(CO)_{12}$ (16 mg), and the solution is heated at 135 °C under 7 atm of ammonia for 20 h. Following distillation a 68% yield of nonvolatile products is obtained with $\bar{M}_n$ = 1200 daltons.

(c) $Ru_3(CO)_{12}$ (25 μmol) is added to 2.40 g of the volatile fraction collected from run 2 (Table III) at 60–80 C (500 μm) which consists of a mixture of cyclomers (x = 3–6; 25%) and linear oligomers (x = 3–6). The solution is heated for 2 h at 60 °C followed by 2 h at 90 °C under 1 atm of ammonia. Following distillation, a 45% yield of nonvolatile products is obtained (60% yield of the linear oligomers G and H in the starting mixture) with $\bar{M}_n$ = 1000 daltons.

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Registry No. (1)(2) (copolymer), 103692-00-8; $(HSiMe_2NHSiMe_2H)(NH_3)$ (copolymer), 103692-02-0; $Ru_3(CO)_{12}$, 15243-33-1; $H_4Ru_4(CO)_{12}$, 34438-91-0; $Fe(CO)_5$, 13463-40-6; $Fe_3(CO)_{12}$, 17685-52-8; $Os_3(CO)_{12}$, 15696-40-9; $H_2Os_3(CO)_{10}$, 41766-80-7; $Rh_6(CO)_{16}$, 28407-51-4; $Ir_4(CO)_{12}$, 18827-81-1; Pt, 7440-06-4; C, 7440-44-0; PtO_2, 1314-15-4; $AlCo_3$, 7446-70-0; H_2SO_4, 7664-93-9.

Kinetics of the Thermal Rearrangement of Chloromethyldimethylsilane: Some Observations on 1,2-Shifts in Silicon-Containing Radicals

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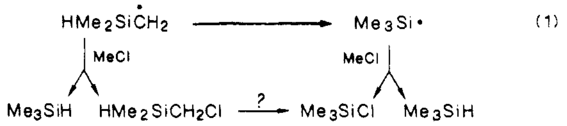
The kinetics of the thermal rearrangement of chloromethyldimethylsilane to trimethylchlorosilane have been measured alone, in the presence of several traps for reactive intermediates and in the presence of a radical source. The role and energetics of 1,2-shifts in α-silylmethyl or silyl radicals in the mechanism of rearrangement of this and other chloromethylsilane are discussed.

Introduction

Gas kinetic measurements in the pyrolysis of allyltrimethylsilane with and without added methyl chloride enabled two concurrent primary processes to be distinguished, viz., radical-forming homolysis and retroene elimination of dimethylsilene.[1] These methods have been applied to the mechanism of pyrolysis of a number of other alkenylsilanes, including 4-(dimethylsilyl)-1-butene;[2] this butenylsilane dissociates to give an allyl radical and

Scheme I



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