J. Org. Chem. 1983, 48, 2539–2543 2539

donium iodide, was immersed in an oil bath kept at 105 °C, whereupon the yellow solid decomposed to a purplish-red liquid. An ^1H NMR spectrum of the decomposition mixture (in 0.5 mL of $CDCl_3$) was distinct from that of the starting iodonium salt and virtually identical with that of a mixture of authentic *p*-chloroiodobenzene and authentic 2-iodo-5-methylfuran. The decomposition was "clean", and the integration is consistent with a 1.04:1.00 molar mixture (ArI:furI) of the two components.

The iodide salt corresponding to **15** (R = 3-Me) had the expected percent iodine content ($\Delta\% = +0.34$). The iodide salt corresponding to **11** (R = 4-Br) was not subjected to combustion analysis.

Authentic Iodofurans. 2-Iodo-5-(trimethylsilyl)furan, 2-iodo-5-methylfuran, and 2-iodofuran, being expected products from the thermal decompositions of the iodide analogues of **11** (R = 4-Br), **13** (R = 4-Cl), and **15** (R = 3-Me), were required as ^1H NMR standards. They were prepared by the direct lithiation of 2-(trimethylsilyl)furan, 2-methylfuran, and furan, respectively, in Et_2O with *n*-butyllithium in hexane and subsequent treatment of the lithiofurans thus produced with I_2 in Et_2O. The crude iodofurans were isolated after an aqueous sodium thiosulfate workup, and their ^1H NMR spectra (in $CDCl_3$) were recorded. 2-Iodo-5-(trimethylsilyl)furan and 2-iodi-5-methylfuran were "purified" by distillation, but they still retained dark coloration. 2-Iodofuran, also dark in color, was not further purified. Their NMR spectra revealed only minor impurities, one of which is probably *n*-octane, and were really quite clean. The ^1H NMR spectrum of 2-iodofuran has been described in the literature ("infinite" dilution, cyclohexane) as that of an XYZ spin system whose chemical shifts compare favorably with those measured by us.[11]

2-Iodo-5-(trimethylsilyl)furan: ^1H NMR ($CDCl_3$) δ 0.26 (s, 9 H), 6.48 (s, 2 H).

2-Iodo-5-methylfuran:[21] ^1H NMR ($CDCl_3$) δ 2.30 (d, 3 H, very close spacing at 10-ppm sweep width with one peak being more intense than the other), 5.85 (m, 1 H), 6.34 (m, 1 H, appears as a d at 10-ppm sweep width but shows evidence of fine structure at broader sweep width).

2-Iodofuran:[22] ^1H NMR ($CDCl_3$) δ 6.29 (m, 1 H), 6.50 (m, 1 H), 7.50 (m, 1 H) at 10-ppm sweep width; at 5-ppm sweep width, the m at δ 6.29 appears to be a pair of overlapping doublets, the m at δ 6.50 appears as a "distorted" triplet of doublets, and the m at δ 7.50 appears as a pair of closely spaced overlapping doublets [lit.″ ^1H NMR (cyclohexane) δ 6.17, 6.42, 7.37].

None of the iodofurans were subjected to C and H analysis. 2-Iodo-5-(trimethylsilyl)furan was subjected to iodine analysis; $\Delta I\% = -4.82\%$.

Registry No. **9** (R = H), 27126-76-7; **9** (R = 2-Me), 73177-97-6; **9** (R = 3-Me), 84383-97-1; **9** (R = 4-Me), 73177-96-5; **9** (R = 4-F), 84383-77-7; **9** (R = 4-Cl), 73178-07-1; **9** (R = 4-Br), 73178-08-2; **9** (R = 4-I), 73178-09-3; **9** (R = 4-Ph), 73178-11-7; **10**, 1578-29-6; **11** (R = H), 85925-18-4; **11** (R = 2-Me), 85925-20-8; **11** (R = 3-Me), 85925-22-0; **11** (R = 4-Me), 85925-24-2; **11** (R = 4-F), 85925-26-4; **11** (R = 4-Cl), 85925-28-6; **11** (R = 4-Br), 85925-30-0; **11** (R = 4-I), 85925-32-2; **11** (R = 4-Ph), 85925-34-4; **11·I** (R = 4-Br), 85925-35-5; **12**, 13271-75-5; **13** (R = 2-Me), 85925-37-7; **13** (R = 3-Me), 85925-39-9; **13** (R = 4-Me), 85925-41-3; **13** (R = 4-F), 85925-43-5; **13** (R = 4-Cl), 85925-45-7; **13** (R = 4-Br), 85925-47-9; **13** (R = 4-I), 85939-46-4; **14**, 1578-33-2; **15** (R = H), 85925-49-1; **15** (R = 2-Me), 85925-51-5; **15** (R = 3-Me), 85925-53-7; **15** (R = 4-Me), 85925-55-9; **15** (R = 4-F), 85925-57-1; **15** (R = 4-Cl), 85925-59-3; **15** (R = 4-Br), 85925-61-7; **15** (R = 4-I), 85925-63-9; **15·I** (R = 3-Me), 85925-64-0; furan, 110-00-9; 2-methylfuran, 534-22-5; *o*-iodotoluene, 615-37-2; *o*-(diacetoxyiodo)toluene, 31599-59-4; *p*-chloroiodobenzene, 637-87-6; (4-chlorophenyl)-2-(5-methylfuryl)iodonium iodide, 85925-65-1; 2-iodo-5-(trimethylsilyl)furan, 85939-47-5; 2-iodo-5-methylfuran, 85925-66-2; 2-iodofuran, 54829-48-0.

Supplementary Material Available: Further experimental details on the syntheses of this study (10 pages). Ordering information is given on any current masthead page.

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(21) Gilman, H.; Wright, G. F. *J. Am. Chem. Soc.* **1933**, *55*, 3302.

(22) Gilman, H.; Mallory, E.; Wright, G. F. *J. Am. Chem. Soc.* **1932**, *54*, 733.

Homogeneous Catalytic Formation of Carbon–Nitrogen Bonds. 2. Catalytic Activation of the Silicon–Nitrogen Bond[†]

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Received November 8, 1982

The catalytic formation of new carbon–nitrogen single bonds can be promoted via catalytic activation of silicon–nitrogen bonds. Silazanes, compounds containing Si–N bonds, will react, in the presence of a catalyst, with compounds containing carbon–oxygen double bonds to form new C–N and Si–O bonds concurrently. Thus, CO_2 and phenyl isocyanate can be reacted with a number of silazane compounds to give urethane and urea derivatives in 60–90% yields. In the absence of catalysts, the identical reactions either do not proceed or go to less than 20% conversion. Aldehydes and ketones also react in a similar manner to give imines and enamines, respectively. A variety of group 8 metals have been found to activate the Si–N bond in the catalytic formation of $PhCH{=}NPh$ from $PhNHSiM_3$ and PhCHO. Iron and rhodium catalysts were found to be the most active for this reaction. The catalytic activation of Si–N bonds was also found useful in the ring-opening oligomerization of $\overline{-[(CH_3)_2SiNH]_4-}$ in the presence of $(Me_3Si)_2NH$.

The chemistry that is the subject of this preliminary report arises as a result of our continuing interest in developing new catalytic methods for the formation of C–N bonds. A second directive for pursuing the following studies was the knowledge that silicon compounds are excellent oxygenophiles, and, as such, the formation of Si–O bonds could be the driving force that promotes catalytic reactions. Consequently, our initial goal was to develop simple catalytic reactions in which C–N and Si–O bonds are formed simultaneously.

One logical approach was envisioned in which compounds containing Si–N bonds (silazanes) were reacted with compounds containing C–O multiple bonds via cat-

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[†] Previous paper in this series: Laine, R. M.; Cho, B. R.; Wilson, R. B., Jr. *J. C_1 Mol. Chem.*, in press.

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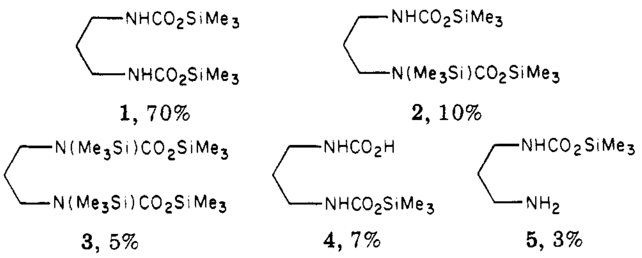
Chart I


1, 70%
2, 10%
3, 5%
4, 7%
5, 3%

alytic activation of the Si–N bond. Although such reactions are known to occur in some instances in the absence of catalysts,[1,2] a search of the literature did not reveal any examples of catalytic activation of the Si–N bond, despite the fact that silicon compounds have been shown to participate in a wide variety of catalytic reactions. A review by Curtis[3] indicates that one can catalytically cleave and reform (redistribute) silicon–oxygen, silicon–halogen, silicon–hydrogen, silicon–carbon, and even silicon–silicon bonds.[3] Thus, it seemed reasonable to expect that Si–N bonds could also be catalytically activated.

In a recent paper, Süss-Fink[4] reported that the ruthenium-catalyzed hydrosilylation of carbon dioxide, CO_2, gave good yields of silyl formates (eq 1). These results

$$Et_3SiH + CO_2 \longrightarrow HC(O)OSiEt_3 \tag{1}$$

suggested that it might be possible to catalyze a similar reaction by substituting silazanes for silanes to form silylurethanes (eq 2). Such a reaction would result in the

$$(R_3Si)_2NH + CO_2 \longrightarrow R_3NHC(O)OSiR_3 \tag{2}$$

simultaneous formation of C–N and Si–O bonds and serve as a test case for our two directives.

Results and Discussion

We report here reactions, which are the first examples of transition-metal-promoted catalytic activation of the Si–N bond, that may be of use to the synthesis chemist. We also describe several previously unknown reactions that may be of exceptional promise to the polymer chemist. As indicated in reactions 3–6, it is possible to catalytically promote the formation of C–N bonds by reacting silazanes with CO_2 by using a ruthenium carbonyl catalyst.

$$PhNHSiMe_3 + CO_2 \xrightarrow{Ru_3(CO)_{12}/100\ °C/2\ h} PhNHCO_2SiMe_3 \tag{3}$$

$$PhNHSiMe_3 + CO_2 \xrightarrow[THF]{Ru_3(CO)_{12}/110\ °C/10\ h} PhNHC(O)NHPh + (Me_3Si)_2O \tag{4}$$

$$CH_2(CH_2NHSiMe_3)_2 + CO_2 \xrightarrow{Ru_3(CO)_{12}/110\ °C/2\ h} Me_3SiO_2CHN(CH_2)_3NHCO_2SiMe_3 \tag{5}$$

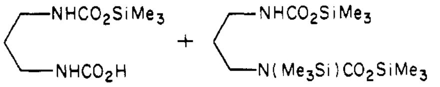
$$(Me_3Si)_2NH + CO_2 \xrightarrow{Ru_3(CO)_{12}/110\ °C/10\ h} Me_2SiNHCO_2SiMe_3 \tag{6}$$

Rhodium [as $Rh_6(CO)_{16}$] can also be used in reactions 3–6. The crude yields for these reactions are 60–90%, with the isolated yields being somewhat less. Blank reactions run in the absence of catalyst gave less than 20% conversion and in the case of eq 4 gave only small amounts of the urethane observed in eq 3.

A more in-depth analysis of reaction 5 provides some interesting observations. For example, GC/MS analysis of the products gives the product distribution shown in Chart I.

The starting material $[CH_2(CH_2NHSiMe_3)_2]$ is pure according to GC/MS analysis; therefore, the origin of compounds **2**–**5** must result from exchange of Me_3Si groups as exemplified by reaction 7.

$$2CH_2(CH_2NHCO_2SiMe_3) \longrightarrow$$


(7)

This observation is surprising in view of the fact that silicon–oxygen bonds (bond dissociation energy = 128 kcal/mol) are substantially stronger than silicon–nitrogen bonds (bond dissociation energy = 100 kcal/mol).[5] It seems reasonable to assume that carboxyl substitution on the nitrogen atoms in **1** enhances the electronegativity of the nitrogen sufficiently to promote formation of an unusually strong silicon–nitrogen bond, which accounts for formation of **2**–**5**.[6]

The next step in our study was to use a CO_2 analogue such as phenyl isocyanate (eq 8 and 9). Reaction 8 goes

$$PhN{=}C{=}O + (Me_3Si)_2NH \xrightarrow[20\ h]{Ru_3(CO)_{12}/150\ °C} (PhNH)_2CO \tag{8}$$

$$PhN{=}C{=}O + PhNHSiMe_3 \xrightarrow[45\ min]{Ru_3(CO)_{12}/110\ °C} (PhNH)_2CO \tag{9}$$

to completion in 45 min, whereas the blank reaction (without catalyst) gives no product under the same conditions after 2 days.

The mechanism by which diphenylurea forms in eq 8 or 9 is unclear at present. It is disconcerting that the product is always diphenylurea because one would expect to obtain at least a silylated analogue of diphenylurea in reaction 9.[2] However, the expected intermediate, $PhN(Me_3Si)C(O)NHPh$, is known to silylate such weakly acidic hydrogens as those in malonate ester.[5c] Moreover, given our observations on reaction 5, it is likely that the intermediate silylates the remaining $PhNHSiMe_3$ to produce $PhN(Me_3Si)_2$. Furthermore, as noted in the Experimental Section, we isolate, in low yield, a compound whose spectral characteristics suggest that it is the compound $PhN[C(O)NHPh]_2$. This compound would result from reaction of the proposed intermediate $PhN(Me_3Si)C(O)NHPh$ with a second $PhN{=}C{=}O$ followed by Me_3Si for H exchange.

With simpler, but perhaps more useful reactants, considerable rate enhancements were observed in the ruthenium-catalyzed reactions relative to the uncatalyzed reactions. Thus, the imine in eq 10 and the enamine in eq 11 are formed in extremely high yield under conditions

$$PhCHO + PhNHSiMe_3 \rightarrow PhCH{=}NPh + (Me_3Si)_2O \tag{10}$$

$$CH_3C(O)CH_2CH_3 + PhNHSiMe_3 \xrightarrow[20\ h]{Ru_3(CO)_{12}/100\ °C} CH_3C(NHPh){=}CHCH_3 + (Me_3Si)_2O \tag{11}$$

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(1) (a) Comi, R.; Franck, R. W.; Reitano, M.; Weinreb, S. M. *Tetrahedron Lett.* **1973**, *33*, 3107–9. (b) Selin, T. G. U.S. Patent *Chem. Abstr.* **1972**, *76*, 45258*a*.

(2) Morton, D. W.; Neilson, R. H. *Organometallics* **1982**, *1*, 289–95.

(3) Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213–55.

(4) Süss-Fink, G.; Reiner, J. *J. Organomet. Chem.* **1981**, *221*, C36–8.

(5) (a) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246–52. (b) Rochow, E. G. *Pure Appl. Chem.* **1966**, *13*, 247–62. (c) "Silicon Compounds Register and Review"; Petrarch Systems, Inc.: Bristol, PA, 1982.

(6) One set of products that we have considered that contain the $N{=}C(OSiMe_3)_2$ moiety rather than the $N(Me_3Si)CO_2SiMe_3$ moiety appear to be proscribed by the ^1H NMR data and the evidence (M. T. Zoeckler, unpublished work) that these compounds can readily lose CO_2. CO_2 loss would not be expected from $N{=}C(OSiMe_3)_2$. However, a tautomeric mixture of the two species cannot be ruled out at present.

Table I. Comparison of the Catalytic Activities of Various Group 8 Metals When Used as Catalysts for Reaction 10[a]

catalyst precursor	% conversion[b]	turnover frequency[c]
$Fe(CO)_5$	95	134
$Fe_3(CO)_{12}$	90	121
$Ru_3(CO)_{12}$	24	34
$NaHRu_3(CO)_{11}$	<3	
$Os_3(CO)_{12}$	4	4
$Co_2(CO)_8$	85	117
$Rh_6(CO)_{16}$	87	120
$Ir_4(CO)_{12}$	7	5
$(Ph_3P)_4Pd$	5	6
$H_2(Ph_3P)_3Ru(CO)$	1	
d	1	

[a] Reactions were run in sealed-glass reactors in which were mixed 0.05 mmol of catalyst precursor, 14 mmol of PhNH $SiMe_3$, 14 mmol of PhCHO, 2.8 mmol of PhOPh as an internal standard, and 2.0 mL of THF. Reactions were heated at 100 °C for 2 h and analyzed by gas chromatography. [b] Values are percent conversion of reactants to products. [c] Turnover frequency = moles product/moles catalyst precursor/hour. [d] Blank reaction; no catalyst added.

where the starting compounds are essentially unreactive in the absence of catalyst. Of importance here is that reactions 3–11 are all conducted under essentially neutral conditions, making them quite useful when the reactant molecule has acid- or base-sensitive functional groups. (See ref 7 for alternate methods of synthesizing enamines.)

With regard to catalysts, the results shown in Table I indicate that several of the group 8 metals are active catalysts for reaction 10. To date, of those catalysts examined, $Fe(CO)_5$ provides the highest catalytic activity.

While the exact reaction mechanism(s) must await further study, a logical sequence of events for the CO_2 insertion reactions, based on the work of Suss-Fink and of Curtis, is shown in Scheme I. It could be argued that

Scheme I

$$M + PhNHSiMe_3 \rightarrow PhNHMSiMe_3$$

$$PhNHMSiMe_3 + CO_2 \rightarrow PhNHCO_2MSiMe_3$$

$$PhNHCO_2MSiMe_3 \rightarrow M + PhNHCO_2SiMe_3$$

$$PhNHMSiMe_3 + PhNHCO_2SiMe_3 \rightarrow M + (Me_3Si)_2O + (PhNH)_2CO$$

or $$PhNHCO_2SiMe_3 \rightarrow PhNCO + Me_3SiOH$$

$$Me_3SiOH + PhNHSiMe_3 \rightarrow (Me_3Si)_2O + PhNH_2$$

$$PhNH_2 + PhN{=}C{=}O \rightarrow (PhNH)_2CO$$

but given eq 8 and 9: $$PhN{=}C{=}O + PhNHMSiMe_3 \rightarrow PhN(Me_3Si)C(O)MNHPh$$

$$PhN(Me_3Si)C(O)MNHPh \rightarrow M + PhN(Me_3Si)C(O)NHPh$$

$$PhN(Me_3Si)C(O)NHPh + PhNHSiMe_3 \rightarrow (PhNH)_2CO + PhN(Me_3Si)_2$$

in actuality the catalytic reactions 3–11 do not involve the catalytic activation of the Si–N bond but rather involve catalytic activation of the other reactants. One additional set of reactions that was run based on the following rationale indicates otherwise.

If Si–N bonds are being catalytically activated in the above reactions, then there appears to be an application to polymer chemistry that could have far-reaching effects in the area of polysilazane chemistry.

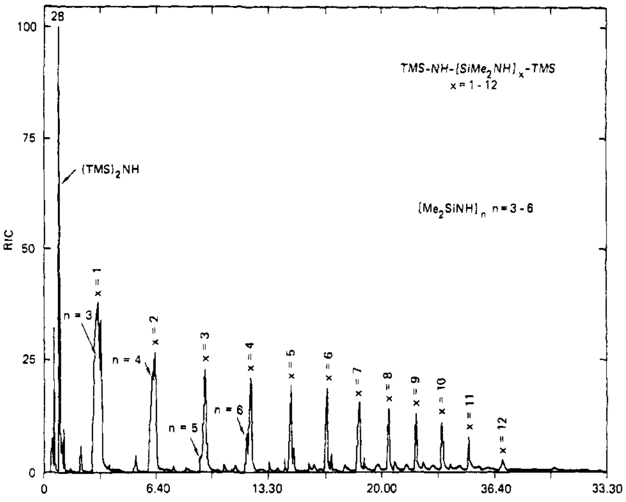

Figure 1. Ruthenium-catalyzed formation of oligomers from $[Me_2SiNH]_n$ and $(Me_3Si)_2NH$.

Consider the catalytic ring opening of octamethyltetrasilazane (**6**, $-\overline{[(CH_3)_2SiNH]_4}-$). With the proper catalyst, it might be possible to catalytically open the ring in **6** and couple one ring-opened intermediate with another to obtain chain growth. If a compound is added that reacts to give chain termination [e.g., $(Me_3Si)_2NH$], it should be possible to produce long-chain polymers with the repeating unit $-(CH_3)_2SiNH-$. These products would be polysilazane analogues (silazones) of polysiloxanes (silicones). Depending on the concentration of the chain-terminating compound relative to the chain-propagating ring compound, one should be able to control the polymer chain length. We tested these ideas by running reactions 12 and 13.

$$\mathbf{6} + 2.5(Me_3Si)_2NH \xrightarrow[110\ °C/20\ h]{Ru_3(CO)_{12}} Me_3Si-[NHSi(CH_3)_2]_n-NHSiMe_3 \quad (n = 1\text{–}6) \tag{12}$$

$$2.5\mathbf{6} + (Me_3Si)_2NH \xrightarrow[110\ °C/20\ h]{Ru_3(CO)_{12}} Me_3Si-[NHSi(CH_3)_2]_n-NHSiMe_3 \quad (n = 1\text{–}12) \tag{13}$$

As shown by the GC/MS results in Figure 1 for reaction 13, we succeeded in opening the rings and producing long-chain oligomers. In addition, by controlling the concentration of **6** relative to $(Me_3Si)_2NH$ (ratio of 1:2.5 in reaction 12 and 2.5:1 in reaction 13), we were able to control the average molecular weight distribution of the oligomers.

Previously, oligomers such as those prepared in eq 13 could only be prepared in low yield (~10%) after 10 days of reaction time under more severe conditions according to reaction 14.[8]

$$\mathbf{6} + NH_3\ (10\ atm) \rightarrow NH_2-[NHSi(CH_3)_2]_n-(CH_3)_2SiNH_2 \tag{14}$$

It is somewhat early to speculate on the mechanism of Si–N bond activation. However, in view of the mechanisms proposed by Curtis for transition-metal-catalyzed siloxane redistribution reactions, we can present the tentative general mechanisms for reactions 11 and 13 shown in Scheme II.

In analogy to the Curtis work, the intermediacy of a metal-complexed silicon–nitrogen double bond seems reasonable in view of the formation of Me_3SiNH-

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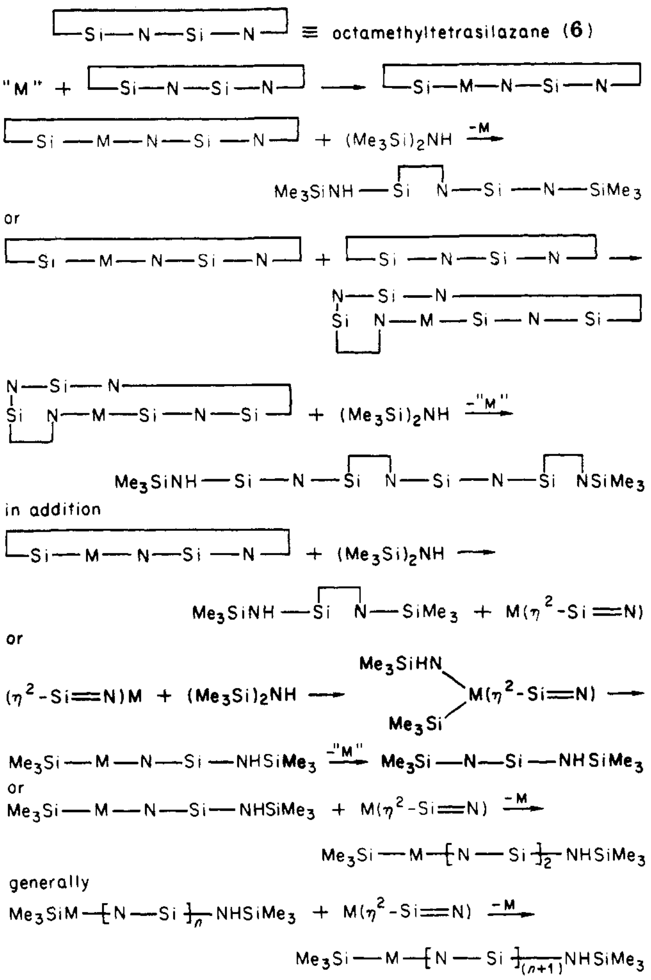
(7) Cook, A. G., Ed. "Enamines, Synthesis, Structure and Reactions"; Marcel Dekker: New York, 1969.

(8) Redl, G.; Rochow, E. G. *Angew. Chem.* **1964**, *76*, 650–2.

Scheme II



$[(CH_3)_2SiNH]_n$–$SiMe_3$, where $n = 1$, although repeated "clipping" of the longer chains to give $n = 1$ is still possible.

Summary

We have demonstrated that catalytic formation of new C–N bonds can be promoted by the catalytic activation of Si–N bonds. Thus, a variety of silazanes will react in the presence of several group 8 metal catalysts with compounds containing carbon–oxygen double bonds to form C–N and Si–O bonds concurrently. In our preliminary investigations, we have established that CO_2 and phenyl isocyanate can be reacted with several silazanes to form urethane and urea derivatives in 60–95% yield. In the absence of catalyst, these reactions give at most a 20% yield of the same products under comparable conditions. Aldehydes and ketones react with silazanes to give imines and enamines. Furthermore, we have been able to use the catalytic activation of Si–N bond as a means of producing high molecular weight oligomers containing the $-(CH_3)_2SiNH-$ unit. This observation suggests that it may eventually be possible to synthesize silazone analogues of silicones.

Considerable work remains to develop the best catalysts for the above-described reactions and to fully explore the generality of these reactions.

Experimental Details

General Procedures. Solvents were purified via distillation from suitable drying agents under a nitrogen atmosphere. Benzaldehyde, phenyl isocyanate, and *N*-(trimethylsilyl)aniline were distilled under N_2 and stored under N_2 prior to use. $NaHRu_3(CO)_{11}$ was prepared by the method of Shore.[9] All silazanes, with the exception of 1,3-bis[(trimethylsilyl)amino]propane, were purchased from Petrarch, distilled under N_2, and stored under N_2 before use.

Analyses for the studies shown in Table I were performed on a Hewlett-Packard 5711 gas chromatograph equipped with a 1.5 m × 0.325 cm column packed with 5% Carbowax 20M on acid-washed Chromosorb W and with FID. Infrared spectra were obtained by using a Perkin-Elmer 281 IR spectrophotometer. NMR spectra were taken on a Varian EM-360. GC/MS analyses were performed by using an LKB-9000 mass spectrometer or a Ribermag R 10-10C.

1,3-Bis[(trimethylsilyl)amino]propane. The title compound was prepared by the method of Birkhoffer[10] and characterized by mass spectroscopy (electron impact): *m/e* (relative intensity) 218 (2), 203 (12), 129 (90), 114 (61), 102 (35), 100 (60), 88 (37), 73 (100), 59 (22), 45 (15); ^1H NMR [pyridine, $(CH_3)_4Si$] δ 2.70 (CH_2CH_2NH), 1.40 (quintet, $CH_2CH_2CH_2$), 0.75 (br s, NH?), 0.08 (Me_3Si); pure by GC/MS.

$PhNHCO_2SiMe_3$. In an oven-dried, general-purpose, quartz-lined, Parr bomb reactor (34 mL volume) with a magnetic stir bar were placed 1.84 mL (10.5 mmol) of *N*-(trimethylsilyl)aniline and 48 mg (0.075 mmol) of $Ru_3(CO)_{12}$. The bomb was flushed three times with nitrogen and twice with CO_2 and pressurized with 300 psi of CO_2. After 20 h at 100 °C, the bomb was cooled to room temperature, depressurized, and opened. The product was 1.66 g (76% yield) of an orange solid. Recrystallization from hexane/THF removed most of the catalyst, leaving a gray powder, mp 125–130 °C. Sublimation under reduced pressure gave fine white needles: mp 134 °C; mass spectrum, *m/e* (relative intensity) 209 (M^+, 30), 194 (13), 165 (18), 150 (100), 129 (8), 75 (42), 73 (56); IR (KBr) 3300 (s), 3030 (w), 2950 (w), 2320 (m), 1660 (s), 1590 (m), 1520 (s), 1440 (m), 1310 (m), 1270 (m), 1250 (m), 1180 (w), 1045 (w), 1020 (w), 850 (s), 745 (m), 715 (w), 690 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25 (m, 5 H), 0.28 (s, 9 H).

$(PhNH)_2CO$ from $PhNHSiMe_3$ and CO_2. The same procedure as described above was followed except that the bomb was pressurized with 200 psi of CO_2, and the reaction was conducted at 150 °C for 20 h. The product mixture, crystals mixed with a red-brown gum, was rinsed from the reactor with acetone, and the crystals (0.36 g) were isolated by suction filtration. A second crop (0.17 g) was obtained by chilling the filtrate in ice, giving a combined yield of 48%: mp 248 °C; mass spectrum, *m/e* (relative intensity) 212 (M^+, 17), 93 (100); IR (KBr) identical with the Aldrich spectrum of diphenylurea. Note that the reaction run with 2.0 mL of THF solvent at 110 °C gives the same or better yields after 20 h of reaction time.

$(PhNH)_2CO$ from PhN=C=O. In a 34-mL quartz-lined bomb reaction were mixed 1.0 mL (9.2 mmol) of phenyl isocyanate, 1.0 mL (5.7 mmol) of *N*-(trimethylsilyl)aniline, and 48 mg (0.075 mmol) of $Ru_3(CO)_{12}$. The bomb was flushed twice with nitrogen, pressurized with 300 psi of nitrogen, and then stirred at 100 °C for 20 h. The product, a semisolid material, was rinsed from the reactor with ether. Three crops of crystals were collected: 0.17 g, mp 145 °C; 0.64 g, mp 245 °C dec; 0.51 g, mp 245 °C dec.

The second and third crops were diphenylurea (95% yield, based on $PhNHSiMe_3$), as shown by IR. The first crop was a mixture of diphenylurea and a compound with the following spectral characteristics: mass spectrum, *m/e* (relative intensity) 331 (M^+, 7), 212 (34), 119 (28), 93 (100); IR (KBr) 3300 (m), 3170 (m), 3050 (m), 1695 (s), 1665 (s), 1590 (s), 1520 (br), 1490 (s), 1430 (s), 1310 (s), 1260 (s), 1175 (s), 1095 (w), 1070 (w), 1025 (w), 895 (w), 860 (w), 830 (w), 750 (m), 685 (m) cm^{-1}. The reactants, the mass spectrum, and the IR spectrum suggest that this product is $PhN[C(O)NHPh]_2$.

Reaction of $CH_2(CH_2NHSiMe_3)_2$ with CO_2. In a quartz-lined bomb reactor were mixed 2.0 mL of THF, 2.56 g (11.7 mmol) of 1,3-[(trimethylsilyl)amino]propane, and 32 mg (0.05 mmol) of $Ru_3(CO)_{12}$. The reactor was sealed, degassed as described above with CO_2, charged to 750 psi of CO_2, and heated to 110 °C for 1 h, at which time 1.9 equiv of CO_2 were taken up, and no further reaction was observed.

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A white, highly crystalline solid was filtered off and identified as $CH_2(CH_2NHCO_2SiMe_3)_2$, GC/MS analysis revealed the presence and allowed the identification of compounds **2**–**5**. GC/MS characterization for these compounds gives the following results for compound **1**: electron-impact (EI) mass spectrum, *m*/*e* (relative intensity) 172 (4), 157 (52), 100 (12), 75 (100), 73 (23), 45 (22), 44 (22); chemical ionization (CI, NH_3) mass spectrum, *m*/*e* (relative intensity) 307 (56), 217 (20), 191 (21), 173 (45), 101 (100), 75 (35); negative chemical ionization (NCI, with NH_3) mass spectrum, *m*/*e* (relative intensity) 241 (18), 171 (100), 99 (30), 89 (42). For compound **2**: EI mass spectrum, *m*/*e* (relative intensity) 273 (4), 157 (40), 147 (67), 100 (12), 75 (100), 73 (59), 59 (18), 45 (27); CI (NH_3) mass spectrum, *m*/*e* (relative intensity) 379 (5), 289 (19), 173 (31), 101 (100), 90 (16), 75 (17); NCI mass spectrum, *m*/*e* (relative intensity) 245 (5), 171 (100), 99 (22), 89 (40). Compound **3** gave the following spectra: EI mass spectrum, *m*/*e* (relative intensity) 450 (3), 435 (29), 246 (27), 232 (55), 218 (43), 147 (32), 73 (100); CI mass spectrum, *m*/*e* (relative intensity) 451 (100), 361 (10), 289 (27), 173 (13); NCI mass spectrum, *m*/*e* (relative intensity) 243 (4), 171 (100), 89 (6). Compound **4** was determined by difference, as it decomposes on GC/MS analysis to give spectra as found for compound **5**. **4** gave the following: EI mass spectrum, *m*/*e* (relative intensity) 100 (17), 75 (100), 56 (9), 47 (13), 45 (18); CI mass spectrum, *m*/*e* (relative intensity) 191 (100), 101 (96), 75 (93); NCI mass spectrum, *m*/*e* (relative intensity) 117 (17), 99 (53), 89 (100). Compound **5** has the identical pattern but can be differentiated from **4** by further silylating the reaction solution with $CF_3SO_3SiMe_3$ and running the GC/MS to determine the amounts of **4** that have been doubly and triply silylated [e.g., $(Me_3Si)_2N(CH_2)_3$–$N(Me_3Si)CO_2SiMe_3$, *m*/*e* 406]. This procedure allows the determination of amounts of **4** present as well.

The yields of these compounds as determined by GC were ca. 70% for **1**, 10% for **2**, 5% for **3**, and 10% for **4** and **5** combined. Compound **1** was further characterized as follows: ^1H NMR (Me_2SO-d_6) δ 5.40 (t, NH?); 3.42 (q, CH_2NH), 1.80 (quintet, CH_2CH_2N), 0.26 (s, $OSiMe_3$); ^1H NMR (pyridine) δ 3.35 (q), 1.78 (quintet), 0.28 ($OSiMe_3$); IR (KBr) 3340 (br s), 2950 (s), 2880 (br s), 1670 (s), 1575 (br s), 1490 (br s), 1390 (ms), 1325 (br s), 1280 (ms), 1253 (ms), 1155 (m), 1135 (mw), 1060 (m), 1020 (w), 840 (s), 765 (mw); mp 85–87.

Compounds **2** and **3** were also characterized by ^1H NMR. Clean NMR samples were prepared by treating **1** with $CF_3SO_3SiM_3$ in pyridine. For compound **2**: ^1H NMR (pyridine) δ 3.30 (quintet, CH_2CH_2N), 1.78 (quintet?, $CH_2CH_2CH_2$) 0.28 (s), 0.34 (s, Me_3Si). Compound **3** has essentially the same spectrum, however, the integrations for the silyl groups are different but as expected (see ref 6).

Reaction of $(Me_3Si)_2NH$ with CO_2. In a magnetically stirred, quartz-lined bomb reactor of 34-mL volume were mixed 32 mg (0.05 mmol) of $Ru_3(CO)_{12}$ and 2.0 mL of $(Me_3Si)_2NH$. The reactor was sealed, pressurized to 300 psi with CO_2, and heated at 100 °C for 12 h. When the reactor cooled, no liquid remained, and the product, $Me_3SiNHC(O)OSiMe_3$, was sublimed prior to analysis: IR (KBr) 3230 (s), 2950 (s), 2895 (mw), 2790 (w), 1675 (br s), 1400 (m, sh), 1330 (s), 1245 (s), 1050 (s), 880 (m, sh), 850 (br s), 810 (m, sh), 745 (m), 723 (m), 642 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.5 (br s, NH), 0.30 (s, 9 H, Me_3SiN), 0.21 (s, 9 H, Me_3SiO); NCI mass spectrum, *m*/*e* (relative intensity) 206 (100). A blank reaction (without catalyst) gave 10–15% conversion.

Reaction of $PhNHSiMe_3$ with PhCHO. In a magnetically stirred, sealed, glass reactor of 30-mL volume were mixed 0.05 mmol of catalyst precursor (see Table I), 14 mmol of $PhNHSiMe_3$, 14 mmol of PhCHO, 2.8 mmol of PhOPh as an internal standard, and 2.0 mL of THF. The reactor was heated at 100 °C for 2 h, and the product was analyzed by GC. The product yields for the various catalysts and the catalytic activities for these catalysts are listed in Table I.

Authentic PhCH=NPh was prepared by reaction of PhCHO and $PhNH_2$ and used for the GC standards. The product isolated from the reactions was found to be identical, spectrally, with the authentic PhCH=NPh. Blank reactions gave essentially no product.

Reaction of $PhNHSiMe_3$ with 2-Pentanone. In a magnetically stirred glass reactor were mixed 2.5 mL (14 mmol) of $PhNHSiMe_3$, 1.5 mL of 2-pentanone, and 32 mg (0.05 mmol) of $Ru_3(CO)_{12}$. The reactor was sealed under N_2 and heated at 100 °C for 20 h. GC analysis indicated 70% conversion to enamine as identified by mass spectroscopy; EI mass spectrum, *m*/*e* (relative intensity) 161 (20), 146 (25), 118 (57), 77 (100), 51 (63), CI (NH_3) mass spectrum, *m*/*e* (relative intensity) 162 (100), 146 (12), 133 (12), 118 (22); NCI (NH_3) mass spectrum, *m*/*e* (relative intensity) 160 (100); ^1H NMR ($CDCl_3$) δ 6.88 (br m, 6 H, ArH, =CH), 3.55 (br s, ~1 H, NH), 2.15 (q, CH_2CH_3), 1.57 (s, CH_3C=CH), 0.88 (t, CH_2CH_3). A blank reaction run concurrently gave 10% conversion.

Silazones. In a glass reactor were mixed 4.0 mL (19 mmol) of $(Me_3Si)_2NH$ and 2.1 g (7 mmol) of octamethyltetrasilazane for reaction 12, or 1.0 mL (4.2 mmol) and 3.0 g (10 mmol), respectively, for reaction 13, and 32 mg (0.05 mmol) of $Ru_3(CO)_{12}$. The reactor was sealed and heated at 110 °C for 14 h; the product was then analyzed via a combination of EI, CI, and NCI GC/MS. For reaction 12 the products were solely the silazanes Me_3SiNH–$[(CH_3)_2SiNH]_n$–$SiMe_3$, where n = 1–7, in a normal Schulz–Flory distribution. The analysis for reaction 13 was somewhat more complex and is shown in Figure 1. Similar silazones were also prepared using $Rh_6(CO)_{16}$ as catalyst, and in this case the reaction was complete in 10 h with much the same analysis as that shown in Figure 1.

Typically, the NCI mass spectral fragmentation pattern for Me_3SiNH–$[(CH_3)_2SiNH]_n$–$SiMe_3$ is M – H, M – 18, and M – 32; for the higher molecular weights, M – H is not found. For the cyclic compounds $[(CH_3)_2SiNH]_n$, the NCI mass spectral fragmentation is generally only M – H. The fragmentation patterns for EI, CI, and NCI corroborated the structures of the various oligomeric products.

Acknowledgment. We thank Dr. D. W. Thomas for his exceptional work on the mass spectral analyses. We are also grateful to the U.S. Army Research Office for generous support of this work through Contract DAAG-29-81-K-0086.

Registry No. **1**, 86045-53-6; **2**, 86045-54-7; **3**, 86045-55-8; **4**, 86045-56-9; **5**, 86045-57-0; $PhNHCO_2SiMe_3$, 30882-95-2; $Ru_3(CO)_{12}$, 15243-33-1; CO_2, 124-38-9; $(PhNH)_2CO$, 102-07-8; PhN=C=O, 103-71-9; PhNHC(O)N(Ph)C(O)NHPh, 2645-39-8; $(Me_3Si)_2NH$, 999-97-3; $Me_3SiNHCO_2SiMe_3$, 35342-88-2; PhCHO, 100-52-7; PhCH=NPh, 538-51-2; Me_3SiNH–$[(CH_3)_2SiNH]_n$–$SiMe_3$, 86045-58-1; $Fe(CO)_5$, 13463-40-6; $Fe_3(CO)_{12}$, 17685-52-8; NaH-$Ru_3(CO)_{11}$, 71936-71-5; $Os_3(CO)_{12}$, 15696-40-9; $Co_2(CO)_8$, 10210-68-1; $Rh_6(CO)_{16}$, 28407-51-4; $Ir_4(CO)_{12}$, 18827-81-1; $(Ph_3P)_4Pd$, 14221-01-3; $H_2(Ph_3P)_3Ru(CO)$, 25360-32-1; 1,3-bis[(trimethylsilyl)amino]propane, 63737-72-4; *N*-(trimethylsilyl)aniline, 3768-55-6; 2-pentanone, 107-87-9; 2-(phenylamino)-2-pentene, 24235-21-0; octamethylcyclotetrasilazane, 1020-84-4.