4b, 52547-77-0; **4c**, 124155-99-3; **4d**, 34761-56-3; **4e**, 124175-14-0; **4f**, 69754-59-2; **4g**, 124156-00-9; **4h**, 35281-64-2; **4i**, 124156-01-0; **4j**, 124156-02-1; **4k**, 59148-51-5; **4l**, 124156-03-2; **4m**, 124156-04-3; **4n**, 124156-05-4; **4o**, 69754-58-1; **4p**, 79090-78-1; **4q**, 124156-06-5; **4r**, 124156-07-6; **4s**, 124156-08-7; **4t**, 124156-09-8; **4u**, 124156-10-1; **4w**, 124156-13-4; **11**, 53915-69-8; **12b**, 111847-83-7; **13**, 124155-87-9; **14**, 124155-88-0; **15b**, 69165-98-6; **16**, 61157-32-2; **17**, 124155-91-5; **18**, 124155-92-6; **19**, 124155-93-7; **21**, 124156-19-0; **22**, 124155-95-9; **23**, 124155-96-0; i-PrMgCl, 1068-55-9; t-BuMgCl, 677-22-5; $H_3C(CH_2)_6CHO$, 124-13-0; $(CH_3)_3CCHO$, 630-19-3; PhCHO, 100-52-7; PhCH=CHCHO, 14371-10-9; $(Et)_2CO$, 96-22-0; $(i\text{-}Pr)_2CO$, 565-80-0; $H_3CCOC(CH_3)_3$, 75-97-8; $t\text{-}BuCO(CH_2)_6CH_3$, 61759-36-2; i-PrCOPh, 611-70-1; $H_3CC{\equiv}C(CH_2)_4CH_3$, 2809-67-8; $BrCH_2C{\equiv}CC(CH_3)_3$, 52323-99-6; cyclohexanone, 108-94-1; 2-cyclohexenone, 930-68-7; (1*R*)-(+)-camphor, 464-49-3; 2-adamantanone, 700-58-3; estrone 3-*O*-*tert*-butyldimethylsilyl ether, 57711-40-7.

Supplementary Material Available: Spectral data (IR, ^1H and ^{13}C NMR) of **3p**, **3q**, **4q**, **3r**, **4r**, **3s**, **4s**, **3u**, **4u**, **3v**, **3w**, **3x**, and **3y** and copies of actual ^1H and ^{13}C NMR spectra of **3i**, **4i**, **3l**, **3m**, **3n**, **4n**, **3p**, **3w**, **3y**, **17**, **19**, **21**, **22**, and **23** (32 pages). Ordering information is given on any current masthead page.

Cobalt Carbonyl Catalyzed Hydrosilylation of Nitriles: A New Preparation of *N*,*N*-Disilylamines

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Received July 17, 1989

Cobalt carbonyl catalyzed hydrosilylation of a wide variety of nitriles with $HSiMe_3$ has been examined. The reaction generally proceeded at 60 °C to give *N,N*-disilylamines in good yields. Electron-donating groups on aromatic nitriles facilitated the reaction, and electron-withdrawing groups decreased the rate. The reaction of aliphatic nitriles at 60 °C was sluggish except for cyclopropanenitriles, whereas raising the temperature to 100 °C greatly enhanced the reaction rate. In the case of acrylonitrile, four types of products were obtained. For monosubstituted acrylonitriles, consecutive 1,2- and 1,4-addition of $HSiMe_3$ were observed as a major route to give (*Z*)-*N,N*-disilylenamines exclusively. The introduction of two kinds of alkyl substituents to acrylonitrile lowered the reactivity and reversed the selectivity to give (*E*)-*N,N*-disilylenamines in ca. 20% yield. A plausible reaction pathway discussed.

Transition-metal-catalyzed hydrosilylation of carbonyl compounds, imines, oximes, acetylenes, and olefins has been developed for the last 30 years because of its importance as a method not only for reduction but also for introducing silyl groups into organic molecules.[1] The recent development of asymmetric hydrosilylation has further illustrated the applicability of this process.[2] In contrast to these well-established and useful reactions, little[3] is known about hydrosilylation of the C–N triple bond, since the cyano group has been believed to be inert under the usual hydrosilylation conditions. For example, rhodium(III)-catalyzed hydrosilylation of α,β-unsaturated nitriles has been developed as a method for the preparation of α-silyl nitriles,[4] and molybdenum-catalyzed reduction of α,β-unsaturated nitriles with H_3SiPh gave only alkyl nitriles in good yields.[5] As exceptional cases, Corriu et al. have reported that 1,2-bis(dimethylsilyl)benzene added to aklyl nitriles in the presence of an Rh catalyst to give a mixture of *N,N*-disilylenamines and amines,[6a] and Chalk has found that cobalt carbonyl catalyzed addition of $HSiMe_2Cl$ to $CH_2{=}CH(CH_3)CN$ gave $(CH_3)_2C{=}CHN(SiMe_2Cl)_2$, but in only 20% yield after 6 days.[6b] Recently, we have found that $HSiMe_3$ cleanly added to the C–N triple bond in aromatic nitriles in the presence of a catalytic amount of $Co_2(CO)_8$.[7] This process provides a new

Table I. Cobalt Carbonyl Catalyzed Addition of Trimethylsilane to Aromatic Nitriles[a]

$$ArCN + HSiMe_3 \xrightarrow[\text{CO atm.}]{\text{cat. } Co_2(CO)_8} ArCH_2N(SiMe_3)_2$$

entry	ArCN	yields of product, %[b]
1	C_6H_5CN	61
2	$2\text{-}CH_3C_6H_4CN$	11 (22)
3	$3\text{-}CH_3C_6H_4CN$	57 (68)
4	$4\text{-}CH_3C_6H_4CN$	91
5	$4\text{-}NCCH_2C_6H_4CN$	(36)[c]
6	$4\text{-}CH_3OC_6H_4CN$	67 (88)
7	$4\text{-}(CH_3)_2NC_6H_4CN$	51 (73)
8	$3\text{-}ClC_6H_4CN$	(50)[d]
9	$4\text{-}ClC_6H_4CN$	(53)[e]
10	$4\text{-}CH_3CO_2C_6H_4CN$	(46)[e]
11	1-naphtyl nitrile	0
12	2-naphtyl nitrile	68

[a] Reaction conditions: nitrile (2.5 mmol), $HSiMe_3$ (25 mmol), $Co_2(CO)_8$ (0.2 mmol), $CH_3C_6H_5$ (10 mL), CO atmosphere, 60 °C, 20 h. [b] GLC yields in parentheses. [c] $Co_2(CO)_8$ (0.625 mmol) was used. [d] 48 h. [e] 40 h.

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[1] (a) Lukevics, E.; Belyakova, Z. V.; Pomerantseva, M. G.; Voronkov, M. G. *J. Organomet. Chem. Chem. Libr.* **1977**, *5*, 1. (b) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407. (c) Ojima, I.; Kogure, T. In *Rev. Silicon, Germanium, Tin, Lead Compd.* **1981**, *5*, 8. (d) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983.

[2] For review, see: (a) Brunner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 897. (b) Ojima, I.; Hirai, K. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, p 103.

[3] (a) Calas et al. have reported that the addition of $HSiEt_3$ to PhCN in the presence of ZnI_2 gave $PhCH{=}NSiEt_3$: (a) Frainnet, E.; Llonch, J. P.; Dubourdin, F.; Calas, R. *Bull. Soc. Chim. Fr.* **1966**, 1172. (b) Calas, R. *Pure. Appl. Chem.* **1966**, *13*, 61.

[4] (a) Ojima, I.; Kumagai, M.; Nagai, Y. *Tetrahedron Lett.* **1974**, 4005. (b) Ojima, I.; Kumagai, M.; Nagai, Y. *J. Organomet. Chem.* **1976**, *111*, 43.

[5] Keinan, E.; Perez, D. *J. Org. Chem.* **1987**, *52*, 2576.

[6] (a) Corriu, R. J. P.; Moreau, J. J. E.; Pataud-Sat, M. *J. Organomet. Chem.* **1982**, *228*, 301. (b) Chalk, A. J. *J. Organomet. Chem.* **1970**, *21*, 207.

[7] Murai, T.; Sakane, T.; Kato, S. *Tetrahedron Lett.* **1985**, *26*, 5145.

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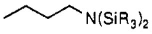
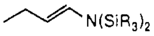
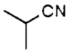
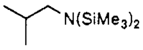
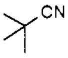
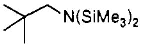
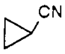
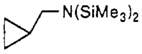
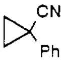
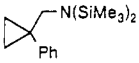
Table II. Cobalt Carbonyl Catalyzed Addition of Hydrosilanes to Aliphatic Nitriles[a]

entry	nitrile	products	yields, %[b]
	 1		
1		R = Me 6a 44 %	7a 20 %
2		R = OEt[c] 6b 31 %	7b 8 %
3	 2	 8	100 % (26 %)[d]
4	 3	 9	100 %[e]
5	 4	 10	87 %
6	 5	 11	88 %

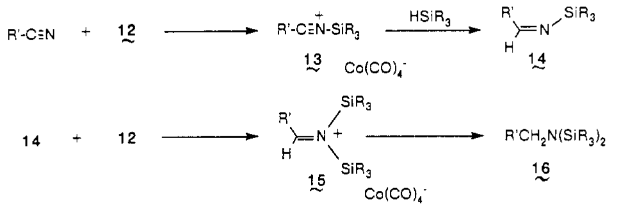
[a] Reaction conditions are as follows unless otherwise noted: nitrile (2.5 mmol), $HSiMe_3$ (25 mmol), $Co_2(CO)_8$ (0.2 mmol), PPh_3 (0.4 mmol), $CH_3C_6H_5$ (10 mL), 100 °C, 20 h, CO atmosphere. [b] GLC yields. [c] $HSi(OEt)_3$ (10 mmol) and $CH_3C_6H_5$ (5 mL) were used. [d] 60 °C without PPh_3. [e] $P(OEt)_3$ (0.4 mmol) was used.

synthetic method for preparation of *N*,*N*-bis(trimethylsilyl)amines, which have been prepared generally from primary amines and often used when the reaction with organic compounds bearing primary amino groups are carried out under basic conditions.[8] Herein we report the scope and limitations of this cobalt carbonyl catalyzed hydrosilylation reaction of nitriles.

Results and Discussion

Aromatic Nitriles. Initially, cobalt carbonyl catalyzed reactions of 4-methylbenzonitrile with a hydrosilane were studied. Although the addition reaction in the presence of $Co_2(CO)_8$ formed only a small amount of hydrosilyated product at 25 °C, raising the temperature to 60 °C facilitated the conversion to *N*,*N*-bis(trimethylsilyl)-4-methylbenzylamine (71% yield, R = 4-$CH_3C_6H_4$ in Table I). Further, a carbon monoxide atmosphere enhanced the yield of this reaction, probably due to the stabilization of the catalyst species. Formally, the carbon–nitrogen triple bond is doubly reduced by the addition of two molecules of a hydrosilane.

Scheme I



$HSiMe_2Ph$, H_2SiPh_2, and $HSi(OEt)_3$ were examined as hydrosilane reagents. However, they gave complex mixtures or resulted in the recovery of the starting material. Interestingly, $HSiEt_2Me$ and $HSiEt_3$ also gave rise to the same mixture in low yields despite only having longer alkyl chains than $HSiMe_3$.

As shown in Table I, the catalytic reaction of aromatic nitriles having substituents generally proceeded smoothly at 60 °C to give the corresponding *N*,*N*-disilylamines in fair to good yields. There are some comments that should be noted. First, the electronic factor of the aromatic ring highly affected the reaction rate, i.e., electron-donating groups facilitated the reaction, and electron-withdrawing groups decreased the rate (entries 5–10). Second, the reaction with ortho-substituted nitriles was very slow, probably because of steric congestion (entries 2, 11). Third, the hydrosilylation is site specific with respect to the aromatic cyano group at this temperature (entry 5). Fourth, functional groups such as methoxy, dimethylamino, chloro, and methoxycarbonyl survived the reaction conditions (entries 6–10).

Aliphatic Nitriles. The results of the cobalt carbonyl catalyzed reaction of aliphatic nitriles with $HSiMe_3$ are presented in Table II. As can be predicted from entry 5 in Table I, the reaction at 60 °C was quite slow except for the case of cyclopropyl nitriles. The hydrosilylation of **4** and **5** proceeded smoothly at 60 °C to yield the corresponding *N*,*N*-disilylamines selectively in high yields (entries 5 and 6). In this case the product of cleavage of the cyclopropane ring was not observed.[9]

On the other hand, alkyl-substituted nitriles **1**, **2**, and **3** required higher temperatures to undergo the reaction effectively. However, when the temperature was simply raised to 100 °C, the yields of the products were rather low, and black metal was precipitated after the reaction for 20 h. At this temperature, the decomposition of the catalyst may be competitive with the process. When the phosphine derivatives, such as triphenylphosphine and triethoxy phosphite, were employed to stabilize the catalyst, hydrosilylation of **2** and **3** proceeded smoothly to give the corresponding *N*,*N*-disilylamines in excellent yields. For **1**, (*E*)-*N*,*N*-disilylenamine **7** was obtained together with **6**. The reaction of **1** with $HSi(OEt)_3$ also proceeded smoothly, unlike the case of aromatic nitriles, but the ratio of **6** and **7** was unchanged.

Mechanistic Aspects. On the basis of our results and some other related results,[10,11] a plausible reaction pathway of the present reaction is proposed in Scheme I. The

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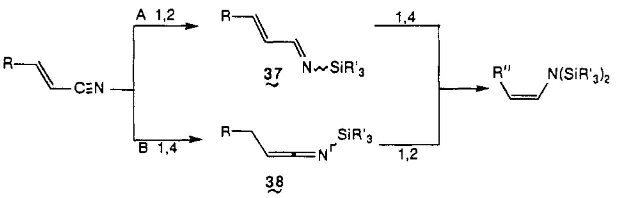
[8] (a) Fleming I. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. P., Eds.; Pergamon Press: Oxford, 1979; Vol. III, pp 542–686. (b) Colvin, E. *Silicon in Organic Synthesis*; Butterworths; 1981; pp 314–320. (c) Corriu, R. J. P.; Huynh, V.; Iqbal, J.; Moreau, J. J. E. *J. Organomet. Chem.* **1984**, *276*, C61. (d) Corriu, R. J. P.; Moreau, J. J. R. In *Selectivity-a Goal for Synthetic Efficiency*; Bartmann, W., Trost, B. M., Eds.; Verlag Chemie: Weinheim, 1984; pp 21–41. (e) Morimoto, T.; Takahashi, T.; Sekiya, M. *J. Chem. Soc., Chem. Commun.* **1984**, 794. (f) Okano, K.; Morimoto, T.; Sekiya, M. *J. Chem. Soc., Chem. Commun.* **1984**, 883. (g) Bestmann, H. J.; Wolfel, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 53. (h) Morimoto, T.; Aono, M.; Sekiya, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1055. (i) Corriu, R. J. P.; Huynh, V.; Moreau, J. J. E. *Tetrahedron Lett.* **1984**, 1887. (j) Okano, K.; Morimoto, T.; Sekiya, M. *Chem. Pharm. Bull.* **1985**, *33*, 2228. (k) Morimoto, T.; Sekiya, M. *Chem. Lett.* **1985**, 1371. (l) Corriu, R. J. P.; Moreau, J. J. E.; Vernhet, C. *Tetrahedron Lett.* **1987**, *28*, 2963. (m) Bestmann, H. J.; Wolfel, G.; Mederer, K. *Synthesis* **1987**, 848. (n) Kira, M.; Nagai, S.; Nishimura, M.; Sakurai, H. *Chem. Lett.* **1987**, 153. (o) Dicko, A.; Montury, M.; Baboulene, M. *Tetrahedron Lett.* **1987**, *28*, 6041. (p) Igueld, S.; Baboulene, M.; Dicko, A.; Montury, M. *Synthesis* **1989**, 200. (q) Capella, L.; Degl'Innocenti, A.; Reginato, G.; Ricci, A.; Taddei, M.; Seconi, G. *J. Org. Chem.* **1989**, *54*, 1473.

[9] The reaction between Me_3SiI and cyclopropyl phenyl ketone is accompanied with ring cleavage of the cyclopropyl group: Miller, R. D.; McKean, D. R. *Tetrahedron Lett.* **1979**, 2305.

[10] (a) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1967**, *89*, 1640. (b) Baay, Y. L.; MacDiarmid, A. G. *Inorg. Chem.* **1969**, *8*, 986. (c) Sisak, A.; Ungvary, F.; Marko, L. *Organometallics* **1986**, *5*, 1019.

[11] The reaction of the system $HSiR_3/CO/Co_2(CO)_8$ with olefins and oxygen-containing compounds has been well documented: (a) Murai, T.; Yasui, E.; Kato, S.; Hatayama, Y.; Suzuki, S.; Yamasaki, Y.; Sonoda, N.; Kurosawa, H.; Kawasaki, Y.; Murai, S. *J. Am. Chem. Soc.* **1989**, *111*, 7938. (b) Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 837 and references cited therein.

Scheme II



active catalyst may be the (trialkylsilyl)cobalt carbonyl (**12**), which is easily generated from a hydrosilane and dicobalt octacarbonyl (eq 1).[10] By the nucleophilic attack

$$2\ HSiR_3 + Co_2(CO)_8 \longrightarrow \underset{12}{2\ R_3SiCo(CO)_4} + H_2 \qquad (1)$$

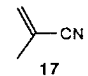
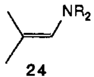
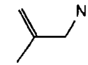
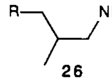
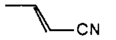
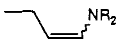
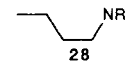
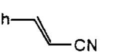
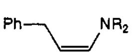
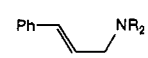
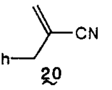
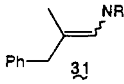
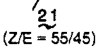
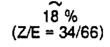
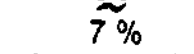
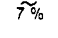
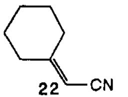
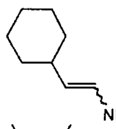
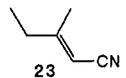
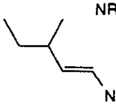
of the nitrogen lone pair of a nitrile to **2**, the *N*-silylnitrilium ion intermediate (**13**) and $Co(CO)_4^-$ would be formed. Then, hydrogen transfer to **13** from $HSiR_3$ or more likely from $HSiR_3Nu$, a pentacoordinate silicon where Nu^- may be $Co(CO)_4^-$ or any heteroatom center in the system, would give silylimine **14**. This step can be supported by the fact that reduction of *N*-alkylnitrilium ion with $HSiEt_3$ easily took place to give alkylamine.[13] A similar process may be repeated from **14** to give the final product **16**. The intermediacy of **14** seems to be reasonable since the reaction of isolated **14** (R' = Ph)[14] with $HSiMe_3$ under the present reaction conditions proceeded smoothly to form $PhCH_2N(SiMe_3)_2$ in high yield.[15] According to the results in Table I and those of cyclopropyl nitriles **4** and **5**, the rate-determining step of the reaction would be the formation of *N*-silylnitrilium (**13**) and/or *N*,*N*-disilyliminium (**15**) ion intermediates. Furthermore, since **14** (R' = Ph) was consumed faster than PhCN, when both were reacted with $HSiMe_3$, the reaction rate would be predominantly dependent on the step giving **13**.

The formation of *N*,*N*-disilylenamine **7** would be accounted for by hydrogen abstraction from the *N*,*N*-disilyliminium ion intermediate analogous to **15**. Interestingly, only the *E* isomer was obtained, and this is in marked contrast to the result of cobalt carbonyl catalyzed hydrosilylation of ketones giving enol silyl ethers as a mixture of *Z* and *E* isomers.[16]

α,β-Unsaturated Nitriles. Finally, hydrosilylation of α,β-unsaturated nitriles was of interest, since they were expected to give several products. However, when $HSiMe_3$ was employed, (*Z*)- or (*E*)-*N*,*N*-disilylenamines were selectively obtained as shown in Table III, although the reaction with $HSi(OEt_3)_3$ and H_2SiPh_2 gave a mixture of N,N-disilylated products. For nitriles **18** and **19**, (*Z*)-enamines were exclusively obtained, whereas the reaction of **20**, **21**, **22**, and **23** gave (*E*)-enamines in low to moderate yields. To the our best knowledge, this is the first example of consecutive 1,2- and 1,4-reduction of α,β-unsaturated nitriles, giving vinylamines[17] as a protected form with silyl groups, since the parent vinylamines have been known to decompose gradually at temperatures higher than −50 °C.[18] Furthermore, the usefulness of *N*,*N*-disilylenamines in organic synthesis has been demonstrated,[19] and the present reaction provides a new route to *Z* isomers which has not been easily accessible by the known methods.[20]

The reaction pathway to *N*,*N*-disilylenamines would involve *N*-silyl-1-aza-1,3-diene intermediate **37** (path A in Scheme II).[21] The selective formation of *Z* isomers would

Table III. Cobalt Carbonyl Catalyzed Addition of Trimethylsilane to α,β-Unsaturated Nitriles[a]

entry	nitrile	products[b,c] yields, %		
1	 17	 24 53 %	 25 7 %	 26 17 %
2	 18 (Z/E = 37/63)	 27 58 % (Z/E = 83/17)	 28 4 %	
3	 19 (Z/E = 16/84)	 29 64 %	 30 15 %	
4	 20	 31 42 % (Z/E = 14/86)		
5	 21 (Z/E = 55/45)	 32 18 % (Z/E = 34/66)	 33 7 % (Z/E = 63/37)	 34 7 %
6	 22	 35 20 %[d] (Z/E = 10/90)		
7	 23	 36 14 %[d]		

[a] Reaction conditions are as follows unless otherwise noted: nitrile (2.5 mmol), $HSiMe_3$ (25 mmol), $CH_3C_6H_5$ (10 mL), 60 °C, 20 h. [b] GLC yields. [c] R represents $SiMe_3$. [d] PPh_3 (0.4 mmol) was added at 100 °C.

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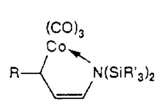
(20) For *N*,*N*-bis(trimethylsilyl)enamines: (a) Walter, W.; Luke, H.-W. *Angew. Chem.* **1977**, *89*, 550. (b) Bassindale, A. R.; Brook, A. G.; Jones, P. F.; Stewart, J. A. G. *J. Organomet. Chem.* **1978**, *152*, C25. (c) Churakov, A. M.; Ioffe, S. L.; Khasapov, B. N.; Tartakovskii, V. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, 129. (d) Sales, F.; Serratosa, F. *Tetrahedron Lett.* **1979**, 3329. (e) Corriu, R. J. P.; Huynh, V.; Moreau, J. J. E.; Pataud-Sat, M. *J. Organomet. Chem.* **1983**, *255*, 359. (f) Ahlbrechet, H.; Duber, E.-O. *Synthesis* **1982**, 273. (g) Okazaki, R.; O-oka, M.; Tokitoh, N.; Shishido, Y.; Inamoto, N. *Angew Chem., Int. Ed. Engl.* **1981**, *20*, 799. (h) Ahlbrechet, H.; Duber, E.-O. *Synthesis* **1983**, 56. (i) Picard, J.-P.; Aziz-Elysusufi, A.; Calas, R.; Dunogues, J.; Duffaut, N. *Organometallics* **1984**, *3*, 1660. (j) Okazaki, R.; O-oka, M.; Tokitoh, N.; Inamoto, N. *J. Org. Chem.* **1985**, *50*, 180. For *N*,*N*-(*o*-phenylenedisilyl)enamines: (k) Corriu, R. J. P.; Moreau, J. J. E. *J. Chem. Soc., Chem. Commun.* **1980**, 278. (l) Corriu, R. J. P.; Moreau, J. J. E.; Pataud-Sat, M. *J. Org. Chem.* **1981**, *46*, 3374. (m) Corriu, R. J. P.; Moreau, J. J.E.; Patuad-Sat, M. *Organometallics* **1985**, *4*, 623.

(21) Two 1,2-additions of a hydrosilane followed by isomerization of the C=C double bond may be possible. However, this can be eliminated by the fact that the ratio of **24** to **25** was unchanged even after a longer reaction time.

be due to the five-membered intermediate **39**, followed by oxidative addition of $HSiR_3$ and reductive elimination of the alkyl group and hydrogen to give the *Z* isomer. The intermediacy of **39** can be supported by the reaction with **20**, where the methylene group of **20** is converted to a methyl group placed on the cis position of the *N*,*N*-disilylamino group in **31**. When alkyl substituents were on both α and β or both β and β positions, steric congestion would retard the formation of **39**.



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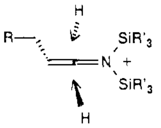

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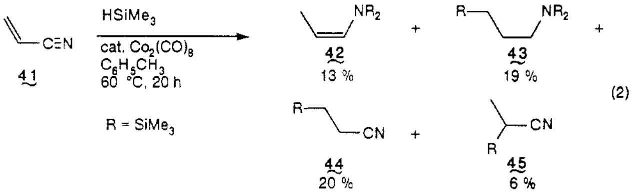
Alternatively, *N*-silylketeneimine intermediate **38** in Scheme II may be possible. However, if hydrogen approaches the *N*,*N*-disilyliminium intermediate **40** from the sterically vacant site in the 1,2-addition of $HSiR_3$ to **38**, more substituted nitriles such as **21**, **22**, and **23** should give *Z* isomers preferentially compared to **18**, **19**, and **20**. Nevertheless, at this point evidence for and/or against the intermediacy of **37**, **38**, **39**, and **40** cannot be provided. Further studies to investigate the mechanism are necessary.[22]

The reaction of acrylonitrile (**41**) gave (Z)-N,N-disilylenamine (**42**) in low yield (eq 2). Instead, addition of a hydrosilane across the C–C double bond became competitive to give **43**, **44**, and **45** as other products. This is not an unexpected result, since terminal olefins have been known to undergo cobalt carbonyl catalyzed hydrosilylation.[24] Interestingly, the present reaction is in marked contrast to a similar reaction with $CH_2{=}CHCOOMe$, giving $Me_3SiCH{=}CHCOOMe$ as a major product.[25] Attempts to improve the yield of **42** failed. For example, total yields of the products decreased to 35%, and **43** was the major product under the reaction conditions adopted for the alkyl nitriles, i.e., at 100 °C with PPh_3.



In conclusion, the combination of $HSiMe_3$ and the cobalt carbonyl catalyst turned out to be effective for reducing nitriles to *N*,*N*-disilylamines. Even at 100 °C, the catalyst has survived the reaction conditions involving amino compounds capable of coordinating to transition metals. The present reaction provides not only a new route to stereochemically defined *N*,*N*-disilylenamines but also additional applicability of the transition-metal-catalyzed hydrosilylation process.

Experimental Section

^{1}H NMR spectra were recorded at 60, 90, or 270 MHz. ^{13}C NMR spectra were recorded at 67.8 MHz. Mass spectra were recorded at 20 eV. Analytical gas chromatography (GLC) was carried out with a flame ionization detector, using a 6 m × 3 mm stainless steel column packed either with 5% silicone OV-1 supported on 60–80-mesh Uniport HP or with 2% silicone OV-1 supported on 60–80-mesh Chromosorb WAW DMCS. Preparative GLC were performed on a 2 m × 10 mm stainless steel column packed with 5% silicone OV-1 supported on 60–80-mesh Uniport HP. Bulb-to-bulb distillation was carried out with a Kugelrohr apparatus.

Materials. Toluene and 1,2-dichloroethane were distilled from phosphorous pentoxide and CaH_2, respectively. Diethyl ether and *n*-hexane were distilled from sodium metal. $Co_2(CO)_8$ was purchased from Strem Chemical Co., recrystallized from *n*-hexane (25 °C to -20 °C), and stored under a carbon monoxide atmosphere in a refrigerator. Triethyl phosphite was distilled in vacuo prior to use. 4-(Cyanomethyl)benzonitrile,[26] 4-anisonitrile,[27] methyl 4-cyanobenzoate,[28] **19**,[29] **20**,[30] **21**,[31] **22**,[32] and **23**[33] were prepared by the literature methods. Other nitriles are commercially available. Trimethylsilane was prepared by the known procedure[32] and stored in a special stainless bottle.[11a]

General Procedure for the Reaction of Nitriles with $HSiMe_3$ in the Presence of a Catalytic Amount of $Co_2(CO)_8$. A 10-mL, two-necked, round-bottomed flask equipped with an efficient dry ice condenser and a Teflon-coated magnetic stirrer bar was flame-dried, charged with $Co_2(CO)_8$ (0.068 g, 0.2 mmol), and then fitted with a serum cap and CO balloon. To this flask was added $HSiMe_3$ (2.83 mL, 25 mmol) with a special apparatus[11a] at -20 °C, and the solution was stirred for ca. 5 min. To the resulting solution were added toluene (10 mL) and nitrile (2.5 mmol) in this order. The temperature of the reaction mixture was raised to 60 °C, and the solution was stirred for 20 h. Solvent was removed in vacuo, and the residue was dissolved in *n*-hexane, filtered, and concentrated, followed by bulb-to-bulb distillation to give the desired *N*,*N*-disilylamine as a colorless liquid. In some cases this was further purified by preparative gas chromatography.

1,1,1-Trimethyl-*N*-(cyclopropylmethyl)-*N*-(trimethylsilyl)silanamine (10): bp 90 °C (18 mm); IR (neat) 3090, 2960, 1284, 1258, 1166, 1060, 1015, 941, 907, 869, 837, 763 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 18 H, Si-CH_3), 0.15 (m, 2 H, CH_2), 0.40–0.47 (m, 2 H, CH_2), 0.67–0.82 (m, 1 H, CH), 2.68–2.74 (m, 2 H, CH_2-N); MS *m/e* 215 (M$^+$, 17), 200 (63), 173 (29), 73 (68). Anal. Calcd for $C_{10}H_{25}NSi_2$: C, 55.74; H, 11.69; N, 6.50. Found: C, 55.74; H, 11.85; N, 6.53.

1,1,1-Trimethyl-*N*-[(2-phenylcyclopropyl)methyl]-*N*-(trimethylsilyl)silanamine (11): bp 130 °C (1 mm); IR (neat) 3100, 3090, 3030, 2950, 2910, 1880, 1610, 1588, 1503, 1450, 1417, 1377, 1349, 1300, 1251, 1170, 1108, 1060, 1027, 980, 926, 896, 830, 764, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$ δ 0.11 (s, 18 H, Si-CH_3), 0.65 (m, 2 H, CH_2), 0.81 (m, 2 H, CH_2), 3.15 (s, 2 H, CH_2-N), 7.14–7.37 (m, 5 H, Ar); MS *m/e* 291 (M$^+$, trace), 276 (5), 174 (100), 86 (16), 73 (38). Anal. Calcd for $C_{16}H_{29}NSi_2$: C 65.91; H, 10.03; N, 4.80. Found: C, 65.55; H, 10.16; N, 4.91.

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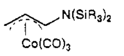
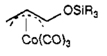
(22) Another mechanism, involving (π-allyl)cobalt intermediate i, may be possible. But it has been reported that anti isomer ii is preferencially formed by the reaction of $CH_2{=}CHCHO$ with **12**[23a] and that alkylation of (π-allyl)cobalt complex gives *E* olefins.[23b,c] Even so, the intermediacy of a syn (π-allyl)cobalt complex analogous to i cannot be completely ruled out, since the syn complex has been prepared by alkylation of a diene–cobalt complex and further alkylation gave *Z* olefins.[23d]



i



ii

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1,1,1-Trimethyl-*N*-(2-methyl-1-propenyl)-*N*-(trimethylsilyl)silanamine (24): bp 50 °C (2 mm); IR (neat) 2975, 1653, 1450, 1436, 1401, 1381, 1345, 1297, 1248, 1143, 1029, 8965, 874, 835, 766, 751 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.05 (s, 18 H, Si-CH$_3$), 1.54 (d, *J* = 1.3 Hz, 3 H, CH$_3$), 1.62 (d, *J* = 1.1 Hz, 3 H, CH$_3$), 5.57 (m, 1 H, =CH); MS *m/e* 215 (M$^+$, 34), 200 (100), 172 (30), 142 (20), 126 (35), 112 (10), 73 (73). Anal. Calcd for $C_{10}H_{25}NSi_2$: Si, 55.74; H, 11.69; N, 6.50. Found: C, 55.68; H, 11.88; N, 6.44.

(*Z*)-1,1,1-Trimethyl-*N*-1-butenyl-*N*-(trimethylsilyl)silanamine (27): bp 70 °C (16 mm); IR (neat) 2975, 1632, 1454, 1394, 1262, 1248, 1134, 1070, 1048, 1012, 968, 940, 889, 830, 755, 732 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.08 (s, 18 H, Si-CH$_3$), 0.93 (t, *J* = 7.6 Hz, 3 H, CH$_3$), 2.03 (doublet-quintet, *J* = 7.5 and 1.7 Hz, 2 H, CH$_2$), 5.04 (q, *J* = 7.1 Hz, 1 H, =CHC), 5.71 (dt, *J* = 7.5 and 1.7 Hz, 1 H, =CH-N); MS *m/e* 215 (M$^+$, 31), 200 (100), 172 (30), 126 (35), 112 (35), 73 (82). Anal. Calcd for $C_{10}H_{25}NSi_2$: C, 55.74; H, 11.69; N, 6.50. Found: C, 55.79; H, 11.88; N, 6.58.

(*Z*)-1,1,1-Trimethyl-*N*-(3-phenyl-1-propenyl)-*N*-(trimethylsilyl)silanamine (29): bp 130 °C (4 mm); IR (neat) 3080, 3040, 3025, 2975, 2910, 1627, 1600, 1493, 1450, 1388, 1250, 1097, 1069, 1031, 998, 966, 941, 924, 869, 832, 737 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.14 (s, 18 H, SiCH$_3$), 3.43 (dd, *J* = 6.8 and 1.8 Hz, 2 H, CH$_2$), 5.31 (dt, *J* = 7.3 and 6.8 Hz, 1 H, =CHC), 5.91 (dt, *J* = 7.3 Hz and 1.8 Hz, 1 H, =CHN), 7.16–7.34 (m, 5 H, Ar); MS *m/e* 277 (M$^+$, 51), 262 (48), 204 (78), 172 (54), 73 (100). Anal. Calcd for $C_{15}H_{27}NSi_2$: C, 64.91; H, 9.81; N, 5.05. Found: C, 64.63; H, 10.05; N, 5.13.

(*E*)-1,1,1-Trimethyl-*N*-(3-phenyl-2-propenyl)-*N*-(trimethylsilyl)silanamine (30): bp 130 °C (4 mm); IR (neat) 3085, 3050, 2975, 2920, 1650, 1630, 1599, 1578, 1496, 1447, 1405, 1354, 1253, 1103, 1072, 1030, 1008, 965, 943, 909, 883, 835, 752, 727 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.13 (s, 18 H, Si-CH$_3$), 3.63 (dd, *J* = 4.9 and 1.6 Hz, 2 H, CH$_2$), 6.15 (dt, *J* = 15.8 and 4.9 Hz, 1 H, =CHCN), 6.45 (dt, *J* = 15.8, 1.6 Hz, 1 H, =CHPh), 7.18–7.37 (m, 5 H, Ar).

Mixture of (*Z*)- and (*E*)-1,1,1-trimethyl-*N*-(3-phenyl-2-methyl-1-propenyl)-*N*-(trimethylsilyl)silanamines 31 (*Z*/*E* = 14/86): bp 100 °C (0.3 mm); IR (neat) 3090, 3060, 2980, 1643, 1600, 1494, 1452, 1251, 1178, 1126, 965, 875, 838, 751, 700, 677, 615 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.07 (s, 15.4 H, Si-CH$_3$ of (*E*)-**31**), 0.13 (s, 2.6 H, Si-CH$_3$ of (*Z*)-**31**), 1.45 (d, *J* = 1.5 Hz, 2.6 H, CH$_3$ of (*E*)-**31**), 1.49 (d, *J* = 1.5 Hz, 0.4 H, CH$_3$ of (*Z*)-**31**), 3.26 (br s, 1.7 H, CH$_2$ or (*E*)-**31**), 3.44 (br s, 0.3 H, CH$_2$ of (*Z*)-**31**), 5.78 (m, 0.1 H, =CH of (*Z*)-**31**), 5.80 (m, 0.9 H, =CH of (*E*)-**31**), 7.16–7.30 (m, 5 H, Ph) [The stereochemistry was supported by the NOE measurement conducted on a JEOL-GX 270 (270 MHz) instrument as follows. Irradiation of CH$_2$ of (*Z*)-**31** at 3.26 enhanced the intensity of =CH by 16%, whereas no effect was observed in the case of (*E*)-**31**.]; ^{13}C NMR (CDCl$_3$) δ 1.6 (Si-CH$_3$ of (*E*)-**31**), 1.8 (Si-CH$_3$ of (*Z*)-**31**), 15.2 (CH$_3$ of (*E*)-**31**), 19.2 (CH$_3$ of (*Z*)-**31**), 36.9 (CH$_2$ of (*Z*)-**31**), 43.1 (CH$_2$ of (*E*)-**31**), 125.8 (Ph of (*Z*)-**31**), 125.9 (Ph of (*E*)-**31**), 128.1 (Ph of (*Z*)-**31**), 128.2 (Ph of (*E*)-**31**), 128.7 (Ph of (*Z*)-**31**), 128.9 (Ph of (*E*)-**31**), 129.0 (Ph of (*Z*)-**31**), 129.2 (Ph of (*E*)-**31**); MS *m/e* 291 (M$^+$, 15), 276 (19), 218 (100), 73 (76). Anal. Calcd for $C_{16}H_{29}NSi_2$: C, 65.91; H, 10.03; N, 4.80. Found: C, 65.93; H, 10.08; N, 4.69.

Mixture of (*Z*)- and (*E*)-1,1,1-trimethyl-*N*-(2-methyl-1-butenyl)-*N*-(trimethylsilyl)silanamines 32 (*Z*/*E* = 34/66): bp 100 °C (18 mm); ^{1}H NMR (CDCl$_3$) δ 0.049 (s, 11.8 H, Si-CH$_3$ of (*E*)-**32**), 0.051 (s, 6.2 H, Si-CH$_3$ of (*Z*)-**32**), 0.93 (t, *J* = 7.5 Hz, 1 H, CH$_3$ of (*Z*)-**32**), 0.98 (t, *J* = 7.5 Hz, 2 H, CH$_3$ of (*E*)-**32**), 1.53 (d, *J* = 1.5 Hz, 2.0 H, =CCH$_3$ of (*E*)-**32**), 1.59 (d, *J* = 1.5 Hz, 1.0 H, =CH$_3$ of (*Z*)-**32**), 1.96 (dq, *J* = 7.5 and 0.9 Hz, 1.3 H, CH$_2$ of (*E*)-**32**), 2.07 (dq, *J* = 7.5 and 0.9 Hz, 0.7 H, CH$_2$ of (*Z*)-**32**), 5.54 (m, 0.3 H, =CH of (*Z*)-**32**), 5.61 (m, 0.7 H, =CH of (*E*)-**32**).

Mixture of (*Z*)- and (*E*)-1,1,1-trimethyl-*N*-(2-cyclohexyl-1-ethenyl)-*N*-(trimethylsilyl)silanamines 35 (*Z*/*E* = 10/90): bp 100 °C (3 mm); IR (neat) 2940, 2880, 1638, 1445, 1398, 1303, 1250, 1150, 1134, 1090, 978, 943, 892, 871, 836, 752 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.10 (s, 2.3 H, Si-CH$_3$ of (*Z*)-**35**), 0.11 (s, 15.7 H, Si-CH$_3$ of (*E*)-**35**), 0.90–1.40 (m, 6 H, CH$_2$), 1.53–1.80 (m, 4 H, CH$_2$), 1.90 (m, 1 H, CH), 4.88 (dd, *J* = 9.9 and 7.5 Hz, 0.1 H, =CHC of (*Z*)-**35**), 4.89 (dd, *J* = 13.6 and 7.8 Hz, 0.9 H, =CHC of (*E*)-**35**), 5.62 (dd, *J* = 7.5 Hz and 0.9 Hz, 0.1 H, =CHN of (*Z*)-**35**), 5.79 (dd, *J* = 13.6 and 0.9 Hz, 0.9 H, =CH-N of (*E*)-**35**); MS *m/e* 269 (M$^+$, 50), 254 (30), 226 (100), 196 (22), 172 (37), 147 (26), 73 (99). Anal. Calcd for $C_{14}H_{31}NSi_2$: C, 62.38; H, 11.59; N, 5.20. Found: C, 62.41; H, 11.82; N, 5.43.

(*E*)-1,1,1-Trimethyl-*N*-(3-methyl-1-pentenyl)-*N*-(trimethylsilyl)silanamine (36): bp 100 °C (18 mm); IR (neat) 2975, 1637, 1452, 1403, 1378, 1248, 1155, 1109, 972, 945, 873, 836, 750 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.12 (s, 18 H, Si-CH$_3$), 0.86 (t, *J* = 7.3 Hz, 3 H, CH$_3$), 0.96 (d, *J* = 6.8 Hz, 3 H, CH$_3$), 1.27 (m, 2 H, CH$_2$), 1.94 (m, 1 H, CH), 4.79 (dd, *J* = 13.7 and 8.5 Hz, 1 H, =CHC), 5.78 (dd, *J* = 13.7 and 0.7 Hz, 1 H, =CHN); MS *m/e* 243 (M$^+$, 16), 228 (27), 214 (100), 147 (14), 140 (12), 126, 73 (60).

Acknowledgment. We thank Professors N. Sonoda and S. Murai, Osaka University, for valuable discussions. Shin-Etsu Chemical Industries Co., Ltd., kindly provided the chlorosilanes.

Supplementary Material Available: Spectral data for the products in Table I and compounds **6**–**9** (6 pages). Ordering information is given on any current masthead page.