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ADDITION OF TRIMETHYLSILYL CYANIDE TO ALLENES WITH THE AID OF A PALLADIUM OR NICKEL CATALYST

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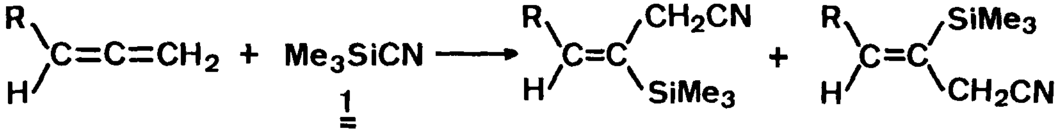
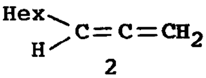
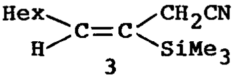
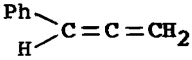
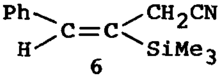
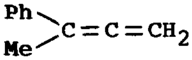
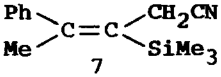
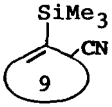
Summary: The reaction of allenes with trimethylsilyl cyanide in the presence of a palladium or nickel catalyst provides functinalized vinylsilanes in good yields.

We have reported a new palladium-catalyzed reaction of trimethylsilyl cyanide (**1**) with acetylenes.1) This reaction represents the first example for the addition of silyl cyanide across a carbon-carbon multiple bond. In order to extend the scope of the new catalytic reaction of **1**, have been studied the reactions of **1** with allenes in the presence of a transition metal complex. We now wish to report that a palladium or nickel complex catalyses the addition of **1** to allenes. The new reaction gave functinalized vinysilanes in good yields.

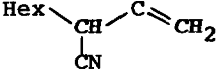


The representative results are shown in Table 1. The reaction of 1,2-nonadiene (**2**) with **1** gave mainly vinylsilane **3E**,2) along with **3Z** and **4** in low yields (entries 1-5). In all products the trimethylsilyl group is found at the central carbon atom of allene. The stereochemistry of vinylsilanes **3E** and **3Z** was determined on the basis of ^{1}H NMR.3)4) The stereochemistry was further confirmed by protodesilylation (I_2/H_2O)5) of **3E** leading to 3-(**Z**)-decenitrile (**5**).6) The reaction rate was accelerated by the addition of pyridine. The role of pyridine, however, is not clear. A number of other additive, including amines (Et_3N, bipyridyl, N,N-dimethylaniline, and N,N-dimethylaminopyridine), triphenylphosphite, and Lewis acids ($AlCl_3$, and $ZnCl_2$) were examined, but no improvement in regio- and

Table 1. The Reaction of Allenes with Me_3SiCN (1) in the presence of Palladium or Nickel Catalyst[a]

entry	allene		product[b]
	catalyst	additive	
	 2		 3
1	$PdCl_2$	-	70% (E/Z=89/11)[d]
2	$PdCl_2$	pyridine	66% (E/Z=95/5)[d]
3[c]	$PdCl_2$	pyridine	62% (E/Z=92/8)[d]
4	$PdBr_2$	pyridine	87% (E/Z=89/11)[d]
5	$NiCl_2$	DIBAH	54% (E/Z=72/28)[e]
			 6
6	$PdCl_2$	pyridine	67% (E/Z=88/12)
7	$PdBr_2$	pyridine	75% (E/Z=89/11)
8	$NiCl_2$	DIBAH	48% (E/Z=54/46)
			 7
9	$PdBr_2$	pyridine	60% (E/Z=67/33)[f]
10	$NiCl_2$	DIBAH	58% (E/Z=64/36)[f]
			
11	$PdBr_2$	pyridine	59% 8
12	$NiCl_2$	DIBAH	78%

[a] All reactions were carried out on a scale as described in the text unless otherwise noted. [b] GLC yields based on allenes. [c] Triethylsilyl cyanide (Et_3SiCN) was used in place of **1**. [d] **4** was obtained in 3-7% yield in each cases. [e] **4** was obtained in 20% yield. [f] Stereochemistry was tentatively assigned.



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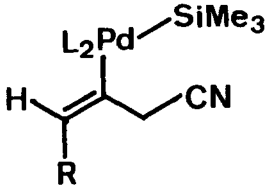
stereoselectivity was realized. The use of triethylsilyl cyanide in place of **1** did not affect the selectivity (entry 3). Other palladium catalysts which showed a catalytic activity for the reaction of **2** were $Pd(OAc)_2$, $(PhCN)_2PdCl_2$, and $Pd(PPh_3)_4$. The reaction can also be effected by $NiCl_2$/DIBAH, but the regio- as well as stereoselectivity decreased (entry 5).

The reaction of phenylallene with **1** resulted in the addition of **1** to the terminal carbon-carbon double bond of allene and vinylsilanes were obtained as a mixture of stereoisomers **6E** and **6Z**7) (entries 6-8). No regioisomer (analogous to **4**) was detected spectrometrically in the crude reaction mixture. In case of 1,1-methylphenylallene, the reaction proceeded with low stereoselectivity (entries 9 and 10).8) The reaction of 1,2-cyclononadiene with **1** also gave the addition product **8**9) (entries 11 and 12).

No detailed rationale could be given about the mechanism of the present reactions. We feel it necessary to contemplate three possible reaction pathways. Firstly, addition of Pd-CN to the coordinated allene could occur in the similar sense to chloropalladation of allene,10) generating silylvinylpalladium complex **9**, followed by reductive elimination to afford the product. Secondly, addition of Pd-Si to allene may give π-allyl palladium complex **10**, followed by attack of CN^- to the terminus. Finally, the path via a complex **11** could be considered.



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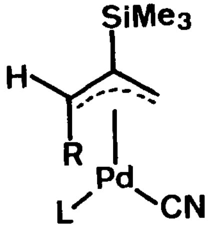

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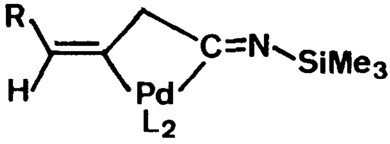

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The studies to explore and extend the utility of this novel transition metal-catalyzed reaction of **1** are under investigation and will be reported in due course.

Typical Experimental Procedure

A mixture of 2.5 mmol (0.31 mL) of phenylallene, 5 mmol (0.67 mL) of **1**, 0.1 mmol (18 mg) of $PdCl_2$, and 0.2 mmol (16 μL) of pyridine in toluene (5 mL) was heated under reflux (bath temperature 120-130°C) with stirring for 20 h under nitrogen. The resulting solution was analyzed by GLC on Shimazu Hicap-CBP1 capillary column with reference to an internal standard (n-pentadecane). Solvent was removed in vacuo and the residue was distilled by bulb-to-bulb distillation (bp 150-160°C/15 mmHg) to give a mixture of **6E** and

6Z, which were essentially pure (280 mg, 59 % yield). The analytical sample was obtained by preparative TLC (Merk Kieselgel 60F-254) using 10% EtOAc in hexane, as an eluent.

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2) All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, IR, and mass spectral data and elemental analyses.

3) T. H. Chan, W. Mychajlowskij, and R. Amouroux, Tetrahedron Lett., 1605 (1977).

4) Selected ^{1}H NMR data of **3E**, **3Z**, and **4** are as follows. **3E:** 0.15 (s, Si-CH_3), 3.08 (s, -CH_2-), 5.97 (t, J=7.2 Hz, =CH). **3Z:** 0.20 (s, Si-CH_3), 3.05 (s, -CH_2-), 6.32 (t, J=7.0 Hz, =CH). **4:** 0.17 (s, Si-CH_3), 3.32 (t of ABq, J=5.6, 8.7 Hz, -CH-CN), 5.60 (d, J=1.0 Hz, =CH_2), 5.97 (d, J=1.0 Hz, =CH).

5) K. Utimoto, M. Kitai, and H. Nozaki, Tetrahedron Lett., 2825 (1975).

6) The stereochemistry of **5** was confirmed by the vicinal olefinic coupling constant (J=10.5 Hz) in the ^{1}H NMR spectrum.

7) **6E:** ^{1}H NMR ($CDCl_3$) δ 0.28 (s, Si-CH_3), 3.24 (d, J=1.3 Hz, -CH_2-), 7.02 (d, J=1.3 Hz, =CH), 7.24-7.39 (m, Ph). ^{13}C NMR ($CDCl_3$) δ -1.58 (Si-CH_3), 18.48 (-CH_2-), 118.72 (CN). IR (neat) 2250 (CN). **6Z:** ^{1}H NMR ($CDCl_3$) δ 0.00 (s, Si-CH_3), 3.26 (d, J=1.7 Hz, -CH_2-), 7.19-7.32 (m, Ph), 7.51 (d, J=1.7 Hz, =CH). ^{13}C NMR ($CDCl_3$) δ -0.23 (Si-CH_3), 25.84 (-CH_2-), 118.42 (CN). IR (neat) 2225 (CN). mass spectrum (E/Z mixture) 215 (M^+). Anal Calcd for $C_{13}H_{17}NSi$ (E/Z mixture) : C, 72.50; H, 7.96; N, 6.50. Found: C, 72.79; H, 8.07; N, 6.69.

8) Stereochemistry of **7E** and **7Z** is tentatively assigned. **7E:** ^{1}H NMR ($CDCl_3$) δ 0.50 (s, Si-CH_3), 2.30 (s, -CH_3), 3.36 (s, -CH_2-), 7.25-7.65 (m, Ph). ^{13}C NMR ($CDCl_3$) δ -0.23 (Si-CH_3), 19.56 (-CH_3), 23.03 (-CH_2-), 118.52 (CN), 145.13 (=CH), 154.24 (=C-). **7Z:** ^{1}H NMR ($CDCl_3$) δ 0.00 (s, Si-CH_3), 1.74 (s, -CH_3), 3.04 (s, -CH_2-), 7.25-7.55 (m, Ph). ^{13}C NMR ($CDCl_3$) δ -0.14 (Si-CH_3), 21.73 (-CH_3), 25.43 (-CH_2-), 119.37 (CN), 143.52 (=CH-), 154.00 (=C-). IR (neat, E/Z mixture) 2250 (CN). mass spectrum (E/Z mixture) 229 (M^+). Anal. Calcd for $C_{14}H_{19}NSi$ (E/Z mixture): C, 73.30; H, 8.35; N, 6.11. Found: C, 73.36; H, 8.25; N, 6.09.

9) ^{1}H NMR ($CDCl_3$) δ 0.19 (s, Si-CH_3), 1.30-2.50 (m, -CH_2-), 3.78 (dd, J=4.0, 10.3 Hz, -CH-), 6.08 (t, J=8.6 Hz, =CH). IR (neat) 2230 (CN). mass spectrum 221 (M^+). Anal. Calcd for $C_{13}H_{23}NSi$: C, 70.52; H, 10.47; N, 6.33. Found: C, 70.22; H, 10.44; N, 6.40.

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