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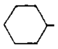
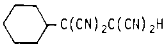
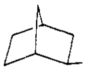
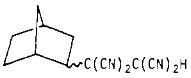
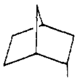
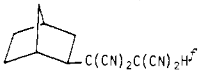
Alkylation of Tetracyanoethylene with Organopentafluorosilicates: Implication of One-Electron-Transfer Mechanism[1]

Sir:

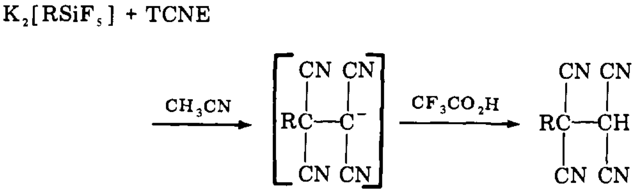
Remarkable attention has been given to the elucidation of the mechanism of cleavage of carbon-metal bonds and the importance of an electron-transfer process has been suggested not only for transition metal alkyls but also for main group organometallics.[2] Alkyl carbon-silicon bonds in hexacoordinate organopentafluorosilicates, $K_2[RSiF_5]$, are now known to be cleaved readily by the action of various electrophiles or oxidizing agents which do not affect those in neutral tetracoordinate silanes.[3] However, a fundamental insight into how carbon-silicon bonds in organosilicates are cleaved has not yet been obtained. To test whether an electron-transfer mechanism is possible for carbon-silicon bond cleavage reactions, we have investigated the reaction of alkylpentafluorosilicates with tetracyanoethylene (TCNE)[4] which is considered to be a typical one-electron acceptor. We describe here the first case of alkylation of TCNE with alkylpentafluorosilicates and several experimental results consistent with a one-electron-transfer mechanism.[5]

Table I. Reaction of Alkylpentafluorosilicates with TCNE in CH_3CN^a

R in $K_2[RSiF_5]$	conditions	product^b	yield (%)^c
CH_3-	rt, 1 h		0^d
C_2H_5-	rt, 1 h	$C_2H_5C(CN)_2C(CN)_2H$	11
n-C_8H_{17}-	3 °C, 0.5 h	n-$C_8H_{17}C(CN)_2C(CN)_2H$	64
	3 °C, 8 h		34
 (*exo* 100%)	3 °C, 8 h	 (*exo*/*endo* = 1/1)^e	19
 (*endo* 95%)	3 °C, 8 h		5

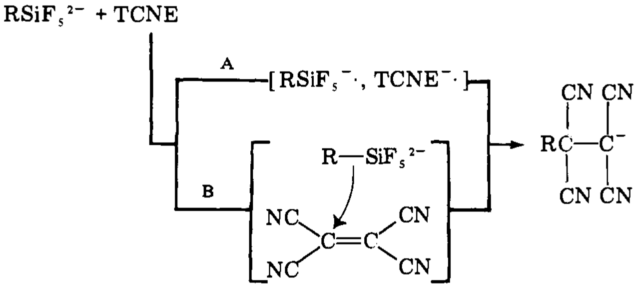
^{a} $K_2[RSiF_5]$ (5.0 mmol) was allowed to react with 1.0 mmol of TCNE in 10 mL of CH_3CN and decomposed with trifluoroacetic acid. ^{b} Identified by ^{1}H NMR, IR, and MS spectra and elemental analyses. ^{c} Isolated yield based on TCNE. ^{d} Methylpentafluorosilicate and TCNE were recovered unchanged. ^{e} Determined by ^{1}H NMR. ^{f} Only exo isomer was observed by ^{1}H NMR.

The addition of TCNE to a suspension of n-octylpentafluorosilicate in acetonitrile at −40 °C under an atmosphere of nitrogen resulted in the formation of a deep blue mixture. On warming to 3 °C it turned to grayish green and gradually became dark brown in 0.5 h. After treatment with trifluoroacetic acid, 1,1,2,2-tetracyanodecane (**1**, R = C_8H_{17}),[6] the alkylation product, was isolated in 64% yield. The results obtained with several alkylpentafluorosilicates are summarized in Table I.[7]



2 **1**

While no electronic spectral evidence for participation of charge-transfer complexes in the present reaction was obtained owing to the insolubility of potassium organopentafluorosilicates in organic solvents, electron spin resonance (ESR) studies have proven the formation of the TCNE anion radical. Thus, shaking a degassed acetonitrile solution of TCNE with powder of octylpentafluorosilicate gave intense ESR absorptions due to the TCNE anion radical ($a_N = 0.157_1$ mT, $g = 2.0027_7$).[8]



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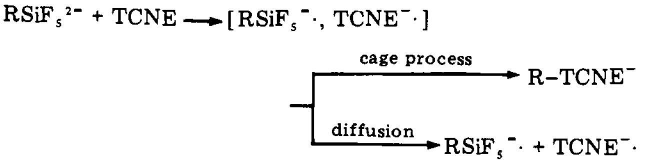
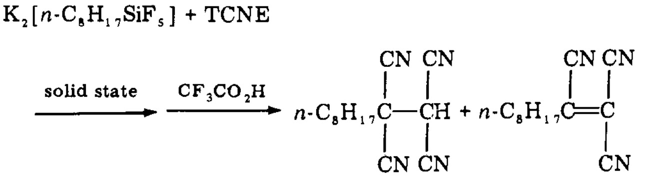
The ESR monitoring of the reaction mixture revealed, if qualitatively, that TCNE anion radicals appeared to be accumulated as the reaction proceeded. These facts strongly suggest that the present reaction proceeds by an initial one-electron transfer from silicate to TCNE (route A) rather than a direct electrophilic alkyl transfer (route B), and that there may be some leakage of radical species from the cage.

Although kinetic data were not available, the relative reactivities of alkylpentafluorosilicates shown in Table I provide further support for the electron-transfer mechanism. While the methylsilicate failed to react with TCNE probably because of the low electron-donating ability of the methyl group, cyclohexyl- and 2-norbornylsilicates reacted in spite of steric hindrance. These facts are also consistent with the electron-transfer mechanism in which the electron-donating ability of an alkyl group is more important than steric factors.[4b]

The following observation is also worth noting. In the reaction of *exo*-2-norbornylpentafluorosilicate[1] with TCNE a 1:1 mixture of *exo*- and *endo*-(2-norbornyl)-1,1,2,2-tetracyanoethane[9] was formed, whereas from *endo*-2-norbornylsilicate[1] only one isomer of the alkylation products was obtained, which was identified as the exo isomer by its ^{1}H NMR spectrum.[10] This stereochemical result[12] suggests a partial diffusion of the norbornyl radical from a cage arising from the exo silicate. In the main reaction course, there must be some interaction between carbon and silicon atoms during the transfer of an alkyl group to the TCNE anion radical or TCNE. Alkyl transfer may occur not only within a cage, but also after diffusion of radical species.[13]



Similar alkylation reactions also took place in the solid state. Mixing of powdered octylpentafluorosilicate and TCNE under vacuum resulted in a violet mixture which showed intense ESR absorptions due to the TCNE anion radical.[14] Stirring the solid mixture at 3 °C for 8 h, followed by quenching with trifluoroacetic acid, afforded 1,1,2,2-tetracyanodecane (**1**, R = C_8H_{17}) and 1,1,2-tricyano-1-decene (**3**) in 80 and 13% yields, respectively. The latter is considered to be formed by elimination of hydrogen cyanide from the cyanocarbanion intermediate **2** under reduced pressure.[4a] The successful electron-transfer reaction in the solid state indicates that an electron-transfer process can occur at the solid surface of organopentafluorosilicates.



$$K_2[n\text{-}C_8H_{17}SiF_5] + TCNE \xrightarrow{\text{solid state}} \xrightarrow{CF_3CO_2H} n\text{-}C_8H_{17}C(CN)_2\text{—}CH(CN)_2 + n\text{-}C_8H_{17}C(CN)\text{=}C(CN)_2$$

80% **3**, 13%

In conclusion the reaction of organopentafluorosilicates with TCNE proceeds through an initial one-electron transfer. The ease of one-electron release from organopentafluorosilicates suggests their relatively low ionization potentials and the possibility that their reactions with other oxidizing agents may also involve such an electron-transfer process. Further mechanistic studies are now in progress.

Acknowledgment. We thank the Ministry of Education for the Grant-in-Aid for Scientific Research (No. 303523) and Shin-etsu Chemical Co., Ltd., for support of the work, and Dr. M. Ohuchi of JEOL Ltd. for measurements of ^{13}C NMR spectra.

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(5) Allyltrimethylsilane has been reported to react with TCNE to form 4,4,5,5-tetracyano-1-pentene after hydrolysis.[4g]

(6) $n^{20}{}_D$ 1.4585; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.90 (t, J = 6 Hz, 3 H), 1.1–2.0 (m, 12 H), 2.1–2.4 (m, 2 H), 4.45 (s, 1 H) ppm; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 110.68 (s), 107.37 (s), 39.59 (s), 35.82 (t), 31.64 (t), 31.59 (d), 28.91 (t, t), 28.42 (t), 25.64 (t), 22.57 (t), 14.02 (q) ppm; MS (24 eV) *m/e* (%) 215 ($M^+ - HCN$, 1), 214 (2), 200 (7), 186 (25), 172 (28), 159 (22), 158 (17), 145 (18), 144 (11), 117 (31), 69 (11), 57 (100), 43 (98), 41 (27); IR (neat) 2925 (s), 2855 (m), 2265 (vw), 1415 (s), 1376 (w), 895 (w), 758 (m), 738 (m), 721 cm^{-1} (w). Calcd for $C_{14}H_{18}N_4$: C, 69.39; H, 7.49; N, 23.12. Found: C, 69.52; H, 7.55; N, 23.21. Similar alkylation products have been obtained by the reaction of TCNE with Grignard reagents and other metal alkyls.[4a,b]

(7) All products exhibited consistent ^{1}H NMR, IR, and MS spectra and elemental analysis.

(8) ESR parameters for TCNE anion radical generated by reduction with potassium metal in 2-methyltetrahydrofuran were $a_N = 0.157_2$ mT and $g = 2.0027_9$.

(9) Determined by comparison of intensities of ^{1}H NMR (100 MHz) signals of the methine proton $-C(CN)_2H$. These methine signals arising from two stereoisomers occur as a very close doublet around 4.4 ppm in $CDCl_3$, but shift upfield and separate sufficiently so that the intensities in a mixture of benzene and $CDCl_3$ containing a small amount of trifluoroacetic acid can be measured.

(10) Only one methine proton $-C(CN)_2H$ was observed by ^{1}H NMR and it was identified as the exo isomer by the inspection of the spin coupling pattern of the norbornyl 2-methine proton[11] (δ 2.25 ppm, br t, J = 6.8 Hz).

(11) Flautt, T. J.; Erman, W. F. *J. Am. Chem. Soc.* **1963,** *85*, 3212.

(12) Similar stereochemical phenomena have been observed for the bromine cleavage of *exo*- and *endo*-2-norbornylsilicate.[1]

(13) The latter step may be followed by several radical chain processes which are consistent with all of the present observations, e.g.,

$$RSiF_5^{-}\cdot + TCNE \rightarrow R\text{–}TCNE\cdot + SiF_5^{-}$$

$$R\text{–}TCNE\cdot + RSiF_5^{2-} \rightarrow R\text{–}TCNE^{-} + RSiF_5^{-}\cdot$$

$$RSiF_5^{-}\cdot \rightarrow R\cdot + SiF_5^{-}$$

$$R\cdot + TCNE \rightarrow R\text{–}TCNE\cdot$$

We thank one of the referees for suggestions of radical chain mechanisms.

(14) The ESR spectrum of the solid mixture measured at 77 K coincides with that of a frozen 2-methyltetrahydrofuran solution of potassium tetracyanoethylenide observed at 77 K.

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Titanium-Mediated Methylene-Transfer Reactions. Direct Conversion of Esters into Vinyl Ethers

Sir:

To date, the direct methylenation of esters (eq 1) via phosphorus ylides has not proven to be a generally viable synthetic operation.[1,2] However, recent studies by Schrock[3] and Tebbe[4] show that the more electrophilic "transition metal ylides" such

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