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Structure and Reactivity of 1-Isothiocyanatosilatrane: The First Silatrane with a Direct Si−NCS Bond

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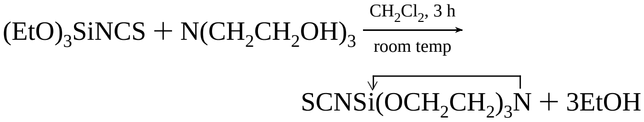
Introduction

Silatranes (cyclic organosilicon ethers of tris(2-oxyalkyl)-amines) constitute a unique class of pentacoordinate silicon compounds and thus have been extensively studied for the past 3 decades.[1] Numerous publications have appeared in the literature throwing light on various structural aspects, including the N→Si transannular bond in the distorted trigonal bipyramid geometry at the silicon atom.[1−3] These compounds are also important because of the stereoelectronic influence of the silatranyl group in shaping the reactivity of the exocyclic functional groups apical to the transannular bond.[4−8] The molecules have also created interest because of their applications in medicine and agriculture.[9] All of these factors have contributed to understand the structure−reactivity relationship in these types of compounds by incorporating modifications in the silatranyl group (mostly replacing O with N, C, or S) or in the exocyclic group opposite to the transannular N→Si bond. The literature, however, records that the silatranes with exocyclic inorganic functionalities have received much less attention.

1-Isothiocyanatosilatrane, **1**, is accessible under mild conditions by the classical approach.



$$(EtO)_3SiNCS + N(CH_2CH_2OH)_3 \xrightarrow[\text{room temp}]{CH_2Cl_2,\ 3\ h} SCNSi(OCH_2CH_2)_3N + 3EtOH$$

The reaction proceeds with remarkable selectivity with retention of the Si−N(CS) bond. Multinuclear (^{13}C, ^{29}Si and ^{14}N) NMR studies and X-ray crystal structure analyses have revealed some novel features of the molecule. These are supported by its chemical reactivity as well as semiempirical calculations. The details are reported in this paper.

Spectral Studies

The new silatrane **1** has been characterized by elemental analyses, IR, multinuclear (^1H, ^{13}C, ^{29}Si and ^{14}N) NMR, and mass spectroscopy. IR spectra in Nujol/acetonitrile solution show a ν_{NCS} absorption at 2110 cm^{-1}. In addition, the bands at 940, 910, and 660 cm^{-1} are attributed to the silatranyl skeletal vibrations with the predominant contribution from the N→Si dative bond.[10] The mass spectrum (EI, 70 eV) clearly reveals the parent ion, M^+ at *m*/*z* 232. The base peak at *m*/*z* 174 corresponds to the $[M^+ - NCS]$ ion.

Multinuclear (^1H, ^{13}C, ^{14}N and ^{29}Si) NMR spectra are consistent with the structure. There are some noteworthy features in the spectra (Figure 1). For example in the ^{13}C NMR spectrum, the isothiocyanato carbon resonates as a 1:1:1 triplet due to coupling to a quadrupolar ^{14}N nucleus [$J\ (^{13}C-^{14}N) = 26.17$ Hz]. ^{29}Si NMR spectrum also shows a similar pattern arising due to $^{29}Si-^{14}N$ coupling ($J = 28.47$ Hz). This coupling is further confirmed by the ^{14}N NMR spectrum of the silatrane. The direct observation of such concomitant heteronuclear couplings between ^{14}N (NCS) and the neighboring nuclei (^{13}C and ^{29}Si) at room temperature is unprecedented in organosilicon isothiocyanates. In principle, such couplings are attributed to increased quadrupolar relaxation of the ^{14}N nucleus as well as a minimal electric field gradient at nitrogen atom.[11]

Crystal Structure

The ORTEP plot of **1** showing atomic labelling scheme is shown in Figure 2. Crystal data, atomic coordinates, and selected bond lengths and angles are given in Tables 1−3, respectively. X-ray crystal structure reveals that the molecule adopts almost regular trigonal bipyramidal geometry with ∠O(1)−Si−O(2) = 120.6(1), O(1)−Si−O(3) = 120.0(1), O(2)−Si−O(3) = 118.8(1), and N(1)−Si−N(2) = 179.5(1)°. The inclusion of the axial disposition of the N(1)−Si−N(2) moiety is the first example observed in the structural chemistry of silatranes. With regard to the geometrical features of the Si−N−C−S fragment, the structure reveals near linearity of Si−N(2)−C(7) [174.7(3)°]. In silyl isothiocyanates, the linearity of the Si−N−C fragment has long been under speculation,[12,13] with the maximum observed angle of 170.2° found in triphenylisothiocyanatosilane in the solid state.[14] In gas phase, the deviation from linearity of this fragment has been attributed to "vibrational shrinkage"; while in the crystal systems, this departure seems to be associated with intermolecular interactions between the N atom of one molecule and the Si atom of another molecule.[13] However, the crystal structure of **1** does not reveal such an intermolecular association.

The transannular N(1)→Si bond length 2.007(3) Å in **1** is the shortest reported so far in neutral silatranes. The shortest distance known so far is 2.010(5) Å.[2c] In spite of the short N(1)→Si dative bond, no significant variations are discerned in the opposite apical Si−N(2) bond length, 1.800(3) Å (the

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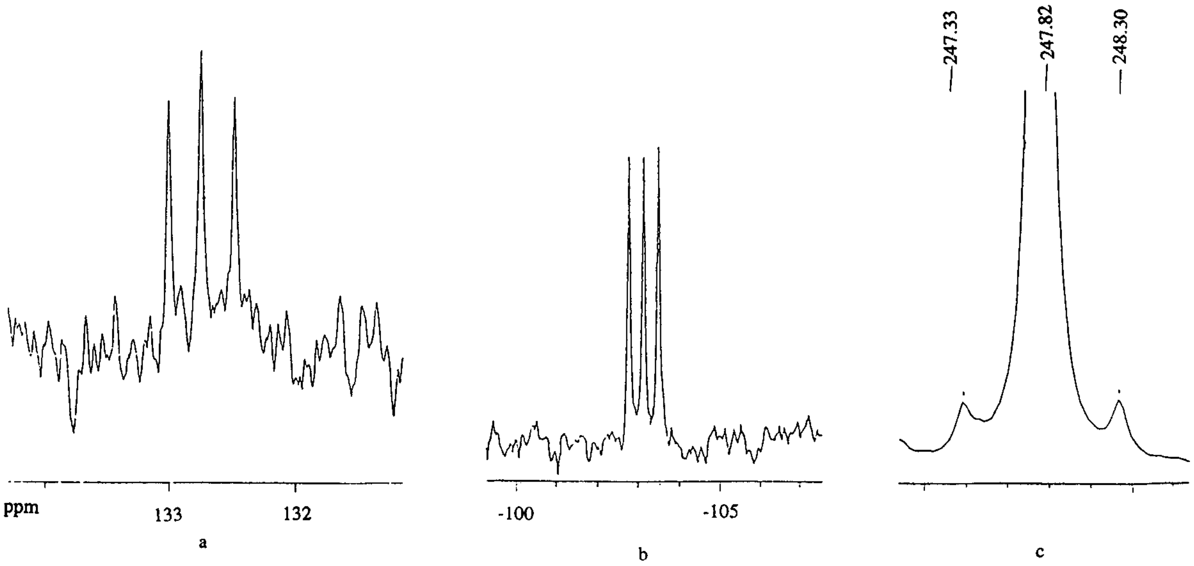

Figure 1. Partial multinuclear (a) ^{13}C, (b) ^{29}Si, and (c) ^{14}N NMR spectra of **1** showing ^{13}C−^{14}N, ^{29}Si−^{14}N, and ^{14}N−^{29}Si couplings.

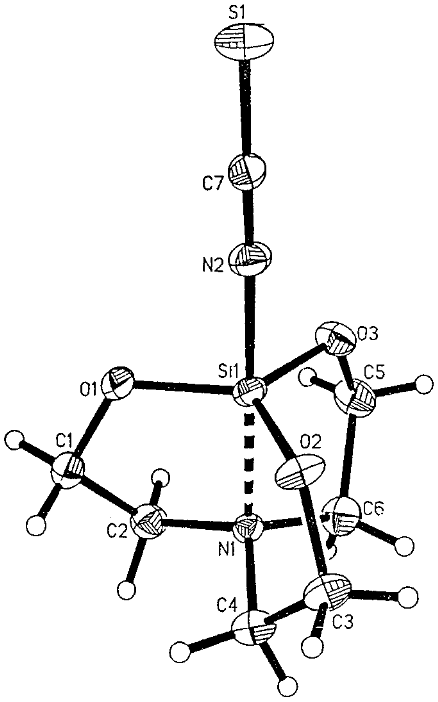

Figure 2. Molecular structure of **1** in the crystal (ORTEP plot, probability level 30%), showing the atomic numbering scheme.

theoretical Si−N covalent bond length in five-coordinate organosilicon compounds is 1.80 Å).[15] Thus the difference between the dative and covalent Si−N bond distance (0.20 Å) is minimal.

In general, the isothiocyanate group is considered to be electron withdrawing in nature which functions through an inductive effect. However, it may also be electron-releasing via a resonance effect. Several resonating structures are believed to contribute to the bonding in the isothiocyanato group when attached to silicon.[16] In the present silatrane, the structural features such as near linearity of Si−N−C fragment and short Si-N(2) bond may suggest significant contributions of structures **I** and **III**.

$$\mathrm{Si^{-} \cdots N^{+}{=}C{=}S \rightleftharpoons Si{-}N{=}C{=}S \rightleftharpoons}$$

I **II**

$$\mathrm{Si{-}N^{+}{\equiv}C{-}S^{-}}$$

III

Table 1. Crystallographic Data and Experimental Parameters for **1**

empirical formula	$C_7H_{12}N_2O_3SSi$
fw	232.3
color; habit	colorless, parallelepiped
cryst size (mm)	0.25 × 0.50 × 0.60
cryst syst	orthorhombic
space group	*Pbca* (No. 61, D_{2h}^{15})
a, Å	13.035(6)
b, Å	12.242(5)
c, Å	13.012(4)
V, Å^3	2080(2)
Z	8
d(calcd), mg/m^3	1.484
λ(Mo Kα) Å	0.710 73
T, K	296
2θ range, deg	4.0−50.0
scan type	$2\theta-\theta$
no. of reflcns collcd	2127
no. of indep reflcns	1846
no. of obsd reflcns (m)	1207 [$F > 6.0\sigma F$)]
no. of paramrs refined (n)	127
final R indices (obsd data),^{a} %	$R = 3.63$, $R_w = 4.73$
R indices (all data), %	$R = 6.12$, $R_w = 5.41$
goodness-of-fit (S)^b	1.32
largest difference peak, e Å^{-3}	0.26

^{a} $R = (\Sigma||F_o| - |F_c||/\Sigma|F_o|)$. $R_w = [(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$. ^{b} $S = [\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

Reactivity

As compared to the chemistry of organic isothiocyanates,[17] the related chemistry of organoisothiocyanatosilanes is relatively much less studied. This is partly attributed to the susceptibility of the Si−N(CS) bond toward hydrolysis and alcoholysis and its tendency to undergo disproportionation reactions in the presence of various Lewis acids.[18−20] However, preliminary studies reveal that the reactivity of 1-isothiocyanatosilatrane toward alcohols, amines and Lewis acids differ from that of tetracoordinate silicon analogs. The results are summarized in Scheme 1.

Reactions with Alcohols and Amines. 1-Isothiocyanatosilatrane is stable toward hydrolysis and alcoholysis. The com-

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Scheme 1

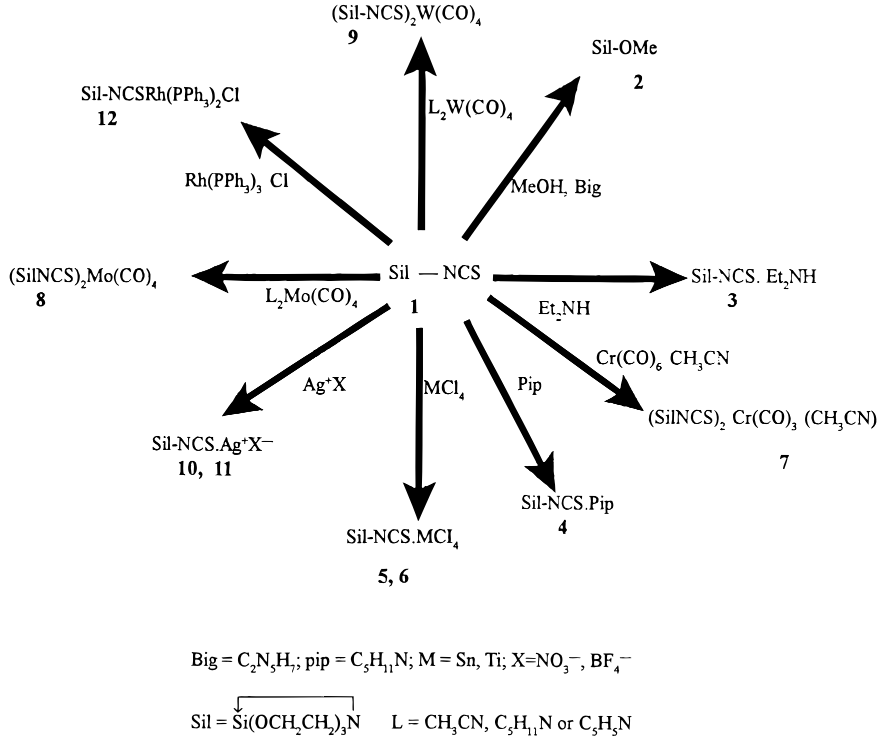
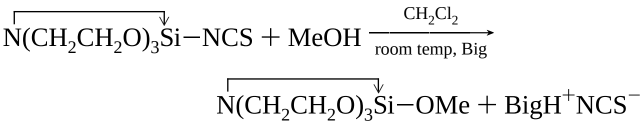


Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for **1**

	x	*y*	*z*	*U*(eq)[a]
Si(1)	634(1)	2144(1)	7746(1)	36(1)
S(1)	2580(1)	112(1)	9931(1)	64(1)
O(1)	1372(2)	3213(2)	7906(2)	54(1)
O(2)	−372(2)	1954(2)	8480(2)	51(1)
O(3)	800(2)	1343(2)	6747(2)	51(1)
N(1)	−256(2)	3085(2)	6853(2)	35(1)
N(2)	1437(2)	1309(3)	8552(2)	53(1)
C(1)	1063(3)	4246(3)	7499(3)	61(1)
C(2)	388(3)	4041(3)	6577(3)	57(1)
C(3)	−1346(2)	2384(3)	8171(3)	55(1)
C(4)	−1161(3)	3363(3)	7487(3)	54(1)
C(5)	404(3)	1671(3)	5775(3)	62(1)
C(6)	−520(3)	2405(3)	5951(3)	57(1)
C(7)	1919(2)	811(3)	9137(2)	42(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor, i.e., $U_{eq} = {}^1/_3\Sigma_i\Sigma_j\mathbf{U}_{ij}a_i{}^*a_j{}^*a_i{\cdot}a_j$.

pound shows little tendency to decomposition in air and can be recovered unchanged from refluxing methanol/ethanol even after 24 h. However in presence of a strong base such as biguanide (Big, $C_2N_5H_7$), the silatrane undergoes a facile substitution reaction with methanol to afford 1-methoxysilatrane.



$$N(CH_2CH_2O)_3Si{-}NCS + MeOH \xrightarrow[\text{room temp, Big}]{CH_2Cl_2} N(CH_2CH_2O)_3Si{-}OMe + BigH^+NCS^-$$

Elemental analyses and IR, multinuclear (^{1}H, ^{13}C, ^{29}Si) NMR, and mass spectral data are consistent with those reported earlier.[1a]

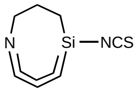
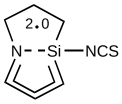
The reactions of 1-isothiocyanatosilatrane with N-donor bases such as piperidine and diethylamine afford a white, hygroscopic solid in each case. Elemental analyses and mass spectral data (Experimental Section) suggest them to be 1:1 adducts of the parent silatrane with the base. IR spectra of the complexes reveal that the ν_{NH} mode has suffered a spectral shift to lower frequency (~80 cm^{-1}) relative to the uncoordinated amines (ν_{NH}: 3320−3300 cm^{-1}). In the multinuclear NMR spectra, the heteronuclear couplings due to ^{14}N (NCS) nucleus with the adjacent ^{29}Si and ^{13}C nuclei, as observed in the parent silatrane (vide infra), are lost. For example, ^{29}Si NMR spectra reveal a single resonance in each case at δ −103.7 (for **1**·Et$_2$NH, **3**) and −100.7 ppm (for **1**·pip, **4**). ^{13}C and ^{14}N NMR spectra show only a marginal upfield shift (~5−8 ppm) of NCS carbon and nitrogen nuclei in these adducts. These results may point to the fact that competitive interactions of the bridgehead nitrogen and of the base exist with silicon.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for **1**

Si(1)−O(1)	1.637(2)	Si(1)−O(2)	1.639(2)
Si(1)−O(3)	1.642(3)	Si(1)−N(1)	2.007(3)
Si(1)−N(2)	1.800(3)	S(1)−C(7)	1.594(3)
O(1)−C(1)	1.429(4)	O(2)−C(3)	1.432(4)
O(3)−C(5)	1.425(4)	N(1)−C(2)	1.484(4)
N(1)−C(4)	1.479(4)	N(1)−C(6)	1.479(4)
N(2)−C(7)	1.160(4)	C(1)−C(2)	1.510(6)
C(3)−C(4)	1.512(5)	C(5)−C(6)	1.520(5)
O(1)−Si(1)−O(2)	120.6(1)	O(1)−Si(1)−O(3)	120.0(1)
O(2)−Si(1)−O(3)	118.8(1)	O(1)−Si(1)−N(1)	87.4(1)
O(2)−Si(1)−N(1)	87.5(1)	O(3)−Si(1)−N(1)	87.8(1)
O(1)−Si(1)−N(2)	92.2(1)	O(2)−Si(1)−N(2)	92.6(1)
O(3)−Si(1)−N(2)	92.6(1)	N(1)−Si(1)−N(2)	179.5(1)
Si(1)−O(1)−C(1)	119.7(2)	Si(1)−O(2)−C(3)	119.6(2)
Si(1)−O(3)−C(5)	119.1(2)	Si(1)−N(1)−C(2)	105.4(2)
Si(1)−N(1)−C(4)	105.7(2)	C(2)−N(1)−C(4)	113.9(3)
Si(1)−N(1)−C(6)	105.7(2)	C(2)−N(1)−C(6)	112.5(3)
C(4)−N(1)−C(6)	112.7(3)	Si(1)−N(2)−C(7)	174.7(3)
O(1)−C(1)−C(2)	108.2(3)	N(1)−C(2)−C(1)	105.6(3)
O(2)−C(3)−C(4)	108.4(3)	N(1)−C(4)−C(3)	105.9(3)
O(3)−C(5)−C(6)	108.7(3)	N(1)−C(6)−C(5)	105.6(3)
S(1)−C(7)−N(2)	179.2(3)		

Reactions with Lewis Acids. The reactivity of 1-isothiocyanatosilatrane with a number of Lewis acids (including hard, soft and borderline acids in Pearson's sense) have been examined (Scheme 1). All the adducts isolated here are stable,

Table 4. Results of Semiempirical Calculations at AM1, PM3, and ZINDO/1 Level for **1**

		PM3			
	AM1				ZINDO/1
binding energy (kcal/mol)	−2593.0	2606.8	2609.2	2604.5	*a*
ΔH_f (kcal/mol)	192.1	205.8	208.3	203.6	*a*
		Optimized Bond Lengths (Å) and Angles (deg)			
N···Si	2.595	3.157	2.429	(2.00 fixed)	2.151
Si−N	1.678	1.748	1.765	1.788	1.954
N−C	1.205	1.206	1.121	1.199	1.217
C−S	1.479	1.525	1.535	1.542	1.645
Si−N−C	177.6	166.4	176.0	176.9	178.0
N−C−S	179.6	178.2	179.7	179.8	179.8
O−Si−N(av)	103.6	106.2	99.5	92.1	96.2
LUMO (eV)	0.39	−0.51	0.06	0.05	2.50
HOMO (eV)	−9.28	−8.69	−8.21	−7.85	−7.84
		Charges			
N(···Si)	−0.342	−0.106	−0.001	0.147	−0.099
O(av)	−0.574	−0.428	−0.417	−0.420	−0.372
Si	1.739	1.182	1.142	1.082	0.896
N(−C−S)	−0.596	−0.125	−0.109	−0.104	−0.313
C	0.040	−0.095	−0.099	−0.099	0.427
S	0.056	−0.130	−0.182	−0.217	−0.510
dipole moment	4.9	6.0	8.8	11.4	13.2
ν(CN) (cm^{-1})	2281	2144	2168	2172	*a*

[a] Not applicable as a single point value.

hygroscopic solids and are soluble in solvents such as CH_3CN, CH_2Cl_2, DMSO, DMF, etc.

The most compelling evidence for the coordination mode of isothiocyanato group in these adducts is given by the IR spectra. In the literature, the frequencies of NCS group are considered as criteria for establishing a variety of coordination modes of this ubiquitous ligand.[21] The ν_{CN} frequencies are generally lower in N-bonded complexes than in S-bonded complexes. The IR spectral absorption along with the assignments of coordination modes of NCS groups in these adducts are consistent with the proposed mode of bonding; e.g. the adducts **5** and **6** are N-bonded and are fragile enough to undergo dissociation in donor solvents such as CH_3CN. The coordinative association of the S-atom is apparent in the majority of the Lewis acids, which include borderline examples of chromium, molybdenum, and tungsten carbonyls (adducts **7**−**12**).

In the multinuclear NMR, the spectral characteristics are similar to those of the parent silatrane. Even more so, chemical shift values and the heteronuclear couplings ($^{13}C-^{14}N$, $^{29}Si-^{14}N$) do not show an acknowledged change. These results reveal that the Si−N(CS) bond in the silatrane is retained under these electrophilic conditions. This is the first example where the coordination chemistry of the isothiocyanate group attached to a silicon atom has been meaningfully studied.

Theoretical Considerations. Various theoretical calculations on the bonding and structure of silatranes are available. The constraints of large size of these molecules limit these studies to semiempirical methods, although a few reports using ab initio methods have also appeared recently.[22]

For 1-isothiocyanatosilatrane, **1**, the influence of the N→Si interactions on its structure and electronic environments is studied using semi-empirical MO calculations at the AM1,[23] PM3,[24] and ZINDO/1[25] levels in combination with molecular dynamic studies. The results are given in Table 4.

The crucial N→Si contact and the linearity of Si−N−C−S moiety is best reproduced in a ZINDO/1 geometry optimization. However, this method does not lend itself to the calculations of spectroscopic properties or energies which can be compared directly to experimental values. The AM1 and PM3 methods, on the other hand, give values between 2.4 and 2.6 Å for the geometry optimized N→Si distance. Furthermore, a second local minimum could also be found with an N→Si separation above 3.1 Å and the nitrogen lone pair pointing away from the silicon atom (exo structure). This situation is calculated to be only 2.5 kcal/mol less stable than the N-inward oriented (endo) isomer.

Concerning the O_3SiNCS geometrical features, the PM3 results are found to be in good agreement with the experimental bond lengths and angles from the X-ray structure determination. The agreement is further improved when the N→Si contact is restrained at 2.0 Å during geometry optimisation (Table 4) [X-ray crystallographic value for the Si−N(1) distance is 2.007(3) Å]. Pushing the nitrogen atom towards silicon requires only 4.7 kcal/mol. In the AM1 and PM3 methods, the silicon atom is not parametrized with a d-function. However, the inclusion of such empty d-functions, even if numerically quite small, would significantly lower this energy.[26]

From PM3 methods, a rather high charge transfer from N→Si onto silicon and further to the sulfur atom is calculated. The charge density increases for the closer N→Si distance (2.00 Å). Thus, sulfur atoms together with oxygen atoms show the highest

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negative electrostatic potentials. Though enhanced basicities of equatorial and apical substituents in silatranes have been observed,[4] yet the transfer of electron density to the tail end of the NCS group is being observed for the first time.

Experimental Section

General Details. All operations were carried out under a dry nitrogen atmosphere. Solvents were freshly distilled under an inert atmosphere from sodium (*n*-hexane), sodium benzophenone ketyl (tetrahydrofuran, diethyl ether), or phosphorous pentoxide (acetonitrile, dichloromethane) before use. Bases such as pyridine, piperidine, and diethylamine (Aldrich) were refluxed over KOH pellets and distilled under a dry nitrogen atmosphere prior to use. Other starting materials such as $SiCl_4$, $SnCl_4$, $TiCl_4$, $AgNO_3$, and $AgBF_4$ were used without further purification. Infrared spectra were routinely obtained as thin films or Nujol mulls on a Perkin-Elmer Model 1430 ratio recording spectrophotometer. ^1H NMR spectra were recorded on a Bruker AM300 instrument, while ^{13}C, ^{29}Si and ^{14}N NMR spectra were obtained on a Bruker AMX-400 spectrometer. Chemical shifts are quoted relative to TMS for ^1H, ^{13}C, and ^{29}Si nuclei and external CH_3NO_2 for the ^{14}N nucleus. Mass spectral measurements (EI, 70 eV) were carried out on a VG Analytical (70-S) spectrometer. C, H, and N analyses were obtained on a Perkin-Elmer Model 2400 CHN elemental analyzer. S and Si were estimated by gravimetric methods.

Preparations. $(EtO)_3SiNCS$,[27] $(Ph_3P)_3RhCl$,[28] *cis*-$W(CO)_4(C_5H_{11}N)_2$,[29] *cis*-$Mo(CO)_4(C_5H_{11}N)_2$,[29] *cis*-$Mo(CO)_4(C_5H_5N)_2$,[30] and biguanide ($C_2N_5H_7$)[31] were prepared from the literature procedures.

$N(CH_2CH_2O)_3Si{-}NCS$ (1). To a stirred solution of triethoxyisothiocyanatosilane (2.2 g, 1.0 mmol) in dry dichloromethane (40.0 mL) was added dropwise triethanolamine (1.3 g, 0.9 mmol) dissolved in the same solvent. A white solid was immediately formed which dissolved after some time to give a pale yellow solution. The contents were stirred at room temperature for 5 h. The solution was concentrated to 15−20 mL, and the white crystalline solid obtained was filtered, washed with small aliquots of dichloromethane, and dried under vacuum. Yield: 1.96 g, 84.48%. Anal. Calcd for $C_7H_{12}O_3N_2SSi$: C, 36.21; H, 5.17; N, 12.07; S, 13.79; Si, 12.07. Found: C, 36.11; H, 5.31; N, 12.12; S, 13.70; Si, 12.15. IR (Nujol, cm^{-1}): 2110 ($\nu_{(as)NCS}$), 910, 940, 660 (skeletal vibrations). ^1H NMR (CD_3CN): δ 4.02 (t, OCH_2), 3.11 (t, NCH_2). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 58.75 (OCH_2), 52.50 (NCH_2), 134.08, 133.82, 133.56 (NCS); J ($^{13}C{-}^{14}N$) = 26.17 Hz. $^{29}Si\{^1H\}$NMR (CD_3CN): −102.67, −103.03, −103.38; $J(^{29}Si{-}^{14}N)$ = 28.47 Hz. $^{14}N\{^1H\}$ NMR (CD_3CN): δ −247.33, −247.82, −248.30; $J(^{14}N{-}^{29}Si)$ = 28.23 Hz. MS (*m*/*z*, assignment, relative intensity): 232, [M^+], 26.75%; 174, [M^+ − NCS], 100%; 130 [M^+ − NCS − OC_2H_4], 13.42%; 86 [M^+ − NCS − $(OC_2H_4)_2$], 8.26%.

$N(CH_2CH_2O)_3Si{-}OMe$ (2). To the suspension of 1-isothiocyanatosilatrane (1.0 g, 4.3 mmol) in dry 1,2-dichloromethane (10 mL) was added a solution of biguanide (0.45 g, 4.3 mmol) in methanol (5 mL). The reaction mixture became clear after 15−20 min. The clear solution was stirred at room temperature for 5 h. A white solid, identified as $C_2N_5H_8{}^+NCS^-$, was filtered off. Solvent was removed from the filtrate, and dry diethyl ether was added. A white solid was obtained, which was filtered and dried under vacuum. Yield: 0.50 g, 56.58%. Anal. Calcd for $C_7H_{15}O_4NSi$: C, 40.97; H, 7.31; N, 6.83; Si, 13.65. Found: C, 40.80; H, 7.23; N, 6.83; Si, 13.50. IR (Nujol, cm^{-1}): 1145 ($\nu_{Si-O(C)}$, 935, 915, 615 (skeletal vibrations). ^1H NMR ($CDCl_3$): δ 3.40 (s, OCH_3), 3.80 (t, OCH_2), 2.92 (t, NCH_2), $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 56.58 (OCH_2), 50.39 (OCH_3), 49.97 (NCH_2). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −95.42. MS (*m*/*z*, assignment, relative intensity): 205, [M^+], 33.65%; 174, [M^+ − OMe], 95.05%.

$N(CH_2CH_2O)_3SiNCS{\cdot}Et_2NH$ (3). To a suspension of 1-isothiocyanatosilatrane (1.0 g, 4.3 mmol) in dry THF (25 mL) was added excess diethylamine (2.2 mL, 21.2 mmol). The contents were heated at 65 °C for 15 h. The resulting clear solution was evaporated to near dryness to yield a sticky mass. The contents were stirred in diethyl ether for 8−10 h. The white solid thus obtained, was filtered, washed with diethyl ether, and dried under vacuum. Yield: 1.0 g, 75.8%. Anal. Calcd for $C_{11}H_{23}N_3O_3SSi$: C, 43.29; H, 7.54; N, 13.77; S, 10.49; Si, 9.18. Found: C, 42.81; H, 7.49; N, 13.65; S, 10.58; Si, 9.20. IR (Nujol, cm^{-1}): 3200 (ν_{NH}), 2070 ($\nu_{(as)NCS}$). ^1H NMR ($CDCl_3$): δ 3.08 (t, OCH_2) 2.8 (t, NCH_2), 3.0 (q, CH_2) 1.3 (t, CH_3) 8.2 (br, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 58.4 (OCH_2), 51.0 (NCH_2), 132.8 (NCS), 42.7, 11.2 $(C_2H_5)_2NH$. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −103.7. $^{14}N\{^1H\}$ NMR ($CDCl_3$): δ −251.8 (NCS), −329.5 (N→Si). MS (*m*/*z*, assignment, relative intensity): 306, [MH^+], 4.4%; 232, [M^+ − $(C_2H_5)_2NH$], 18.0%; 73 [$(C_2H_5)_2NH^+$].

$N(CH_2CH_2O)_3SiNCS{\cdot}C_5H_{11}N$ (4). The reaction of 1-isothiocyanatosilatrane (1.0 g, 4.3 mmol) with piperidine (2.1 mL, 21.3 mmol) was carried out in a manner similar to that described above for **3**. The compound is obtained as a whilte solid (yield 1.1 g, 80.5%). Anal. Calcd for $C_{12}H_{23}N_3O_3SSi$: C, 45.42; H, 7.26; N, 13.24; S, 10.09; Si, 8.83. Found: C, 45.55; H, 7.24; N, 13.08; S, 10.24; Si, 8.80. IR (Nujol, cm^{-1}): 3200 (ν_{NH}), 2070 ($\nu_{(as)NCS}$). ^1H NMR ($CDCl_3$): δ 3.8 (t, OCH_2), 2.8 (t, NCH_2), 3.2 (t), 1.9 (m), 1.8 (m) (piperidine), 5.6 (br, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 57.9 (OCH_2), 50.7 (NCH_2), 132.6 (NCS), 44.7, 22.5, 22.2 (piperidine). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −100.7. $^{14}N\{^1H\}$ NMR ($CDCl_3$): δ −251.7 (NCS), −338.3 (N→Si). MS (*m*/*z*, assignment, relative intensity): 318, [MH^+], 5.6%; 232, [M^+ − $C_5H_{11}N$], 22.2%; 85, [$C_5H_{11}N^+$], 26.6%.

$N(CH_2CH_2O)_3SiNCS{\cdot}TiCl_4$ (5). To a solution of 1-isothiocyanatosilatrane (0.2 g, 0.8 mmol) in dry CH_2Cl_2 (25 mL) was added titanium (IV) chloride (0.1 mL, 0.9 mmol) at room temperature. A yellow solid precipitated out immediately. The contents were stirred for 3 h. The solid obtained was filtered, washed with CH_2Cl_2 and dried under vacuum. Yield: 0.30 g, 83.3%. Anal. Calcd for $C_7H_{12}Cl_4N_2O_3SSiTi$: C, 19.90; H, 2.84; N, 6.63; S, 7.58; Cl, 33.6. Found: C, 19.85; H, 2.79; N, 6.51; S, 7.22; Cl, 34.02. IR (Nujol, cm^{-1}): 1910, 1940 ($\nu_{(as)NCS}$). IR (CH_3CN, cm^{-1}): 2110 ($\nu_{(as)NCS}$). ^1H NMR (CD_3CN): δ 4.0 (t, OCH_2), 3.1 (t, NCH_2). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 58.7 (OCH_2), 52.3 (NCH_2), 133.56, 133.82, 134.08 (NCS); $J(^{13}C^{14}N)$ = 24.17 Hz. $^{29}Si\{^1H\}$ NMR (CD_3CN): δ −102.67, −103.03, −103.38; $J(^{29}Si{-}^{14}N)$ = 28.17 Hz.

$N(CH_2CH_2O)_3SiNCSSnCl_4$ (6). This compound was prepared by a procedure analogous to that described for **5**, using 1-isothiocyanatosilatrane (0.2 g, 0.8 mmol) and tin(IV) chloride (0.1 mL, 0.8 mmol) as reactants. **6** was obtained as a white solid. Yield: 0.35 g, 83.5%. Anal. Calcd for $C_7H_{12}Cl_4N_2O_3SSiSn$: C, 17.05 H, 2.43; N, 5.68; S, 6.44; Cl, 28.82. Found: C, 16.84; H, 2.40; N, 5.46; S, 6.21; Cl, 28.44. IR (Nujol, cm^{-1}): 1940, 1900 ($\nu_{(as)NCS}$). IR (acetonitrile, cm^{-1}): 2110 (ν_{NCS}). ^1H NMR (CD_3CN): δ 4.0 (t, OCH_2), 3.0 (t, NCH_2). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 58.7 (OCH_2) 52.4 (NCH_2), 133.56, 133.82, 134.08 (t, NCS); $J(^{13}C{-}^{14}N)$ = 24.17 Hz. $^{29}Si\{^1H\}$ NMR (CD_3CN): δ −102.67, −103.03, −103.38; $J(^{29}Si{-}^{14}N)$ = 28.17 Hz.

$[N(CH_2CH_2O)_3SiNCS]_2Cr(CO)_3(CH_3CN)$ (7). Chromium hexacarbonyl (0.1 g, 0.45 mmol) in dry CH_3CN (30 mL) was kept at 85 °C for 2 h with constant stirring. 1-Isothiocyanatosilatrane (0.21 g, 0.9 mmol) dissolved in acetonitrile (30 mL) was added in situ, and the clear yellow solution was refluxed at 85 °C for 5−6 h. The solvent was removed under reduced pressure, and dry diethyl ether was added. A pale yellow solid, thus obtained, was filtered and dried under vacuum. Yield: 0.46 g, 81.0%. Anal. Calcd for $C_{19}H_{27}O_9N_5S_2Si_2Cr$: C, 35.57; H, 4.21; N, 10.92; S, 9.98. Found: C, 35.66; H, 4.29; N, 10.80; S, 9.93. IR (Nujol, cm^{-1}): 2100 ($\nu_{(as)NCS}$), 1935, 1900 (ν_{CO}). ^1H NMR ($CDCl_3$ + DMSO-d_6): δ 3.8 (t, OCH_2), 3.0 (t, NCH_2), 2.0 (s, CH_3CN). $^{13}C\{^H\}$ NMR: δ 57.7 (OCH_2), 50.2 (NCH_2), 131.61, 131.41, 131.21 (t, NCS); $J(^{13}C{-}^{14}N)$ = 24.92 Hz; δ 213.1, 212.9 (CO), 117.9, 1.08 (CH_3CN). ^{29}Si NMR (DMSO-d_6): δ −103.46, −103.11, −102.76; $J(^{29}Si{-}^{14}N)$ = 28.62 Hz.

$[N(CH_2CH_2O)_3SiNCS\}_2Mo(CO)_4$ (8). 1-Isothiocyanatosilatrane (2.0 g, 8.6 mmol) in dry CH_2Cl_2 (30 mL) was cannula transferred into *cis*-$Mo(CO)_4L_2$ (L = $C_5H_{11}N$ or C_5H_5N) (4.3 mmol) dissolved in

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CH_2Cl_2 (30 mL). The reaction mixture was heated at 80 °C for 8−10 h. The resulting solution was concentrated to 20 mL, and dry diethyl ether (75 mL) was added to it. A light brown solid was precipitated in each case, which was filtered washed with diethyl ether and dried under vacuum. Yield: 3.50 g, 88.6%. Anal. Calcd for $C_{18}H_{24}MoN_4O_{10}S_2Si_2$: C, 32.14, H, 3.57; N, 8.33; S, 9.52. Found: C, 32.09; H, 3.60; N, 9.21; S, 9.59. IR (Nujol, cm^{-1}): 2090 ($\nu_{(as)NCS}$), 1920 (ν_{CO}). ^1H NMR (CD_3CN): δ 3.8 (t, OCH_2), 2.9 (t, NCH_2). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 57.2 (OCH_2), 49.9 (NCH_2), 132.16, 131.81, 131.46 (t, NCS); $J(^{13}C-^{14}N) = 25.6$ Hz; 204.1 (CO). $^{29}Si\{^1H\}$ NMR (CD_3CN): δ −103.44, −103.28, −103.09, $J(^{29}Si-^{14}N) = 28.6$ Hz.

$[N(CH_2CH_2O)_3SiNCS]_2W(CO)_4$ (9). The title compound was obtained from the reaction of *cis*-$W(CO)_4(C_5H_{11}N)_2$ (2.0 g, 4.3 mmol) with 1-isothiocyanatosilatrane (2.0 g, 8.6 mmol) by following a procedure similar to that described for **8**. The compound was obtained as a light brown solid. Yield: 3.85 g, 84.6%. Anal. Calcd for $C_{18}H_{24}N_4O_{10}S_2Si_2W$: C, 28.42; H, 3.16; N, 7.37; S, 8.42. Found: C, 28.16; H, 3.02; N, 7.11; S, 8.06. IR (Nujol, cm^{-1}): 2090 ($\nu_{(as)NCS}$), 1910 (ν_{CO}). ^1H NMR (CD_3CN): δ 3.8 (t, OCH_2), 2.9 (t, NCH_2). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 57.2 (OCH_2), 50.3 (NCH_2), 132.17, 131.82, 131.47 (t, NCS); $J(^{13}C-^{14}N) = 25.6$ Hz; δ 195.6 (CO). $^{29}Si\{^1H\}$ NMR (CD_3CN): δ −103.50, −103.28, −103.09; $J(^{29}Si-^{14}N) = 28.2$ Hz.

$[N(CH_2CH_2O)_3SiNCS\cdot Ag]^+NO_3^-$ (10). To 1-isothiocyanatosilatrane (1.0 g, 4.3 mmol) in acetonitrile (20 mL) was added a solution of silver nitrate (0.7 g, 4.3 mmol) in acetonitrile (20 mL). The contents were stirred for 4 h under diffused light. The solution was concentrated to 20 mL under reduced pressure. The solid obtained was filtered and dried under vacuum. Yield: 1.50 g, 86.7%. Anal. Calcd for $C_7H_{12}O_6N_3AgSSi$: C, 20.89; H, 2.98; N, 10.45; S, 7.96. Found: C, 20.98; H, 2.89; N, 10.43; S, 3.95. IR (Nujol, cm^{-1}): 2190 ($\nu_{(as)NCS}$), 940, 915, 630 (skeletal vibrations). ^1H NMR (CD_3CN): δ 3.95 (t, OCH_2), 3.08 (t, NCH_2) $^{13}C\{^1H\}$ NMR (CD_3CN): δ 58.10 (OCH_2), 51.92 (NCH_2), 133.60, 132.87, 133.71 (t, NCS); $J(^{13}C-^{14}N) = 24.21$ Hz. $^{29}Si\{^1H\}$ NMR (CD_3CN): δ −102.91, −103.23, −103.51; $J(^{29}Si-^{14}N) = 26.11$ Hz.

$[N(CH_2CH_2O)_3SiNCS\cdot Ag]^+BF_4^-$ (11). The reaction of 1-isothiocyanatosilatrane (1.0 g, 4.3 mmol) and silver tetrafluoroborate (0.8 g, 4.3 mmol) in dry dichloromethane was carried out in a way similar to that described for **10**. A creamish whilte solid was obtained. Yield: 1.64 g, 88.9%. Anal. Calcd for $C_7H_{12}O_3N_2F_4BAgSSi$: C, 19.67; H, 2.81; N, 6.56; S, 7.49. Found: C, 19.56; H, 2.89; N, 6.44; S, 7.38. IR (Nujol, cm^{-1}): 2180 ($\nu_{(as)NCS}$), 940, 915, 620 (skeletal vibrations). ^1H NMR (CD_3CN): δ 3.95 (t, OCH_2), 3.08 (t, NCH_2). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 51.92 (NCH_2), 58.10 (OCH_2), 132.58, 132.84, 133.09 (NCS); $J(^{13}C-^{14}N) = 24.03$ Hz. $^{29}Si\{^1H\}$ NMR (CD_3CN): δ −102.47, −102.85, −103.23; $J(^{29}Si-^{14}N) = 29.46$ Hz.

$[N(CH_2CH_2O)_3SiNCSRh(PPh_3)_2Cl$ (12). To a solution of 1-isothiocyanatosilatrane (0.1 g, 0.43 mmol) in dichloromethane (40 mL) was added a solution of tris(triphenylphosphine)chlororhodium(I) (0.40 g, 0.43 mmol) in dichloromethane (20 mL). After a brief period, a yellow compound precipitated out. The contents were stirred for 5 h. The solid obtained was filtered, washed with diethyl ether, and dried in vacuum. Yield: 0.31 g, 81.5%. Anal. Calcd for $C_{43}H_{42}N_2ClPRhSi$: C, 51.43; H, 4.77; N, 3.13. Found: C, 57.31; H, 4.29; N, 3.41. IR (Nujol, cm^{-1}): 2165 ($\nu_{(as)NCS}$), 935, 900, 620 (skeletal vibrations). ^1H NMR (CD_3CN): δ 3.93 (t, OCH_2), 2.92 (t, NCH_2), 7.1−6.8 (m, phenyl). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 57.29 (OCH_2), 50.97 (NCH_2), 133.09, 132.18, 128.78, 115.11 (phenyl), 132.72, 131.95, 131.19 (t, NCS); $J(^{13}C-^{14}N) = 26.1$ Hz. $^{29}Si\{^1H\}$ NMR (CD_3CN): δ −102.49, −102.09, −101.68, $J(^{29}Si-^{14}N) = 28.60$ Hz.

Crystal Structure Analysis for 1. Crystals of 1-isothiocyanatosilatrane, **1**, were grown at room temperature from an acetonitrile solution of the compound. A suitable crystal was mounted on a glass fiber along the longest dimension, and X-ray diffraction data were collected with a Siemens R3m/V diffractometer (graphite-monochromated Mo Kα radiation, $\lambda = 0.710\,37$ Å). The unit cell dimensions were determined from 24 reflections in the range $15 < 2\theta < 35°$. Data were collected in a nonstandard setting and later transformed to a standard setting of *Pbca* using the matrix 100, 001, $0\bar{1}0$. Intensities of monitor reflections decreased by <1% during 33 h of X-ray exposure. No absorption correction was applied because of a low μ value. There was no evidence of secondary extinction, and therefore no correction was applied. The crystal structure was solved by direct methods and refined by full-matrix least-squares procedures. The system used was Siemens SHELXTL PLUS (VMS). All non-hydrogen atoms were refined anisotropically while hydrogen atoms were included in ideal positions with U fixed at 0.08 Å^2.

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Supporting Information Available: Unit cell packing diagram for **1** and tables of anisotropic displacement coefficients and H-atom coordinates with isotropic displacement coefficients (3 pages). Ordering information is given on any current masthead page.

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