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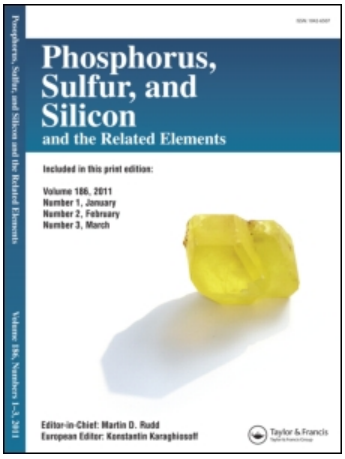

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Synthesis, Characterization and Reactivity of a Novel Six-Membered 1-Isothiocyanato Silatrane

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Synthesis, Characterization and Reactivity of a Novel Six-Membered 1-Isothiocyanato Silatrane

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*The 1-isothiocyanato silatrane, NCSSi[(OC$_6$H$_2$Me$_2$)CH$_2$]$_3$N (**1**), with the silicon atom incorporated in a six-membered ring has been synthesized in high yield by transetherification reaction of triethoxyisothiocyanato silane with tris-(2-hydroxy-3,5-dimethylbenzyl)amine. The new silatrane (compound **1**) reacts with Lewis acids and bases without losing its stability and forms adducts like N[CH$_2$(Me$_2$C$_6$H$_2$O)]SiNCS·AgNO$_3$ (**2**), N[CH$_2$(Me$_2$C$_6$H$_2$O)]SiNCS·TiCl$_4$ (**3**), N[CH$_2$(Me$_2$C$_6$H$_2$O)]SiNCS·SnCl$_4$ (**4**), and N[CH$_2$(Me$_2$C$_6$H$_2$O)]SiNCS·Et$_2$NH (**5**). The novel silatrane, and its adducts have been characterized by elemental analysis, infrared spectroscopy, ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, as well as by mass spectrometry.*

Keywords Hypervalent compound; isothiocyanato silatrane; pentacoordinated silicon; pseudohalogen silatrane; six-membered silatrane

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INTRODUCTION

1-Isothiocyanato silatranes with the silicon atom incorporated in a six-membered ring are reported here for the first time. They are tricyclic neutral pentacoordinated silicon complexes and have a propeller-like geometry as proposed in Figure 1.

Recently the chemistry of hypercoordinated silicon complexes has attracted considerable interest;[1–3] however, 1-isothiocyanato six-membered ring silatranes have not been reported so far. The silatranes were described as non-reactive and little is known about their reactivity.[4] They are of interest because of their application in medicine and agriculture. A number of publications have appeared which put light on various structural aspects including the N→Si transannular

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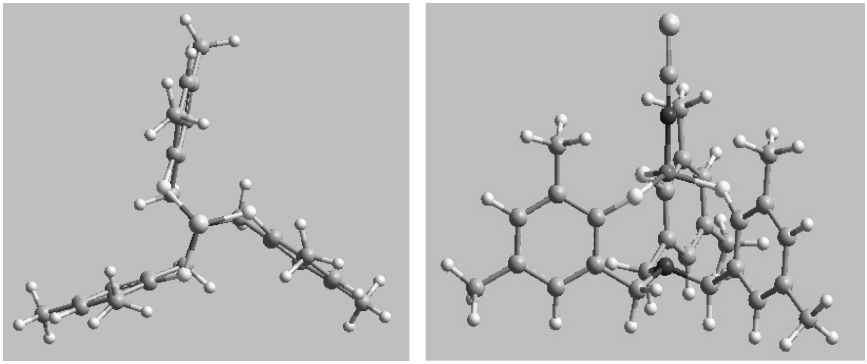

FIGURE 1 Plot of the computed structure of 1-Isothiocyanato silatrane showing the propeller like geometry of the molecule.

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bond in the distorted trigonal bipyramidal geometry at the silicon atom[5–7] of the silatranes. Little attention has been paid in the preparation of silatranes with exocyclic pseudohalogen functionalities.[4–6] In the present study, using a classical approach and under mild conditions, a first 1-isothiocyanato six-membered ring silatrane with more than one reactive center has been prepared as shown in Scheme 1.

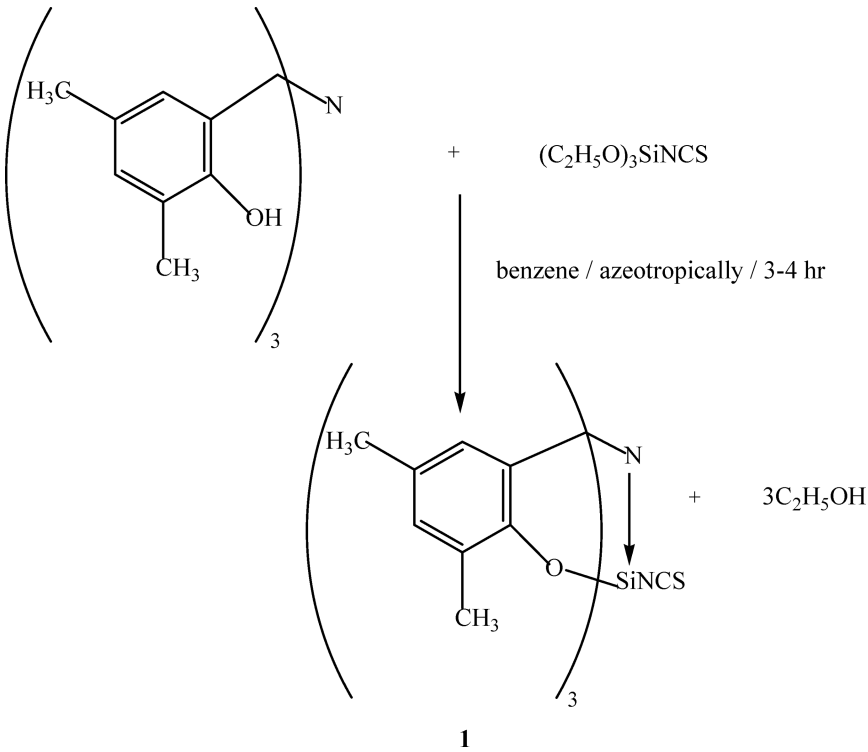
RESULTS AND DISCUSSION

Infrared spectroscopic studies of the compound **1** in nujol show the υNCS absorption at 2115 cm^{-1}. In addition, the band at 1060 cm^{-1} is attributed to the υSi-O(C) vibrations. Bands at 988, 923, and 680 cm^{-1} are attributed to silatranyl skeletal vibrations with the predominant contribution originating from the N→Si dative bond. The mass spectrum (EI, 70 eV) clearly shows the parent ion peak at m/z 502. The base peak at m/z 444 corresponds to the [M^+- SCN] ion.

Multinuclear (^{1}H, ^{13}C, and ^{29}Si) NMR spectra are consistent with the structure shown in Scheme 1. There are some noteworthy features in the spectra. The ^{29}Si NMR spectrum displays a 1:1:1 triplet due to ^{29}Si-^{14}N coupling (J = 33.4 Hz). The observation of such a coupling indicates a less effective quadruple relaxation of the ^{14}N nucleus as well as smaller electric field gradient at nitrogen atom of NCS group.

Reactivity

As compared to the chemistry of organic isothiocyanates, the related chemistry of organoisothiocyanato silanes is little investigated. This is



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SCHEME 1

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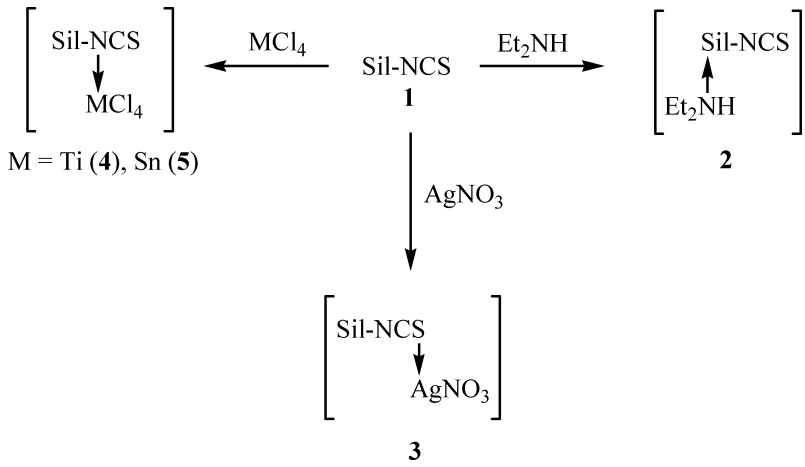
partially attributed to the susceptibility of the Si–NCS bond towards hydrolysis and alcoholysis and its tendency to undergo disproportionation reactions in the presence of various Lewis acids. However, preliminary studies reveal that the reactivity of compound **1** towards Lewis acids differs from that of the tetracoordinated silicon analogues.

Reaction with Alcohols and Amines

Compound **1** is not stable towards hydrolysis and alcoholysis. The compound shows little tendency to decompose in air. Reaction of compound **1** with diethyl amine gives a white hygroscopic solid **2**. Elemental analysis and multinuclear NMR spectroscopy show the product **2** to be the adduct of the silatrane with diethyl amine. The IR spectrum of the complex reveals that υ(NH) is shifted to lower frequency (by $\approx$ 80 cm^{-1}) relative to that of the uncoordinated amine (3320–3300 cm^{-1}). In the ^{29}Si NMR spectrum, no ^{29}Si-^{14}N coupling is observed. The spectrum displays a single resonance at –150.4 ppm. This result may indicate



SCHEME 2

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the presence of interactions of the nitrogen atom of diethyl amine with the silicon atom of compound **1**.

Reaction with Lewis Acids

The reactivity of the compound **1** with a number of Lewis acids has been examined (Scheme 2). All adducts **3–5** are hygroscopic solids and soluble in dimethyl sulfoxide. The most direct evidence for the coordination mode of isothiocyanato group in these adducts is given by the IR spectra. In the literature, the IR frequencies of NCS groups are considered as criteria for establishing a variety of coordination modes of this ligand.[4] The ν(CN) frequencies are generally lower in *N*-bonded complexes as compared to sulfur-bonded complexes. In compound **3** the sulfur atom of the NCS moiety is coordinated to Ag^+ of $AgNO_3$ while in compounds **4** and **5** the nitrogen atom of the NCS group is coordinated to the titanium and the tin atom of $TiCl_4$ and $SnCl_4$, respectively.

The multinuclear NMR data obtained for the compounds **2–5** are identical to those of compound **1** suggesting the dissociation of the adducts in dimethyl sulfoxide. These results reveal that the Si–NCS bond in the compound **1** is retained in the presence of Lewis acids and bases.

Computational Study

It is interesting to compare the N→Si and Si–NCS distances of the present six-membered ring silatrane (Figure 1) with those of related

TABLE I Comparison of the N→Si and Si-NCS Distances Obtained from Semiempirical Calculations for the New Silatrane with Those of Analogous Five-Membered Ring Silatranes.[4]

	N→Si (in Å)		Si-N(CS) (in Å)	
Method	Six-membered (Present)	Five-membered (Ref. 4)	Six-membered (Present)	Five-membered (Ref. 4)
AM1	2.75314	2.595	1.68104	1.678
PM3	2.68297	2.429	1.77277	1.765
MNDO	2.94902	—	1.70913	—
MNDO/d	3.01983	—	1.75976	—
CNDO	2.64542	—	2.06819	—

five-membered ring silatranes.[4] Table I contains the optimized Si-N bond lengths computed using semiempirical methods (AM1[8], PM3[9], MNDO[10], MNDO/d[11] and CNDO[11]). These are compared with the Si-N bond length of analogous five-membered ring silatranes. From the comparison it is apparent that in going from a five to a six membered ring the N-Si distance increases approximately by 0.15 Å and this is attributed to the increase of ring size.

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CONCLUSION

The six-membered silatrane has unique structural properties as observed in the ^{29}Si NMR spectrum for the heteronuclear coupling between ^{29}Si and ^{14}N. The ^{29}Si NMR spectrum of the compound shows a triplet at −149.9 ppm with a ^{29}Sis^{14}N coupling constant of 33.4 Hz. The ^{29}Si chemical shift and a computational study of the molecule both indicate that the Si-N internuclear distance increases in the 1-isothiocynato six membered ring silatrane as compared to analogous 1-isothiocyanato five membered ring silatranes (^{29}Si = −102 ppm)[4]. The new silatrane is found to react with Lewis acids and bases to afford adducts of varying stoichiometry with retention of the Si-NCS bond as well as of the silatranyl framework.

EXPERIMENTAL

All operations were carried out under dry nitrogen atmosphere. Solvents were freshly distilled under an inert atmosphere from sodium (hexane), sodium benzophenone (tetrahydrofuran, diethylether), and phosphorus pentaoxide (acetonitrile and dichloromethane) before use. Bases such as diethyl amine (Aldrich) were refluxed over potassium hydroxide pellets and distilled under dry nitrogen atmosphere before use.

Other starting materials such as silicon(IV) chloride, tin(IV) chloride, titanium(IV) chloride, and silver(I) nitrate were used without further purification. Absolute alcohol (Bengal Chemicals), 2,4-dimethyl phenol (Merck), hexamethylene tetramine (Aldrich) and potassium thiocyanate (Merck) were used as supplied. Tris-(2-hydroxy-3,5-dimethyl benzyl) amine[6]and triethoxy isothiocyanato silane were synthesized according to a procedure reported earlier[12]. Solvents were purified according to standard procedures.[13] IR spectra were obtained as thin films or nujol mulls with a Perkin-Elmer RX-1 FT IR Spectrophotometer. ^{1}H (300.4 MHz), ^{13}C (75.45 MHz) and ^{29}Si (59.60 MHz) NMR spectra were obtained with a Jeol AL 300 instrument. Chemical shifts are reported with respect to TMS as external standard. Mass spectral measurements (EI, 70 eV) were carried out with a VG Analytical (70-S) spectrometer. The elemental analyses were performed using a PERKIN-ELMER (model 2400) C, H, N analyzer. The content of sulfur and silicon was determined by standard gravimetric methods.

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1-Isothiocyanato silatrane (1)

In a round-bottomed flask a solution of triethoxy isothiocyanato silane (1.708 g, 7.73 mmol) and tris-(2-hydroxy-3,5-dimethylbenzyl) amine (3.24 g, 7.73 mmol) in anhydrous benzene (30 mL) was stirred for 4 h at 60–80°C in order to azotropically remove the ethanol formed during the reaction. Thereafter, the solvent was evaporated at room temperature under vacuum. To the viscous liquid anhydrous hexane (20 mL) was added, when a white solid was formed. The solid was filtered under the dry nitrogen atmosphere, washed with hexane (2 mL), and dried under vacuum to give **1**. The compound is hygroscopic and soluble in chloroform and dimethyl sulfoxide. Yield: 3.42 g (88.5%). M.p.: 200–202°C; Anal. calcd. for $C_{28}H_{30}O_3N_2SiS$ (502): C: 67.00; H: 6.00; N: 5.58; S: 6.37; Si: 5.57%. Found C: 66.92; H: 5.99; N: 5.49; S: 6.05; Si: 5.55%. IR (Nujol, KBr, cm^{-1}): $\upsilon = 2115$ (NCS), 1060 (Si-OC), 486 cm^{-1} (NCS). ^{1}H NMR ($CDCl_3$): $\delta = 2.2$ (s, 9H, aryl-Me), 4.2 (s, 6H, NCH_2), 6.9 (s, 3H, aryl-H), 6.9 (s, 3H, aryl-H); ^{13}C NMR ($CDCl_3$): $\delta = 16.2$ (aryl-CH_3), 20.6 (aryl-CH_3), 56.8 (NCH_2), 129.0 (t, $^{1}J_{CN} = 12.8$ Hz, NCS); 124.8, 128.2, 129.3, 129.9, 132.0, and 151.3 (aryl-C). ^{29}Si NMR ($CDCl_3$): $\delta = -149.3$ (t, $^{1}J_{SiN} = 33.4$ Hz). EI-MS: m/z 502, $[M^+]$, 3.75%, m/z 444 $(M\text{-}NCS)^+$ 100%.

Adduct of 1 with Diethyl Amine (2)

Diethylamine (0.40 mL, 5 mmol) was added to a solution of compound **1** (1.40 g, 2.97 mmol) in THF (35 mL). The reaction mixture was refluxed overnight under dry nitrogen atmosphere at 65°C, and a clear solution

was obtained. Thereafter, the solvent was evaporated and diethyl ether (25 mL) was added, and a white solid formed. The solid was filtered under reduced pressure, washed with diethyl ether (2 mL), and dried under vacuum to give **2**. The compound is hygroscopic and insoluble in most solvents except dimethyl sulfoxide. Yield: 1.34 g (83.7%). Anal. calcd. for $C_{32}H_{14}O_3N_3SiS$ (575): C, 66.8; H, 7.1; N, 7.3; S, 5.4; Si, 4.9%. Found: C, 66.6; H, 7.1; N, 7.2; S, 5.5; Si, 4.8%. IR (Nujol, KBr, cm^{-1}): $\upsilon =$ 2069 (NCS), 772 (CS), 3220 (NH), 2923 (CH_2), 1463 (CH_2), 1377 (C = C), and 1072 cm^{-1} (Si-O(C)). ^{1}H NMR (DMSO-d_6): $\delta = 2.1$ (s, 9H, aryl-Me), 2.2 (s, 9H, aryl-Me), 3.9 (s, 6H, NCH_2) 6.6 (s, 3H, aryl-H), 6.8 (s, 3H, aryl-H), 3.0 (q, 4H, $NHCH_2$), 1.4 (t, 6H, CH_3), 8.0 (s, 1H, $NHCH_2CH_3$). ^{13}C NMR (DMSO-d_6): $\delta = 16.5$ (aryl-Me), 20.2 (aryl-Me), 56.2 (NCH_2), 126.7 (NCS), 119.1, 121.1, 124.4, 127.6, 129.9, 150.6 (aryl-C), 11.2 ($NHCH_2$), and 42.6 (CH_3).^{29}Si NMR (DMSO-d_6): $\delta = -150.4$.

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Adduct of 1 with Silver Nitrate (3)

Compound **1** (0.5 g, 0.996 mmol) was placed in a double necked round bottom flask and dissolved in anhydrous dichloromethane (20 mL). Silver nitrate (107.5 g, 0.996 mmol) was added under diffuse light and dry nitrogen atmosphere. The reaction mixture was stirred for 4 h at 25°C. Thereafter, the solvent was evaporated under reduced pressure and upon addition of hexane (20 mL), a white solid was obtained. The solid was filtered under dry nitrogen atmosphere, washed with hexane (2 mL), and dried under vacuum to give **3**. The compound is hygroscopic and insoluble in most solvents except dimethyl sulfoxide. Yield: 0.596 g (89.1%). M.p.: 250°C. Anal. calcd. for $C_{28}H_{30}O_6N_3SiSAg$ (672): C, 50.00; H, 4.47; N, 6.25; S, 4.76; Si, 4.6%. Found: C, 51.11; H, 4.49; N, 6.24; S, 4.69; Si, 4.59%. IR (Nujol, KBr, cm^{-1}): $\upsilon = 2147$ (NCS), 2925 (CH), 1463 (CH_2), 1105 (Si-O), 1677, 1260, and 1300 cm^{-1} (NO_3). ^{1}H NMR (DMSO-d_6): $\delta = 2.2$ (s, 9H, aryl-Me), 2.2 (s, 9H, aryl-Me), 4.2 (s, 6H, NCH_2), 6.7 (s, 3H, aryl-H), 6.8 (s, 3H, aryl-H). ^{13}C NMR (DMSO-d_6): $\delta = 56.6$ (NCH_2), 129.2 (t, $^1J_{CN} = 12.4$ Hz, NCS), 16.9 (aryl-Me), 19.6 (aryl-Me), 116.0, 116.7, 125.7, 128.0, and 150.2 (aryl-C). ^{29}Si NMR (DMSO-d_6): $\delta = -144.9$ (t, $^1J_{SiN} = 33.3$ Hz).

Adduct of 1 with Titanium(IV) Chloride (4)

Equimolar amounts of compound **1** (0.52 g, 1.03 mmol) and titanium(IV) chloride (1.9 g, 1.03 mmol) were mixed together in anhydrous dichloromethane (35 mL). The solution was stirred for 4 h at room temperature, and a yellow solid formed. The solid was filtered under dry nitrogen atmosphere, washed with hexane (5 mL), and dried under

vacuum to give **4**. The compound is hygroscopic and insoluble in most solvents except dimethyl sulfoxide. Yield: 0.57 g, (80.2%). M.p.: 250°C. Anal. calcd. for $C_{28}H_{30}Cl_4O_3N_2SiTi$ (692): C, 48.56; H, 4.34; N, 4.05; S, 4.62; Cl, 20.52; Si, 4.05%. Found: C, 48.07; H, 4.14; N, 3.99; S, 4.53; Cl, 20.61; Si, 4.14%. IR (Nujol, KBr, cm^{-1}): $\upsilon = 2023$ (NCS), 1017 (Si-OC), 810 (CS), 2924(CH), 1463 (CH_2), 1337(C = C). ^{1}H NMR (DMSO-d_6): $\delta = 2.2$ (s, 9H, aryl-Me), 2.2 (s, 9H, aryl-Me), 4.2 (s, 6H, NCH_2), 6.8 (s, 3H, aryl-H), 6.8 (s, 3H, aryl-H). ^{13}C NMR (DMSO-d_6): $\delta = 16.2$ (aryl-Me), 20.0 (aryl-Me), 129.3 (t, $^1J_{CN} = 13.2$ Hz, NCS), 55.2 (NCH_2), 116.5, 126.1, 128.2, 129.0, 133.6, and 150.7 (aryl-C). ^{29}Si NMR (DMSO-d_6): $\delta = -150$ (t, $^1J_{SiN} = 33.1$ Hz).

Adduct of 1 with Tin(IV) Chloride (5)

Tin(IV) chloride (0.5 g, 1.99 mmol) was added to compound **1** (1 g, 1.99 mmol) in anhydrous dichloromethane (35 mL). A white solid was formed. The reaction mixture was stirred for 3 h at room temperature. Thereafter the solvent was evaporated and hexane (20 mL) was added. The solid was filtered under reduced pressure, washed with hexane (5 mL), and dried under vacuum to give **5**. The compound is hygroscopic and insoluble in most solvents except dimethyl sulfoxide. Yield: 1.28 g (84.3%). M.p.: > 250°C. Anal. calcd. for $C_{28}H_{30}Cl_4O_3N_2SiSn$ (764.5): C, 44.04; H, 3.94; N, 3.67; S, 4.19; Cl, 18.61; Si, 3.67%. Found: C, 44.21; H, 3.04; N, 3.58; S, 4.04; Cl, 18.47; Si, 3.27%. IR (Nujol, KBr, cm^{-1}): $\nu =$ 2034 (NCS), 1066 (Si-O), 806 (CS). ^{1}H NMR (DMSO-d_6): $\delta = 2.1$ (s, 9H, aryl-Me), 2.2 (s, 9H, aryl-Me), 4.1 (s, 6H, NCH_2), and 6.9 (6H, s, aryl-H). ^{13}C NMR (DMSO-d_6): $\delta = 16.9$ (aryl-Me), 19.6 (aryl-Me), 127.5 (t, $^1J_{CN} =$ 12.4 Hz, NCS), 55.0 (NCH_2), 115.5, 123.5, 126.1, 131.9, 132.4, and 151.5 (aryl-C). ^{29}Si NMR (DMSO-d_6): $\delta = -147.8$ (t, $^1J_{SiN} = 33.6$ Hz).

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