n-C_4H_9Li in pentane at room temperature for 6 h. $NdCl_3 \cdot xH_2O$ (Research Chemicals, Phoenix, Ariz.) was dehydrated by the method of Taylor and Carter.[7] THF and toluene were distilled from potassium benzophenone ketyl. Pentane was washed with sulfuric acid, dried over $MgSO_4$, refluxed over finely divided $LiAlH_4$, and vacuum transferred. All reactions were performed under nitrogen or argon with standard Schlenk and drybox techniques as appropriate.[8]

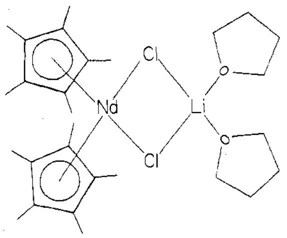
For $[(C_5Me_5)_2NdCl_2][Li(C_4H_8O)_2]$, addition of a white slurry of LiC_5Me_5 (1.66 g, 0.0117 M, in pentane) to a stirred slurry of $NdCl_3$ (1.46 g, 0.005 84 M, in THF) followed by stirring for 2 days at room temperature results in the formation of a cloudy aqua-blue solution. Removal of solvent from this mixture forms a sticky blue-green residue which is extracted with toluene to remove any unreacted $NdCl_3$ and byproduct LiCl. The blue powder obtained by rotary evaporation of the toluene from this solution is extracted with pentane to yield a blue solution from which blue-violet crystals form upon slight cooling (conveniently achieved by partial solvent removal with a rotary evaporator). The solution is quickly filtered, while cold, to isolate the crystalline product. Several crops of crystals are collected by repeating this procedure, leaving an increasingly green mother liquor. The combined microcrystalline product is further purified by cooling a saturated pentane solution at 0 °C until large purple crystals form. The final crystalline yield is 10–15%.[9] Anal. Calcd for $LiNdC_{28}H_{46}Cl_2O_2$: Li, 1.09; Nd, 22.65; C, 52.81; H, 7.28; Cl, 11.13; O, 5.02. Found:[10] Li, 1.01; Nd, 22.78; C, 52.82; H, 7.27; Cl, 11.28; O, 4.84 (by difference).

Results and Discussion

The reaction of $NdCl_3$ with 2 equiv of LiC_5Me_5 forms a crystalline product, I, formulated as $[(C_5Me_5)_2NdCl_2][Li(C_4H_8O)_2]$ based on complete elemental analysis and the following spectral data. Trivalent neodymium is indicated by the near-infrared–visible spectrum of I,[11] which exhibits a characteristic Nd^{3+} pattern, and by the room-temperature magnetic susceptibility,[12] $\chi_g = 8.536 \times 10^{-6}$ cm^3/g, $\mu_{eff} = 3.50$ μ_B, a value in the normal range for Nd^{3+}, 3.3–3.7 μ_B. The ^1H NMR spectrum of I in C_6D_6 exhibits broad resonances at δ 9.18, 1.13, and 0.11 (referenced to C_6H_6) which can be assigned to C_5Me_5 and THF, respectively. In THF, the resonance assigned to C_5Me_5 is found at δ 8.87 (referenced to THF or cyclohexane). The infrared spectrum of I exhibits several weak bands commonly observed in C_5Me_5 complexes,[13] and also displays absorptions at 1045, 915 and 895 cm^{-1} which are consistent with THF coordinated to a cationic center.[14]

The title compound is extremely air and moisture sensitive. Within seconds of air exposure, the complex decomposes to a green powder which turns red-brown upon further standing. These color changes are accompanied by a strong odor of C_5Me_5H. Hydrolytic decomposition of I is also rapid and yields C_5Me_5H.

Based on these data, the most probable structure for I is the chloro-bridged species shown below which allows for complete coordination of the lithium cation. A similar structure has been proposed by Lappert and co-workers for an yttrium complex, $[(Me_3SiC_5H_4)_2YCl_2][Li(C_4H_8O)_2]$.[14]



The attempted sublimation of I results in thermal decomposition at 270 °C. By analogy to the above yttrium case, the green decomposition product may be the neutral dimer, $[(C_5Me_5)_2NdCl]_2$. This latter product may also be present in the mother liquor from which I is obtained, since upon successive crystallizations of I, this solution becomes progressively greener. Removal of solvent from the green mother liquor leaves an oil, however, suggesting that a complex mixture is present as is found in bis(cyclopentadienyl)- and bis(methylcyclopentadienyl)neodymium chloride syntheses.[1] Since synthesis of I may be the only convenient solution route to a pure crystalline bis(cyclopentadienyl)neodymium chloride complex, we are investigating the use of I directly as a synthetic precursor.

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Registry No. I, 73597-12-3.

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(10) Alfred Bernhardt Analytical Laboratories, D-5250 Engelskirchen, Germany.

(11) Near-IR–visible (in THF, λ_{max}, nm (relative intensity, scale 1–100)): 617 (4), 615 (7), 609 (10), 608 (10), 603 (32), 601 (19), 597 (100), 596 (60), 592 (21), 591 (11), 586 (8).

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Formation of 1,1,1-Trimethyl-*N*-sulfinylsilanamine from the Direct Reaction of SO_2 with Hexamethyldisilazane

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The direct, facile reaction between sulfur dioxide and the common silylating agent hexamethyldisilazane (HMDS) resulting in the formation of 1,1,1-trimethyl-*N*-sulfinylsilanamine, $(CH_3)_3Si{-}N{=}S{=}O$ (**1**), has not previously been reported, although sulfur dioxide is known to react with bis(trimethylsilyl)diimine[1] and $Me_3SiHgSiMe_3$[2] to form the unstable bis(trimethylsilyl) sulfoxylate $(CH_3)_3Si{-}O{-}S{-}O{-}Si(CH_3)_3$ (**2**). Compound **1** was first made in 1966 from the reaction of tris(trimethylsilyl)amine with thionyl chloride at 70 °C in the presence of $AlCl_3$ catalyst.[3] Since that time a number of other synthetic methods have also been reported for its formation.[4-8] It should be noted that the germanium

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and tin homologues have also been synthesized.[5,6] Here we report what we believe is the most direct and efficient synthesis of **1** to date.

The silanamine (**1**) and related sulfinylamines have proven useful as synthetic precursors to selected heterocycles,[4,8] symmetric disulfides,[5] and additional sulfinylamines.[5–7,9–12] Preliminary experiments also indicate that **1** has fluorescent properties associated with its ultraviolet absorption bands characterized below, which suggests that the reaction described in this communication may be of considerable interest for trace sulfur dioxide analysis by fluorescent methods.

This reaction was first observed during experiments designed to stabilize by silylation reactive sulfur-containing molecules produced photochemically from SO_2 and hydrocarbons. The results indicated that residual SO_2 in the mixture reacted readily with the silylating reagent to form a new product which was separated by gas chromatography. Verification with anhydrous sulfur dioxide showed that HMDS reacts directly whereas trimethylchlorosilane (TMCS) is unreactive under ambient conditions.

Although **1** can be formed by bubbling SO_2 through pure HMDS or a dilute HMDS pentane solution, a more efficient and preferred procedure was developed. A measured amount (1:1 or 1:3 HMDS:SO_2) of SO_2 was transferred via a mercury-diffusion-pumped high-vacuum line into a liquid-nitrogen-cooled reaction vessel containing degassed HMDS. The reaction was then carried out by closing the Teflon stopcock to the vessel and letting the mixture warm to room temperature. Almost immediately upon melting of the mixture the reaction proceeds to completion forming a finely divided solid. The mixture of products can be removed as a pentane slurry from which the precipitate is filtered. The filtrate can then be collected and the pentane removed by evaporation in a stream of dry nitrogen. Alternately the liquid can be separated from the solid by vacuum distillation. Since the solid readily sublimes at room temperature, distillation either at reduced temperature or via a multiple trap procedure is necessary to ensure separation.

Purification of the product (**1**) was carried out gas chromatographically at 67 °C by using 5% SE-30 silicone oil on 45/60 mesh, acid-washed, DMCS-treated Chromosorb P in a 25 ft × $^1/_4$ in. aluminum column. The product was eluted with a retention volume of 570 mL at a helium carrier flow rate of 60 mL/min and was separated from hexamethyldisiloxane which is invariably present by a difference in retention volume of +120 mL. The pure product was collected at liquid-nitrogen temperature in a 1-mL glass trap fitted with a drying tube at the exit. Collection and storage in a dry atmosphere were included in the procedure because **1** reacts slowly with moisture in the air, leaving a solid white residue on the walls of the container.

It should be noted that the overall reaction is readily reproducible and proceeds in high yield. Although the detailed stoichiometry of the reaction products has not yet been determined with certainty, the amount of **1** produced represents some 22% of the total mass of reactants used. Thus from 60 g of SO_2 and HMDS in a 1:1 mole ratio, 13 g of the silanamine (**1**) is recovered. A further comment on the reaction conditions is also warranted. Whereas the initial studies were carried out under high vacuum to ensure reactant purity, it is clear that such stringent conditions are not required as long as moisture is carefully excluded. In fact this reaction has even been run in the air by simply blowing SO_2 gas through HMDS liquid although a nitrogen atmosphere or modest vacuum conditions at low temperature are preferred.

The pure (>99%) compound **1** has the following physical and spectral characteristics (IR and NMR have been reported previously and compare well). IR: 1302 cm^{-1} (strong) and 1132 cm^{-1} (medium) corresponding to the NSO asymmetric and symmetric vibrations, 570 cm^{-1} (medium) from NSO bending, and 1258 cm^{-1} (strong), 858 cm^{-1} (strong), and 770 cm^{-1} (medium) associated with the Si–CH$_3$ group. 60-MHz ^{1}H NMR: one singlet at $\delta(CCl_4)$ 0.35 (external Me$_4$Si). Mass spectroscopy: m/e (M − 15) = 120 (100%), no parent ion observed which is normal for trimethylsilyl compounds,[13] m/e = 73 (5%) from $Si(CH_3)_3^+$, m/e = 90 (8%) from $HO{-}Si(CH_3)_3^+$, and m/e = 75 (17%) from $HO{=}Si(CH_3)_2^+$, two products expected in the rearrangement of the trimethylsilyl group from nitrogen to oxygen via a four-membered ionic intermediate, and m/e = 46 (40%), probably corresponding to the NS$^+$ residual fragment following the rearrangement. UV: 237 and 295 nm in an absorbance ratio ~10:1, respectively, which are expected for sulfinylsilanamines.[9,14] Anal. Calcd: C, 26.6; H, 6.7; N, 10.4; Si, 20.8; S, 23.7; O, 11.8. Found: C, 26.20; H, 6.95; N, 10.21; Si, 20.46; S, 23.05; O, 12.04.

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Registry No. 1, 7522-26-1; SO$_2$, 7446-09-5; HMDS, 32713-31-8.

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Synthesis of Methylhydrazine in Nonaqueous Solvents

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Interest in the syntheses of hydrazine, methylhydrazine, and 1,1-dimethylhydrazine has developed because of their use as rocket fuels. The synthetic processes reported in the literature for the preparation of these substituted hydrazines in most instances are cumbersome requiring multiple step separations of these hydrazines from dilute aqueous solutions[1–4] and, therefore, are expensive. Apart from cost, some of the processes are known to involve intermediates that are hazardous and carcinogenic.[5] Alternate procedures for synthesizing the substituted hydrazines are, therefore, needed. One of the reactions[6–9] which has been investigated as the basis for an

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