and heated to 75 °C in an oil bath for 2 days. A dark insoluble material deposited inside the tube. A $^1$H NMR spectrum of the toluene-$d_8$ solution revealed resonances arising from complex **4b**. The tube was cracked open and the solution syringed off and placed in a new $^1$H NMR tube. The toluene was blown off under a rapid nitrogen stream and the resulting solid material dissolved in acetone-$d_6$, in which it was more soluble. A spectrum of this solution only revealed resonances arising from **4b**.

**Protonation of 5 To Give NiMo(CO)$_2$($\mu$-$\eta^1$,$\eta^2$-(*E*)-C(Me)=CHMe)($\eta^5$-C$_5$H$_5$)($\eta^5$-C$_5$H$_4$Me)(CO$_2$CF$_3$) (5a) and NiMo(CO)$_2$($\mu$-$\eta^1$,$\eta^2$-(*Z*)-C(Me)=CHMe)($\eta^5$-C$_5$H$_5$)($\eta^5$-C$_5$H$_4$Me)(CO$_2$CF$_3$) (5b).** The isomeric mixture of **5a**/**5b** was prepared in similar fashion to **2a**. Yield: 450 mg, 86%. **5a**:**5b** ≈ 2:1. IR ($\nu$(CO), dichloromethane): 2015 (s), 1808 (s), 1691 (s, $CF_3CO_2$) cm$^{-1}$. IR (Nujol): 2026 (s), 1807 (s), 1693 (s, $CF_3CO_2$) cm$^{-1}$. Anal. Calcd for $C_{19}H_{19}F_3MoNiO_4$: C, 43.51; H, 3.65. Found: C, 42.07; H, 3.65.

**Deuteration Experiments.** $^1$H NMR data (in ppm) are given for the vinylic resonances of the *Z* and *E* monodeutero isomers. $J_{HD}$ values are 1/6 those of corresponding $J_{HH}$ values and are not given. Chemical shifts in parentheses are those of small quantities of the corresponding protio isomer impurity. All experiments were carried out in a degassed Schlenk tube: a representative preparation of **1a**-(*Z*)-$d_1$ is given in full here.

**Preparation of NiW(CO)$_2$($\mu$-$\eta^1$,$\eta^2$-(*Z*)-CH=CHD)($\eta^5$-C$_5$H$_5$)($\eta^5$-C$_5$H$_4$Me)(CF$_3$CO$_2$) (1a-*d*$_1$).** 1 (118 mg, 0.25 mmol) was dissolved in 10 mL of diethyl ether in a degassed Schlenk tube. The solution was cooled in an ice bath, and trifluoroacetic acid-$d_1$ (48 $\mu$L, 0.625 mmol) was added using a microsyringe. The Schlenk tube was placed in an ice bath for 3 days, after which the now yellow black solution was concentrated to a few milliliters in vacuo and placed in a freezer at −20 °C to effect crystallization of **1a**-(*Z*)-$d_1$ (130 mg, 89%). Very slow deuterium scrambling takes place when **1a**-(*Z*)-$d_1$ is dissolved in acetone-$d_6$. After a 7-week period, the ratios of **1a**-(*Z*)-$d_1$ to **1a**-(*E*)-$d_1$ were ≈4.5:1. $^1$H NMR: **1a**-(*Z*)-$d_1$, $\delta$ 5.056 (5.066) [C*H*(2)D=CH]; **1a**-(*E*)-$d_1$, $\delta$ 3.544 (3.553) [C*H*(3)D=CH].

**Preparation of NiW(CO)$_2$($\mu$-$\eta^1$,$\eta^2$-(*Z*)-C(*n*-Pr)=CHD)($\eta^5$-C$_5$H$_5$)($\eta^5$-C$_5$H$_4$Me)(CF$_3$CO$_2$) (3a-(*Z*)-*d*$_1$).** **3** (60 mg, 0.117 mmol) was treated with trifluoroacetic acid-$d_1$ (20 $\mu$L, 0.26 mmol) yielding **3a**-(*Z*)-$d_1$ (66 mg, 90%). **3a**-(*Z*)-$d_1$: $^1$H NMR $\delta$ 4.952 (4.963) [C*H*(2)D=C(*n*-Pr)].

**Preparation of NiW(CO)$_2$($\mu$-$\eta^1$,$\eta^2$-(*Z*)-C(Ph)=CHD)($\eta^5$-C$_5$H$_5$)($\eta^5$-C$_5$H$_4$Me)(CF$_3$CO$_2$) (4a-(*Z*)-*d*$_1$).** The procedure mirrors that of **1a**-(*Z*)-$d_1$. Yield: 82%. When **4a**-(*Z*)-$d_1$ was dissolved in acetone-$d_6$, scrambling of the label to give a 1:1 mixture of **4a**-(*Z*)-$d_1$ and **4a**-(*E*)-$d_1$ took place within 10 h. $^1$H NMR: **4a**-(*Z*)-$d_1$, $\delta$ 4.696 (4.708) [C*H*(2)D=CPh]; **4a**-(*E*)-$d_1$, $\delta$ 3.468 (3.477) [C*H*(3)D=CPh].

**Reaction of 2a with Acetic Acid Affording NiW(CO)$_2$($\mu$-$\eta^1$,$\eta^2$-(*E*)-C(Me)=CHMe)($\eta^5$-C$_5$H$_5$)($\eta^5$-C$_5$H$_4$Me)(CO$_2$Me) (2a′).** **2a** (15 mg, 0.023 mmol) was dissolved in acetone-$d_6$ (≈0.6 mL) and placed in a $^1$H NMR tube. Acetic acid (3.5 $\mu$L, 0.062 mmol) was added: an $^1$H NMR spectrum obtained immediately after addition showed that no reaction had occurred. A spectrum, obtained after a 36-h period, showed resonances assignable to **2a** and **2a′** and to an unidentified organic product.

**X-ray Diffraction Study of 2a.** Crystal data and data collection parameters are tabulated in Table IV. Yellow brown crystals of **2a** were grown from diethyl ether solutions at −20 °C, and a single crystal was selected and mounted on an Enraf-Nonius CAD 4 diffractometer. Unit-cell parameters were based on 25 reflections with $21.9 < \theta < 22.5$. Three standard reflections were monitored every 5000 s of beam time; no decay was observed.

The structure was solved by direct methods and an empirical absorption correction was applied.[39] No correction for extinction was applied, and hydrogen atoms were not refined: their positions were calculated by using idealized geometries and a C–H bond distance of 0.95 Å. For hydrogen atoms of the methyl groups, one atom was located in a Fourier difference map, its position idealized and the remaining hyrogen atomic positions calculated. Refinement converged at $R$ = 0.030 and $R_w$ = 0.043.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the University of Notre Dame, for financial support. We thank the NSF (CHE 8615556) for purchase of a Microvax computer and a diffractometer.

**Registry No.** **1**, 121011-38-9; **1a**, 121029-31-0; **1a**-(*Z*)-$d_1$, 121011-40-3; **1a**-(*E*)-$d_1$, 121054-48-6; **2**, 110512-13-5; **2a**, 121011-41-4; **2a′**, 121011-42-5; **3**, 121011-39-0; **3a**, 121011-43-6; **3a**-(*Z*)-$d_1$, 121011-44-7; **3b**, 121029-32-1; **4**, 110512-17-9; **4a**, 121011-45-8; **4a**-(*Z*)-$d_1$, 121011-46-9; **4a**-(*E*)-$d_1$, 121054-49-7; **4b**, 121011-47-0; **5**, 99280-72-5; **5a**, 121011-48-1; **5b**, 121054-50-0; NiMo(CO)$_2$($\mu$-$\eta^2$,$\eta^2$-PhC$_2$H)($\eta^5$-C$_5$H$_5$)($\eta^5$-C$_5$H$_4$Me), 110512-09-9; NiW(CO)$_4$($\eta^5$-C$_5$H$_5$)($\eta^5$-C$_5$H$_4$Me), 110512-11-3.

**Supplementary Material Available:** Full listings of bond distances, bond angles, anisotropic thermal parameters for nonhydrogen atoms, and positional parameters for hydrogen atoms (9 pages); a listing of structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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# Simple Functional Siloles. 3,4-Dimethylsiloles with Si–F, Si–O, or Si–N Bonds and Other Silicon-Substituted Derivatives

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Stable 1-alkoxy (RO = MeO, $^i$PrO) and 1-dialkylamino ($R_2N$ = $Et_2N$) 1,3,4-trimethylsiloles have been prepared from 1,3,4-trimethylsilole (**1**). The 1-fluoro derivative appears to be less stable, and the synthesis of the 1-chloro derivative failed. 1-*n*-Butyl-, 1-allyl-, and 1-phenylsiloles have also been prepared from **1** and 1-phenyl-3,4-dimethylsilole (**2**) by Si–H substitution using lithium reagents, which can give a second substitution on the exocyclic Si–R bond. The low-temperature reaction of potassium hydride with **1** and **2** did not allow the chemical characterization of corresponding silacyclopentadienide anions.

Having obtained the first stable simple siloles with a silicon–hydrogen bond,[1] the functionalization of these metalloles on the heteroatom appeared possible either by direct substitution of the hydrogen atom or via the cor-

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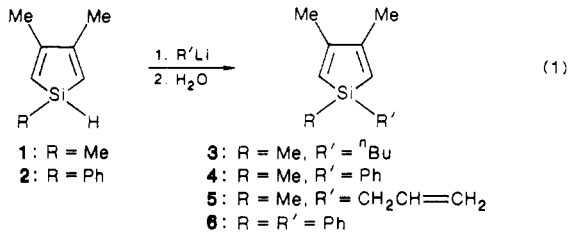
responding silacyclopentadienide anion.

With hydrosiloles **1** and **2**, lithium reagents allowed the preparation of 1-*n*-butyl-, 1-phenyl-, and 1-allylsiloles (**3**–**6**) (eq 1). These 1-substituted siloles are thus obtained in




(1)

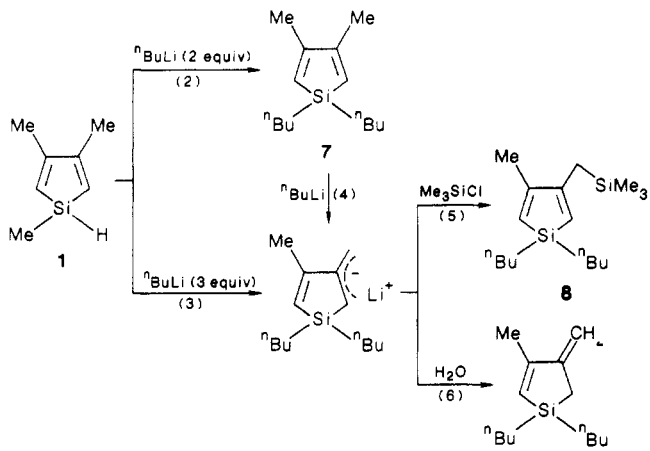
**1**: R = Me
**2**: R = Ph

**3**: R = Me, R′ = $^n$Bu
**4**: R = Me, R′ = Ph
**5**: R = Me, R′ = $CH_2CH{=}CH_2$
**6**: R = R′ = Ph

a more direct way than with the previously described method[2] which is preferable for the preparation of large quantities.

Using 1 equiv of lithium reagent, the only substitution observed in **1** and **2** is that of the hydrogen bonded to the silicon atom. An excess of lithium reagent may lead to a substitution of the exocyclic Si–R bond[3] (Scheme I). Two

**Scheme I**



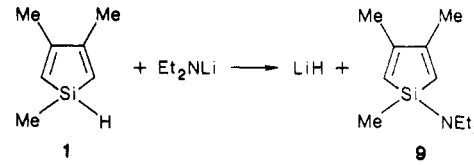

equivalents of BuLi react with **1** to give the dibutyl derivative **7** by substitution of the methyl group on silicon (eq 2). Moreover, a large excess of lithium reagent induces isomerization of the silole **a** into the transoid isomer **b**.[4]


**a** **b**

The formation of an allylic carbanion (eq 3 and 4), silylated by trimethylchlorosilane in the $\gamma$-position (eq 5) or protonated by water in the $\alpha$-position (eq 6), explains this isomerization. In contrast to results obtained with some C-phenylated siloles, we did not observe a reaction of the lithium reagent with the $\pi$ system.[7]

Due to the various transformations into a functional organosilane that a hydrosilane may undergo,[8] the preparation of 1-functional siloles from hydrosiloles **1** and **2** appeared feasible.

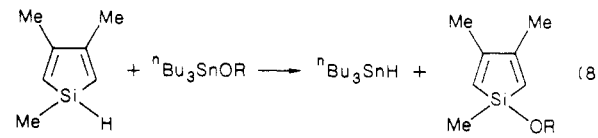
The aminosilole **9** was synthesized by the reaction of $Et_2NLi$ with the silole **1** (eq 7). The stable aminosilole thus obtained was separated by low-pressure distillation.




(7)

**1** **9**

The attempted catalytic alkoxylation of silole **1** by hydrosilylation of acetone or by dehydrocondensation in the presence of methanol failed.[9] The exchange reaction between an alkoxytin and a trialkylsilane does not require catalysis.[11] Already at room temperature, the silole **1** reacts with $Bu_3SnOMe$, giving 1-methoxy-1,3,4-trimethylsilole (**10**) in 80% yield. With $Bu_3SnO^iPr$, the reaction is a little slower and heating (50 °C) the reactants increases the proportion of transoid isomer formed[4] (eq 8).




(8)

**1**

**10**: R = Me
**11**: R = $^i$Pr

The fluorination of methoxysilole **10** was accomplished by using boron trifluoride–diethyl etherate (eq 9). The 1-fluoro-1,3,4-trimethylsilole (**12**), separated by low-pressure trapping, was analyzed by using NMR and GC/MS techniques. The reaction with MeMgI in ether produced 1,1,3,4-tetramethylsilole (**13**).[6] The same fluorosilole **12** was also obtained by the reaction of $Ph_3CBF_4$ with silole **1** in methylene chloride (Scheme II).

The current chlorination methods for hydrosilanes,[8] when applied to silole **1**, met with failure. This was the case for high-temperature reactions ($CCl_4$, $Bz_2O_2$, 100 °C) as well as for room-temperature reactions.[12] Attempts using methoxysilole **10** showed the same results. The conclusion reached is that 1-chloro-1,3,4-trimethylsilole (**14**) is a thermally unstable product. Although surprising at first, this result may be compared to recent results obtained with 1-halo-3,4-dimethylphospholes,[14] which,

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(3) Dubac, J.; Iloughmane, H.; Laporterie, A.; Roques, C. *Tetrahedron Lett.* **1985**, *26*, 1315.

(4) For a discussion on the isomerization **a** ⇄ **b** of the C-methylated siloles and their spectrometric identification, refer to ref 5 and 6.

(5) (a) Laporterie, A.; Manuel, G.; Iloughmane, H.; Dubac, J. *Nouv. J. Chim.* **1984**, *8*, 437. (b) Dubac, J.; Laporterie, A.; Manuel, G.; Iloughmane, H. *Phosphorus Sulfur* **1986**, *27*, 191.

(6) Dubac, J.; Laporterie, A.; Iloughmane, H. *J. Organomet. Chem.* **1985**, *293*, 295.

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(8) (a) Eaborn, C. *Organosilicon Compounds*; Butterworths: London, 1960. (b) Calas, R. *Nouveau Traité de Chimie Minérale*; Pascal, P., Ed.; Masson: Paris, 1965.

(9) Although many transition elements may, with simple siloles, form complexes on the dienic system,[10] some of their derivatives provoke a polymerization of the silole (Dubac, J. et al., unpublished work), in particular chloroplatinic acid.

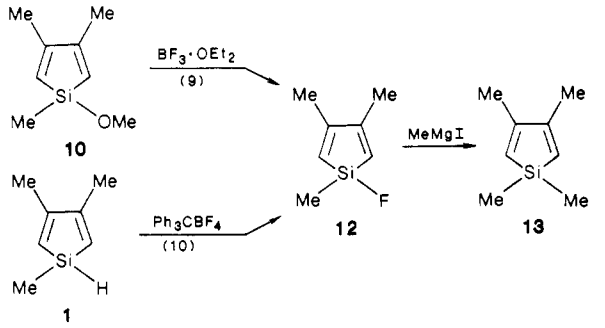
(10) (a) Laporterie, A.; Iloughmane, H.; Dubac, J. *J. Organomet. Chem.* **1983**, *244*, C12. (b) Burns, G. T.; Colomer, E.; Corriu, R. J. P. *Organometallics* **1983**, *2*, 1901. (c) Guimon, C.; Pfister-Guillouzo, G.; Dubac, J.; Laporterie, A.; Manuel, G.; Iloughmane, H. *Ibid.* **1985**, *4*, 636. (d) Ananias de Carvalho, L. C.; Dartiguenave, M.; Dahan, F.; Dartiguenave, Y.; Dubac, J.; Laporterie, A.; Manuel, G. *Ibid.* **1986**, *5*, 2205. (e) Burns, G. T.; Colomer, E.; Corriu, R. J. P.; Lheureux, M.; Dubac, J.; Laporterie, A.; Iloughmane, H. *Ibid.* **1987**, *6*, 1398.

(11) (a) Pijselman, J.; Péreyre, M. *J. Organomet. Chem.* **1973**, *63*, 139. (b) Dubac, J.; Mazerolles, P.; Cavezzan, J.; Quintard, J.P.; Péreyre, M. *Ibid.* **1980**, *197*, 261.

(12) The only case where 1-chloro-1,3,4-trimethylsilole (**14**) has been detected by $^1$H NMR is by the action of $Ph_3CCl$ in $CD_2Cl_2$[13] (20–40 °C): a substitution of the doublets SiMe (**1a** + **1b**) by two singlets (**14a** + **14b**) around 0.4 ppm, the disappearance of the SiH signal. The chloration reaction being rather slow, a degradation of the product was observed.

(13) Corey, J. Y.; West, R. *J. Am. Chem. Soc.* **1963**, *85*, 2430.

**Scheme II**




though unstable, may be stabilized as a pentacarbonyltungsten $\sigma$ complex, and with 1-chloro-2,3,4,5-tetramethylstibole and bismole, which decomposed upon attempted isolation.[15]

As for the kinetically unstable 5-halocyclopentadienes,[16-18] an effect similar to spiroconjugation[19] has been proposed to explain the modifications in the electronic spectra and the chemical reactivity of cyclopentadienone ketals and dioxothiophene.[18-20] The thermal instability of simple group 14 or 15 1-haloheteroles, for which a dimer form has never been identified,[21] could be the result of a more complex phenomenon. It must be noted that if the $\pi$ system is bonded to a transition metal, an unstable silole may be stabilized.[10] The ($\eta^4$-1-chloro-1,3,4-trimethylsilole)tricarbonyliron complex corresponding to the chlorosilole **14** has recently been isolated.[10e] A halosilole may also be stabilized if the ring carbon atoms carry phenyl substituents.[24]

If the chlorosilole **14** is unstable, the same is probably true for a C-unsubstituted chlorosilole such as 1,1-dichlorosilole, which would shed new light on the failures reported in early literature concerning its synthesis.[25]

The silacyclopentadienide anion was first reported in 1961.[26] As in the case of the silole precursor, the synthesis of this anion proved to be faulty.[25c] The metalation of hydrosilanes with potassium hydride, as proposed by Corriu and Guérin,[27] allowed the generation of C-phenylated silacyclopentadienide anions.[28] The reaction of an electrophile with these anions may provide a method of functionalizing the heterocycle.

Although a recent theoretical study showed that the silacyclopentadienide anion's lowest energy state is pyramidal which prevents all resonance between the $\pi$ system and the silicon electron pair,[29] we nevertheless attempted to transform hydrosiloles **1** and **2** into corresponding silacyclopentadienide anions. When treated with potassium hydride in THF in the presence of crown ether (18-crown-6),[28b] the siloles **1** and **2** (3 mmol) show between −50 °C and −30 °C, a slow hydrogen production. The mixture, having turned brown, is treated with $D_2O$ or MeI or $Me_3SiCl$, extracted with pentane, and analyzed by GC/MS. **1** (or **2**) totally disappears, but no trace of the corresponding 1-deuteriated, 1-methylated or 1-trimethylsilylated silole, is ever found. The 3,4-dimethylsilacyclopentadienide anions therefore appear to be unstable entities that decompose too rapidly to be trapped by an electrophile.

Attempts at the preparation of silolium ions derived from **1** and **2** by hydride abstraction are in progress.

## Experimental Section

**1. General Data.** The starting hydrosiloles **1** and **2** have been prepared by flash vacuum pyrolysis of 1-allyl-1,3,4-trimethylsilacyclopent-3-ene and 1-allyl-1-phenyl-3,4-dimethylsilacyclopent-3-ene, respectively.[1] The reactions were carried out from a mixture of silole **1a** or **2a** and its transoid isomer **1b** or **2b** (**1a**/**1b** = 6.14:1, **2a**/**2b** = 9:1).

NMR spectra were recorded on a Varian EM 360 ($^1H$) and on a Brüker AM 300 WB ($^1H$, $^{13}C$, $^{19}F$, $^{29}Si$) spectrometers [$\delta$ in ppm from TMS or $CF_3COOH$ ($^{19}F$)].

**2. Preparation and Identification of Compounds. 1-*n*-Butyl-1,3,4-trimethylsilole (3).** A solution of 10 mmol of *n*-butyllithium (1.6 M in hexane) was added dropwise by using a syringe to a stirred solution of 1.24 g (10 mmol) of hydrosilole **1** in THF (8 mL) cooled at −70 °C. The mixture was allowed to warm to room temperature and stirred there for 2 h. After hydrolysis and extractions ($Et_2O$), the organic solution was concentrated (30 mmHg). Distillation gave **3** (1.50 g) in 85% yield; bp 95–98 °C (13 mmHg). **3a**: $^1H$ NMR (60 MHz, $CCl_4$) $\delta$ 0.08 (s, SiMe), 1.95 (b s, CMe), 5.50 (b s, C=CH), 0.8–1.6 (m, Bu), 4.90 and 5.70 (C=$CH_2$ and C=CH in **3b**). **3a**/**3b** = 4:1. GC/MS: $M^+$ 180 (6), $(M - C_4H_8)^+$ 124 (100%). Compound **3** was identified as the already described product.[3]

**1-Phenyl-1,3,4-trimethylsilole (4).** The silole **4** was prepared from 10 mmol of **1** and 10 mmol of phenyllithium (2 M in $C_6H_6/Et_2O$) by the same process as silole **3** in 87% yield; bp 81–83 °C (0.1 mmHg). **4a**: $^1H$ NMR (60 MHz, $CCl_4$) $\delta$ 0.45 (s, SiMe), 2.03 (b s, CMe), 5.80 (b s, C=CH), 5.12 and 6.00 (C=$CH_2$ and C=CH in **4b**), 7.30 (Ph). **4a**/**4b** = 4.08: 1. Compound **4** was identified as the already described product.[2]

**1-Allyl-1,3,4-trimethylsilole (5).** Silole **5** was prepared from 10 mmol of **1** and 10 mmol of allyllithium (Seyferth method)[30] by the same process in 80% yield; bp 80–82 °C (15 mmHg). **5a**: $^1H$ NMR (60 MHz, $CCl_4$) $\delta$ 0.10 (s, SiMe, **5a**), 0.13 (s, SiMe, **5b**), 1.93 (b s, CMe), 5.48 (b s, C=CH), 4.53–6.13 (CH=$CH_2$). **5a**/**5b** = 4:1. Compound **5** was identified as the already described product.[2]

**1,1-Diphenyl-3,4-dimethylsilole (6).** Silole **6** was obtained from 1 g (5.3 mmol) of hydrosilole **2** and 5.3 mmol of phenyllithium (2 M in $C_6H_6/Et_2O$) by the same process in 72% yield; bp 135–140 °C (0.05 mmHg). **6a**: $^1H$ NMR (60 MHz, $CCl_4$) $\delta$ 2.03 (b s, CMe), 5.95 (b s, C=CH), 5.06 and 6.08 (C=$CH_2$ and C=CH in **6b**), 7.43 (Ph). **6a**/**6b** = 4.1:1 before distillation and 1.5:1 after distillation.

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(15) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310.
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(21) Dimers have been identified in the case of kinetically unstable 1-methylsilole,[22] 1,1-dimethylsilole,[23] and 1,1,3-trimethylsilole.[6] The 1,1-$R_2$-3,4-dimethylsiloles are stable products as monomers, but they isomerize into the transoid form.[4]
(22) Barton, T. J.; Burns, G. T. *J. Organomet. Chem.* **1979**, *179*, C17.
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Compound **6** was identified as the already described product.[2]

**1,1-Di-*n*-butyl-3,4-dimethylsilole (7).** Starting from 1.24 g (10 mmol) of hydrosilole **1**, using 20 mmol of *n*-butyllithium (1.6 M in hexane), by the same process as for **3**, we was obtained 1.58 g (71% yield) of silole **7**, bp 122–125 °C (13 mmHg). **7a**: $^1$H NMR (60 MHz, $CCl_4$) $\delta$ 0.8–1.6 (m, Bu), 1.96 (b s, CMe), 5.50 (b s, C=CH), 4.90 and 5.70 (C=$CH_2$ and C=CH in **7b**). **7a/7b** = 3:1. GC/MS:$M^+$ 222 (2), $(M - C_4H_8)^+$ 166 (39), $(M - 2C_4H_8)^+$ 110 (100%). Compound **7** was identified as the already described product.[3]

**1,1-Di-*n*-butyl-3-((trimethylsilyl)methyl)-4-methylsilole (8).** Similarly, in THF at −70 °C, 3 equiv (30 mmol) of *n*-butyllithium were added to 1.24 g (10 mmol) of hydrosilole **1**. After 2 h at room temperature, the reaction was quenched by 3.3 g (30 mmol) of trimethylchlorosilane. The mixture was hydrolyzed, extracted with $Et_2O$, and distilled. Silole **8** (2.06 g) was obtained in 70% yield; bp 100–102 °C (0.03 mmHg). $^1$H NMR (60 MHz, $CCl_4$): $\delta$ 0.0 (s, SiMe), 0.8–1.6 (m, Bu), 1.81 (s, $SiCH_2C$=C), 1.93 (b s, CMe), 5.27 and 5.53 (m, C=CH). The same silole **8** was obtained from silole **3**, 2 equiv of *n*-butyllithium, and trimethylchlorosilane.[3]

**1-(Diethylamino)-1,3,4-trimethylsilole (9).** The reaction was carried out at −70 °C in anhydrous $Et_2O$ with reactants **1** (1.6 g, 12.9 mmol) and $Et_2NLi$ (12.9 mmol, from $^n$BuLi and $Et_2NH$). The mixture was allowed to warm to rom temperature and stirred for 2 h. The lithium hydride formed was separated by centrifugation and the solution distilled. **9** was obtained in 85% yield (2.14 g); bp 80–82 °C (10 mmHg). **9a**: $^1$H NMR (300 MHz, $C_6D_6$) $\delta$ 0.31 (s, SiMe), 0.22 (s, SiMe in **9b**), 1.84 (d, $^4J$ = 0.9 Hz, CMe), 0.99 and 2.79 (t and q, $^3J$ = 7 Hz, $NEt_2$), 0.92 and 2.73 (t and q, $^3J$ = 7 Hz, $NEt_2$ in **9b**), 5.58 (q, $^4J$ = 0.9 Hz, C=CH), 5.37 and 5.90 (C=$CH_2$ and C=CH in **9b**). **9a/9b** = 4:1 $^{13}$C NMR (75.47 MHz, $C_6D_6$): $\delta$ −6.0(SiMe), 16.0 ($NCCH_3$), 20.3 ($CCH_3$), 40.9 ($NCH_2$), 125.2 ($SiCH$=), 158.5 (=$CCH_3$). $^{29}$Si NMR (59.63 MHz, $C_6D_6$): $\delta$ −3.7. Anal. Calcd for $C_{11}H_{21}NSi$: C, 67.62; H, 10.83. Found: C, 67.5; H, 10.8.

**1-Methoxy-1,3,4-trimethylsilole (10).** The reaction, periodically analyzed by GC, was done without solvent with equimolecular quantities (12 mmol) of silole **1** and methoxytributyltin. The reaction is exothermic. Alkoxysilole **10** (1.48 g, 80% yield) was isolated by distillation and the residue identified as $^n$$Bu_3SnH$; bp 66–68 °C (20 mmHg). **10a**: $^1$H NMR (300 MHz, $C_6D_6$) $\delta$ 0.29 (s, SiMe), 0.22 (s, SiMe in **10b**), 1.79 (d, $^4J$ = 1 Hz, CMe), 3.55 (s, OMe), 3.23 (s, OMe in **10b**), 5.42 (q, $^4J$ = 1 Hz, C=CH), 5.03, 5.13, and 5.82 (C=$CH_2$ and C=CH in **10b**). **10a/10b** = 3:1. $^{13}$C NMR (75.47 MHz, $C_6D_6$): $\delta$ −5.4 (SiMe), 20.5 ($CCH_3$), 50.8 ($OCH_3$), 122.0 ($SiCH$=), 158.8 (=$CCH_3$). $^{29}$Si NMR (59.63 MHz, $C_6D_6$): $\delta$ 8.1. GC/MS: $M^+$ 154 (37), $(M - Me)^+$ 139 (70), $MeOSi^+$ 59 (100%). Anal. Calcd for $C_8H_{14}OSi$: C, 62.28; H, 9.15. Found: C, 62.3; H, 9.1.

**1-Isopropoxy-1,3,4-trimethylsilole (11).** Equimolecular quantities (12 mmol) of silole **1** and isopropoxytributyltin were warmed to 50 °C for 1 h. Isopropoxysilole **11** was separated by distillation (1.31 g, 60% yield); bp 77–80 °C (15 mmHg). **11a**: $^1$H NMR (60 MHz, $C_6D_6$) $\delta$ 0.3 (s, SiMe), 1.9 (b s, CMe), 1.2 and 3.9 (d and sept, $^3J$ = 6 Hz, $O^iPr$), 5.5 (b s, C=CH), 5.1 and 5.9 (C=$CH_2$ and C=CH in **11b**). **11a/11b** = 1.5:1. Anal. Calcd for $C_{10}H_{18}OSi$: C, 65.87; H, 9.95. Found: C, 65.9; H, 9.9.

**1-Fluoro-1,3,4-trimethylsilole (12).** **10** (1.54 g, 10 mmol) (**a:b** = 3:1) was treated by 20 mmol of $BF_3$·$OEt_2$ at 0 °C. The solution was stirred for 5 h at room temperature. After elimination of the remaining $BF_3$ by precipitation with $Me_3N$, the solution was concentrated under a pressure of 300 mmHg. The residue, withdrawn under reduced pressure (1 mmHg), yields a colorless liquid (0.94 g) essentially composed of fluorosilole **12** which is analyzed by NMR and GC/MS. Attempts at distillation under 30 mmHg (under the same conditions as for **1**)[1] lead to its decomposition. **12a**: $^1$H NMR (300 MHz, $C_6D_6$) $\delta$ 0.25 (d, $^3J$(H/F) = 7.4 Hz, SiMe), 0.15 (d, $^3J$(H/F) = 7.2 Hz, SiMe in **12b**), 1.66 (b s, CMe), 5.36 (b s, C=CH), 4.95, 5.10, and 5.70 (C=$CH_2$ and C=CH in **12b**). **12a/12b** = 3:1. $^{13}$C NMR (75.47 MHz, $C_6D_6$): $\delta$ −5.0 (d, $^2J(^{13}C/F)$ = 18 Hz, SiMe), 20.3 ($CCH_3$), 120.1 (d, $^2J(^{13}C/F)$ = 15 Hz, $SiCH$=), 159.7(=$CCH_3$). $^{19}$F NMR (282 MHz, $C_6D_6$): $\delta$ (from $CF_3COOH$) −43.2 (bq, $^3J$ = 7.4 Hz); GC/MS: $M^+$ 142 (64), $(M - Me)^+$ 127 (100%).

The same fluorosilole **12** was obtained by the reaction of 2.64 g (8 mmol) of triphenylmethyl tetrafluoroborate[31] on 1 g (8 mmol) of hydrosilole **1**. During the addition of $Ph_3CBF_4$ in 20 mL of methylene chloride to a solution of silole in 10 mL of the same solvent, the reaction mixture was maintained at 0 °C, then allowed to warm to room temperature, and stirred for 1 h. The solution was concentrated under a pressure of 300 mmHg, and the expected silole separated from $Ph_3CH$ under a pressure of 1 mmHg. The crude withdrawn product (0.6 g), analyzed by NMR and containing essentially the silole **12**, was treated by methylmagnesium iodide in $Et_2O$. After hydrolysis and extractions, the product was identified as 1,1,3,4-tetramethylsilole (**13**) by NMR and GC/MS[6] (80% GC purity).

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