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Silicon Compounds of 1,1-Bis(pyrrol-2-yl)ethenes: Molecular Structures and Chemical and Spectroscopic Properties

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Supporting Information

ABSTRACT: The first examples of silicon compounds of 1,1bis(pyrrol-2-yl)ethenes have been synthesized via salt metathesis from a 2-fold lithiated dipyrromethene and different diorganodichlorosilanes (i.e., dimethyldichlorosilane, diphenyldichlorosilane, and 1,1-dichlorosilacyclobutane). Herein we report on their molecular structures, their optical properties, and some reactivity patterns.

S ince the discovery of the excellent photochemical properties of boron-containing dipyrromethene compounds (Chart 1), such derivatives have been widely explored in the interim. These so-called BODIPYs¹ (boron dipyrromethenes) have found diverse applications such as protein markers, selective ion sensors, and solar cell sensitizers.²⁻⁴ Moreover, the BODIPY moiety has also been introduced into a chelating triphosphane for transition-metal complexation while sustaining its fluorescence properties.⁵





In addition to boron as the most frequently explored central element of dipyrromethene chelates there have also been a considerable number of compounds reported in literature which involve transition metals (e.g., Co, 6 Ni, 7 and Cu⁸) and Zn^{9,10} coordinated by this bidentate ligand system.

In terms of group 13 elements beyond boron the central elements aluminum,¹¹ gallium,¹² and indium^{12a,b} have been successfully introduced into this class of compounds, and dipyrromethene compounds with group 14 elements (germanium¹³ and tin^{13,14}) have been synthesized as well (Chart 1).



In 2011 the notable lack of silicon analogues was closed with an ONNO-functionalized ligand which had also been used for the preparation of an Al complex before.¹⁵ The extension of the classical dipyrrin with adjacent hydroxy anchors promoted complexation of the Si atom (Chart 1).

Following an analogous reaction protocol with the same organochlorosilanes and a structurally related oxygen-free triphenyldipyrromethene, Nabeshima et al.¹⁵ only recovered the unreacted starting material. This hints at certain difficulties in dipyrromethene silicon complexation. With the confidence that silicon should nevertheless be capable of accepting dipyrromethene ligands in its coordination sphere, we successfully addressed this issue with an alternative synthesis route (including lithiation of the ligand) and could overcome preliminary recoils. Unexpectedly, the dipyrromethene ligand used for our investigations gave rise to a 2-fold deprotonated 1,1-bis(pyrrol-2-yl)ethene, the motif of which is retained in the resulting silicon compounds. Therefore, we now report on the first examples of silicon 1,1-bis(pyrrol-2-yl)ethene compounds in detail.

RESULTS AND DISCUSSION

As starting materials we have chosen the easily accessible diethylpentamethyldipyrromethene hydrochloride derivative 1 (Scheme 1),¹⁶ keeping in mind the difficulties reported earlier with meso-phenyl-substituted compounds.¹⁵ Despite their wide exploration as BF₂ complexes, compounds such as 1 and the analogous perchlorate salt 1' still lack crystallographic characterization. We obtained 1 as a bright red powder and were able to convert it into the hydroperchlorate 1', which formed large crystals suitable for X-ray diffraction analysis (Figure 1). The crystal structure of 1, which comprises the same cation, is given in the Supporting Information.

The free base, the 1,1-bis(pyrrol-2-yl)ethene compound 2, was obtained by treatment of 1 with triethylamine (Et_3N), as

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Scheme 1



Figure 1. Molecular structure of 1' in the crystal state. The ellipsoid probability level is set at 50%, and carbon-bound hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and torsion angles (deg): $C2-C3 \ 1.507(2)$; $N1-C1-C2-C3 \ 24.7(2)$, $N2-C4-C2-C3 \ 21.0(2)$. Note that simple atomic labels have been chosen for clarity; they do not correspond to the labels in the CIF file in the Supporting Information.

confirmed by NMR spectroscopy (in accord with data reported earlier by Thompson et al.,¹⁷ who also reported the crystal structure which corresponds to **2** as drawn in Scheme 1). Thompson et al.¹⁷ had obtained crystals of **2** by slow evaporation of a pentane solution. Upon cooling a saturated solution of **2** in hexane, we also obtained crystals which, to our surprise, were revealed to consist of the alternative tautomer, the dipyrromethene **2**' (Figure 2).

For comparison Table 1 gives selected structural features of 2 and 2', which clearly illustrate structural differences between



Figure 2. Molecular structure of 2' in the crystal state. The ellipsoid probability is set at 50%. The C2–C3 bond is situated on a crystallographically imposed 2-fold axis. Therefore, the N and NH sites are disordered in a 50:50 ratio by symmetry. Only one N…NH combination is depicted. Note that simple atomic labels have been chosen for clarity; they do not correspond to the labels in the CIF file in the Supporting Information.

Table 1. Selected Bond Lengths (Å) and Torsion Angles
(deg) of 2' and Related Parameters from $2^{17 a}$

			:	2
		2'		
	C2-C3	1.512(5)	1.338(3)	1.346(3)
	C1-C2	1.415(4)	1.471(3)	1.458(3)
	C2-C4	1.415(4)	1.477(3)	1.473(3)
	N1-C1-C2-C3	179.1(3)	32.8(3)	32.6(3)
	N2-C4-C2-C3	179.1(3)	133.6(2)	144.4(2)
a	contains true ind			

^a2 contains two independent molecules in the crystallographic asymmetric unit.

the two tautomers. Apparently, in solution they coexist in equilibrium, as in both cases they were obtained from similar solvents but at different temperatures. However, variable-temperature NMR studies of **2** in deuterated $[D_{14}]n$ -hexane provided no hints of the presence of any equilibrium. Unexpectedly, only a set of signals characteristic of **2** was detected in solution in a temperature range from -55 to +18 °C.

At this point we applied computational methods¹⁸ to address this issue. The molecular structures of 2 and 2' were optimized as gas-phase structures of isolated molecules at the DFT (MPW1PW91 6-311G(d,p)) level, thus revealing an energy difference between both tautomers of only 0.96 kcal/mol. Single-point energy calculations of the optimized structures with alternative methods and basis sets are in support of the small energetic differences between both tautomers (Table 2). Although 2' is predicted to represent the more stable tautomer in each case, these energy differences point at the coexistence of both tautomeric forms in solution.

Та	ble	e 2.	Calcula	ated	Energy	Dif	fferences	between	2	and	2	ć
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method	$\Delta E \; (\text{kcal/mol})^a$
MPW1PW91	0.96
MP2 6-31G(d)	2.09
B3LYP 6-31G(d,p)	3.53
B3LYP 6-311G+(d,p)	1.23
$^{a}\Delta E = E(2) - E(2').$	

Comparison of the calculated absorption spectra of 2 and 2' (DFT TD-SCF, B3LYP 6-311G*(d,p)) with the experimental spectrum reveals that both 2 and 2' should exhibit two absorption bands in the range 250-500 nm, but the experimental spectrum shows three bands, which can be interpreted as the superposition of the spectra of 2 and 2' (Figure 3). Therefore, we assume that in solution tautomers 2 and 2' both coexist in a rapid exchange equilibrium, thus giving rise to the recorded absorption spectrum as a sum of the spectra of both forms, even though we could not detect 2' by means of NMR spectroscopy.

In a first attempt at synthesizing a silicon complex out of the dipyrromethene ligand 2', we confirmed the earlier finding of Nabeshima et al.:¹⁵ i.e., upon mixing of 2' with SiCl₄ in the presence of Et₃N we found the starting materials unreacted. Therefore, to enhance reactivity, we used *n*BuLi to deprotonate the ligand. Even though we were aiming at the monolithiated dipyrromethene-like ligand (examples had been reported in the literature by Thompson¹⁹), only the dilithiated 1,1-bis(pyrrol-2-yl)ethene 3 was isolated despite the 1:1 stoichiometry of 2' and *n*BuLi used: i.e., compound 3 formed while 50% of the starting



Figure 3. Comparison of absorption spectra recorded for the reaction product 2' and calculated for the different tautomers 2 and 2' (using DFT TD-SCF B3LYP 6-311G*(d,p)).

Scheme 2





Figure 4. Molecular structure of 3.4THF in the crystal state. The ellipsoid probability level is set at 50%. Most hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and torsion angles (deg): Li1–N1 1.976(2), Li1–N2 2.068(2), Li2–N1 2.296(2), Li2–N2 2.035(2); N1–C1–C2–C3 140.7(1), N2–C4–C2–C3 173.7(1). Note that simple atomic labels have been chosen for clarity; they do not correspond to the labels in the CIF file in the Supporting Information.

material 2' remained unreacted (Scheme 2). Compound 3 precipitates almost quantitatively from hexane solution as a bright red and highly air and moisture sensitive powder and can be recrystallized from THF, yielding the corresponding THF solvate 3.4THF. The molecular structure of the latter was confirmed by single-crystal X-ray diffraction analysis (Figure 4).

The lithium atoms in the solvate 3.4THF, which each exhibit a tetrahedral coordination sphere, bridge the two pyrrolide nitrogen atoms and both contain two molecules of THF in the coordination sphere. The Li1...Li2 separation (2.803(3) Å) is significantly longer than in the related structures of *N*-indolyllithium THF solvate (2.57 Å) and *N*-carbazolyllithium THF solvate (2.66 Å).²⁰ The Li–N bond lengths vary in a wide range (1.98–2.30 Å). In contrast to the structure of **2**, both pyrrole nitrogen atoms point to the same side of the molecule, thus resembling a preorganization of the ligand arrangement suitable for formation of silicon complexes.

In further pursuits, compound 3 reacted with a variety of diorganodichlorosilanes with LiCl elimination to furnish the organosilicon compounds 4a-c (Scheme 3). These were





obtained as deep yellow oils and could be recrystallized from hexane, thus yielding crystals suitable for single-crystal X-ray diffraction analysis (Figure 5 and Table 3).

In general, the coordination spheres around the silicon atoms are close to tetrahedral; only the C5-Si1-C6 angle in the silacyclobutane ring of 4c is noticeably smaller due to steric constraints associated with the four-membered ring. The sum of angles about C2 is close to or equal to 360° (>359° in all cases), and the six-membered rings Si1N1C1C2C4N2 exhibit boat conformations. For example, in compound 4a the deviations from the least-squares plane of this six-membered ring are 0.208(1) and 0.231(1) Å in one direction for Si1 and C2, respectively, whereas the other four atoms are displaced into the opposite direction to similar extents (0.112(1),0.108(1), 0.075(1), and 0.144(1) Å for N1, C1, C4, and N2, respectively). As a result of this boat conformation in compounds 4a-c, the angles between the least-squares planes of the pyrrole rings (α) are similar. Nonetheless, one can still find differences between the angles α and one might expect closer analogy between 4a and 4b, since both silicon centers carry acyclic substituents. Thus, differences in their molecular structures hint at some degree of flexibility of this kind of ligand system, which might be of interest in terms of optical properties, especially fluorescence, which is most important for applications of BODIPY derivatives. A planar conjugated system is regarded to enhance the efficiency of fluorescence processes.15

Optical Characterization. Figure 6 shows the absorption spectra of 2 and 4a-c (see also Table 4). All of these compounds exhibit significant absorbances between 400 and 500 nm, thus appearing yellow to the eye. In the UV region the absorbance of 4b distinctly exceeds the others at around 220 nm due to $\pi \rightarrow \pi^*$ transitions of its phenyl substituents.

As Nabeshima et al.¹⁵ observed fluorescence of their SIDIPYs, which comprise the "regular" dipyrromethene backbone (analogously to BODIPYs which are best known



Figure 5. Molecular structures of (from top) compounds $4\mathbf{a}-\mathbf{c}$ in the crystal state. $4\mathbf{a}$ crystallized as the hexane solvate $4\mathbf{a} \cdot 0.5(n$ -hexane); the solvent molecule is omitted for clarity. For $4\mathbf{c}$ only one of the two crystallographically independent molecules from the modification of $4\mathbf{c}$ in space group $P2_1$ is shown. The ellipsoid probability level is set at 50%. Note that simple atomic labels have been chosen for clarity; they do not correspond to the labels in the CIF files in the Supporting Information.

Table 3. Selected Angles (deg) of Compounds 4a-c and 3^{a}

	4a	4b	4c	3		
N1-Si1-N2	100.6(1)	101.2(1)	101.1(1)-102.2(1)			
C5-Si1-C6	111.4(1)	113.8(1)	80.7(1)-82.0(1)			
α	27.1	19.5	18.7–29.1 (av 22.6)	46.5		
$^{a}\alpha$ is the angle between the least-squares planes of the pyrrole rings						
relative to one another.						

for this property), we expected our compounds to exhibit similar optical features. Surprisingly, for compounds **4a**,c as well as for **2** we could not observe any significant fluorescence, as shown by their 3D fluorescence spectra (Figure 7). This might originate from the cross-conjugated 1,1-bis(pyrrol-2-yl)ethene π system. In this context we were then surprised to observe fluorescence for **4b** with absorption and emission maxima at 350 and 534 nm, respectively. We thus conclude that this fluorescence is predominantly due to the phenyl substituents at the silicon center, which seems reasonable since other "simple" diphenylsilicon compounds can also exhibit fluorescence (for example, the emission spectrum of 1,1-dimethyl-3,3,5,5tetraphenylcyclotrisiloxane shows absorption and emission maxima at 388 and 459 nm, respectively).²¹ For compound



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Figure 6. Absorption spectra of **2** and **4a**–**c** (0.05 mM solutions in *n*-hexane, recorded at room temperature, d = 10 mm, quartz cuvette).

Table 4. Absorption Wavelengths λ_{max} (nm) and Extinction Coefficients ε (L mol⁻¹ cm⁻¹) of Compounds 2 and 4a-c (Figure 6)

	$\lambda_{ m max}$	ε
2/2'	455	5133
	297	14069
4a	466	819
	302	8546
4b	503/410	1275/1286
	302	10649
4c	502	224
	304	11753

4b the fluorescence quantum yield $\Phi_{4b} = 0.011 \ (\lambda_{ex} \ 350 \ nm)$ was determined by applying a comparative method²² using anthracene as reference ($\Phi_{anthracene} = 0.27$).²³ Hence, the fluorescence of **4b** is rather poor with respect to what is known for BODIPYs where Φ might reach high values such as 0.95 for 1,3,5,7,8-pentamethyldipyrromethene boron difluoride.²⁴

In order to elucidate the essential differences between the electronic transitions in compounds 4a.b. we have optimized their gas-phase molecular structures and performed TD-DFT calculations (see the Supporting Information). For the SiMe₂ compound 4a we found the UV/vis absorptions around 300 nm (Figure 6) to originate from HOMO \rightarrow LUMO and HOMO-1 \rightarrow LUMO transitions. Whereas HOMO and HOMO-1 are predominantly composed of contributions of the pyrrole π systems, LUMO represents the π^* orbital of the ethene C=C bond; thus, the UV/vis absorption of 4a at ca. 300 nm reflects electron transfer from the conjugated 1,1bis(pyrrol-2-yl)ethene system into the ethene π^* level. In sharp contrast, the UV/vis absorptions observed for compound 4b in the range 300-370 nm (see Figure 6), which give rise to the luminescence of this compound (see Figure 7), originate from transitions from HOMO and HOMO-1 into the orbitals LUMO+1/+2/+3/+4. Whereas HOMO and HOMO-1 of compound 4b resemble the same orbitals as in 4a, the orbitals LUMO+1/+2/+3/+4 of **4b** are predominantly composed of π^* interactions within the SiPh₂ phenyl groups; thus, the UV/vis absorptions of 4b at ca. 300-370 nm reflect electron transfer from the conjugated 1,1-bis(pyrrol-2-yl)ethene system into the phenyl π^* level. Therefore, our calculations confirm that the

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Figure 7. Fluorescence 3D scan spectra of (a) 2, (b) 4a, (c) 4b, and (d) 4c (0.05 mM solutions in hexane, recorded at room temperature, 10×10 mm quartz cuvette). Please note the different scaling for 4b. A linear scale was applied in each case.

 ${\rm SiPh}_2$ moiety alters the nature of electronic transitions in compounds 4.

For a comparison of electronic transitions in dipyrromethene vs 1,1-bis(pyrrol-2-yl)ethene systems, the model compound L^{H} SiMe₂ (a 4a analogue which lacks the alkyl substituents at the pyrrole rings) and the related dipyrromethene $HL^{H}SiMe_{2}F$ were analyzed by TD-DFT. In general, L^{H} SiMe₂ exhibits the same electronic transitions as 4a (slightly blue shifted), whereas $HL^{H}SiMe_{2}F$ exhibits transitions from HOMO/-1/-2 to LUMO, all orbitals of which are composed of π contributions of the dipyrromethene backbone. Whereas the dipyrromethene backbone is rather rigid (as a prerequisite for efficient fluorescence), relaxation of the excited 1,1-bis(pyrrol-2-yl)ethene system (calculated by optimization of the triplet state molecule) involves 90° torsion of the C=CH₂ group with formation of a SOMO which is no longer perpendicular to the idealized plane of the ligand backbone's π -system. Thus, we attribute the nonfluorescence of compound 4a to this kind of mobility of the ligand backbone upon electronic excitation.

Reactivity. It has been demonstrated for silicon enamine complexes that addition of Brønsted acids can convert formally covalent Si–N bonds into dative Si–N bonds and enhance the Si coordination number by Si–X bond formation²⁵ (Scheme 4^{25a}). Since the molecular features of 1,1-bis(pyrrol-2-yl)ethene compounds 4 offer prerequisites for an analogous approach, we tried to convert compounds 4a–c in the manner shown in Scheme 4: i.e., reacting them with a HX equivalent to achieve addition of X⁻ to the silicon center and H⁺ to the =CH₂ moiety, a sequence which should result in the formation of silicon complexes with a "regular" dipyrromethene backbone (as in BODIPYs).

For convenience, as an easy to dispense form of an HX derivative we have chosen p-nitrophenol, which was intended to add to compound **4a** with formation of a pentacoordinate silicon complex. However, despite conduction of the reaction in a 1:1 stoichiometric ratio, this reaction led to the formation of



dimethylbis(p-nitrophenoxy)silane (5) (Scheme 5), which was obtained as an almost colorless crystalline material suitable for

Scheme 5



X-ray diffraction (its structure is given in the Supporting Information). Therefore, to rule out the acidity of *p*-nitrophenol as the source of failure (due to complete displacement of the dipyrromethene ligand), we have chosen the less acidic *p-tert*-butylphenol for further reactions (which were carried out as NMR scale experiments). Despite these considerations of the phenol acidity, we not only observed the formation of multiple compounds but also ²⁹Si NMR spectra

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were lacking signals in a typical range for pentacoordinate silicon compounds. Hence, the reaction did not yield products as expected from Scheme 4 (bottom). Furthermore, in each case also the starting material (4a-c) could be detected in the resulting mixture.

Obviously, as a result of the deficit of Lewis acidity induced by the electron-rich dipyrromethene ligand, the silicon center refused to accept a fifth donor atom, thus sustaining tetracoordination. Therefore, only the most Lewis acidic Si center among compounds 4 (in 4c, due to the ring strain and lower steric demand) was subjected to another reaction which could enhance the coordination number of its Si atom. (The spatial accessibility of the Si atoms of compounds 4 for nucleophiles is illustrated by the space-filling models in Figure 8.)



Figure 8. Space-filling plots of 4a-c. Color code: silicon, pink; nitrogen, blue; carbon, gray; hydrogen, white. Due to the different steric demands of the substituents, the silicon center of 4c exhibits the best accessibility for nucleophiles.

Earlier, it was demonstrated that silacyclobutane derivatives support penta- and hexacoordination of the silicon atom.^{26,27} In general, the acceptance of one or two additional donors D could release the ring strain of silacyclobutanes, as the newly formed geometries bear 90° angles (Scheme 6).



To attain such a geometry, we applied the acac analogue 2-hydroxy-4-methoxybenzophenone in a reaction with 4c to obtain 6c including either a pentacoordinate ($6c^{\circ}$) or a hexacoordinate ($6c^{\circ}$) silicon center (Scheme 7). Once again, this reaction gave rise to a product other than that initially expected, as revealed by a single-crystal X-ray diffraction study (Figure 9). The isolated compound 6c' resulted from a ring-opening reaction of the silacyclobutane and its attack of the dipyrromethene moiety to furnish a new six-membered ring. The 2-oxy-4-methoxybenzophenone ligand only acts as a monodentate donor, thus leaving the silicon center tetracoordinated. Nevertheless, the intended proton shift to the = CH_2 moiety of 4c has taken place.

Ring-opening reactions of silacycloalkanes bearing a higher coordinate silicon atom have already been reported (Scheme 8).²⁶ Corresponding examples also comprise the reclosure of the opened ring in an extended manner together with lowering of the silicon coordination number. The relevant cases illustrated by some examples in Scheme 8 also have the (pseudo)imine carbon atom with its partially positive character as the atom in common, where ring reclosure takes place. Again, in compound **6**c' the former pseudo imine carbon atom of the dipyrromethene system (which formally appears in





Figure 9. Molecular structure of 6c' in the crystal state (one of the three independent molecules of the asymmetric unit). The ellipsoid probability level is set at 30%. Hydrogen atoms are omitted for clarity. Note that simple atomic labels have been chosen for clarity; they do not correspond to the labels in the CIF file in the Supporting Information.

C5

Scheme 8



compounds **6**c) has been the target of the alkyl shift. Even though we were not able to isolate or detect an intermediate with a higher coordinate silicon atom, the reaction might proceed via **6**c⁶ or **6**c⁵ as a transient stage. Inspired by this partial success in the reaction of compound **4**c with 2-hydroxy-4-methoxybenzophenone, we monitored the reaction of a 1:1 stoichiometric solution of dimethylsilicon compound **4a** with 2hydroxy-4-methoxybenzophenone by ¹H, ¹³C, and ²⁹Si NMR spectroscopy, because a related methyl shift (from Si to N=C) is less likely. Unfortunately, this attempt also failed to produce a silicon dipyrromethene compound. Instead, we observed a reaction related to Scheme 5 (i.e., formation of Me₂Si(2-oxy-4methoxybenzophenone)₂).

CONCLUSION

In hexane solution 1,1-bis(pyrrol-2-yl)ethene 2 was found to coexist with its dipyrromethene tautomer 2'. Reaction with *n*BuLi, even in a 1:1 stoichiometric ratio, caused 2-fold lithiation and thus transformation into the more reactive lithiated 1,1-bis(pyrrol-2-yl)ethene derivative 3, which was suitable for synthesizing diorganosilicon compounds 4a-c. Optical characterization of 4a-c showed intense absorbance as for the related BODIPY dyes but significantly different fluorescence properties. From reactions of 4a-c with selected phenolates, thus aiming at the formation of silicon compounds comprising a higher coordinate silicon atom and a dipyrromethene ligand backbone, the expected products could not be isolated. Reaction of 4c with an acac-like ligand led to ring opening of the silacyclobutane ring and formation of the polycyclic product 6c'.

EXPERIMENTAL SECTION

General Considerations. Chemicals commercially available were used as received without further purification. Dimethylethylpyrrole,²⁸ 1,¹⁶ and 2^{17} were prepared according to literature procedures. THF, hexane, and toluene were distilled from sodium benzophenone and were stored over sodium wire (hexane, toluene) or activated molecular sieves 3 Å under an argon atmosphere (THF). All reactions involving organochlorosilanes and/or free dipyrromethene base as well as those interconverting dimethylethylpyrrole were carried out under an atmosphere of dry argon utilizing standard Schlenk techniques.

NMR spectra were recorded on a Bruker Avance III 500 MHz spectrometer (Me_4Si as internal standard, 1 M LiCl in D_2O as external reference).

UV/vis spectra were recorded on a Jasco V-650 spectrophotometer in 10 mm quartz cuvettes, and fluorescence spectra were recorded on a Jasco FP 6500 spectrofluorometer in 10×10 mm quartz cuvettes.

Elemental analyses were performed using an Elementar vario MICRO cube instrument. Single-crystal X-ray diffraction data were collected on a Bruker X8 APEX2 CCD (1', 2', 3) or a STOE IPDS 2/2T single-crystal diffractometer (1, 4a–c, 5, 6c') using Mo K α radiation. The structures were solved by direct methods using SHELXS-97 and refined with full-matrix least-squares methods of F^2 against all reflections with SHELXL-97.²⁹ All non-hydrogen atoms were anisotropically refined. C-bound hydrogen atoms were refined in idealized positions (riding model), and N-bound H atoms were located as residual electron density peaks and were refined isotropically. Ellipsoid plots of the molecular structures were generated with ORTEP³⁰ and POV-Ray.³¹ Space-filling plots were generated with MERCURY.³²

In order to obtain X-ray-quality crystals of compound 1', excess 70% aqueous HClO₄ was added to a sample of 1 in ethanol. The solution thus obtained was then subjected to slow evaporation of the solvent at room temperature. 1' was obtained as large orange crystals with a purplish metallic luster.

The sample 2 derived from 1 (0.10 g, 0.32 mmol) and triethylamine (0.06 g, 0.6 mmol) was recrystallized from the minimum amount of hexane (0.15 mL) and brought to crystallization upon storage at 5 $^{\circ}$ C overnight.

Synthesis of 3. Excess triethylamine (0.40 g, 3.9 mmol) was added to a stirred suspension of 1 (0.61 g, 2.0 mmol) in hexane (20 mL), and the mixture was stirred at 45 °C for 1 h to afford a yellow solution of 2 and a pale precipitate of Et₃NHCl. After it was cooled to room temperature, the mixture was filtered and the residue was washed with hexane (10 mL). From the combined filtrate and washings the volatiles were evaporated under reduced pressure (condensation into a cold trap) and the resulting brownish yellow oil was dissolved in hexane (20 mL). To this solution was added dropwise a solution of nBuLi in hexanes (1.65 mL of a 2.5 M nBuLi solution, 4.1 mmol) at room temperature, whereupon a bright red precipitate was formed which, after stirring for an additional 6 h, was collected on a Schlenk sinter tube and washed with pentane (5 mL). The deep red solid was dried in vacuo and stored under dry argon, as it appeared to be extremely sensitive to air and moisture. Yield: 0.56 g (2.0 mmol, quantitative). $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra indicate the absence of solvent (hexane).

Crystals suitable for X-ray diffraction analysis were obtained upon reflux extraction with THF.

¹H NMR ([D₈]THF, 500 MHz): δ 0.98 (t, 6 H, 7.4 Hz, CH₂CH₃), 2.16 (s, 6 H, pyrrole CH₃), 2.17 (s, 6 H, pyrrole CH₃), 2.39 (q, 4 H, 7.4 Hz, CH₂CH₃), 4.64 (s, 2H C=CH₂). ¹³C{¹H} NMR ([D₈]THF, 125 MHz): δ 14.1 (pyrrole 4 CH₃), 15.5 (pyrrole 2 CH₃), 17.2 (CH₂CH₃), 19.6 (CH₂CH₃), 100.2 (C=CH₂), 115.4, 121.5, 130.9, 136.3, 142.3, (pyrrole ring atoms, methene atom). ⁷Li NMR ([D₈]THF, 194.4 MHz): δ 0.0.

Synthesis of 4a·0.5(hexane). To a solution of 3 (0.56 g, 2.0 mmol) in THF (10 mL) was added dropwise dichlorodimethylsilane (0.26 g, 2.0 mmol) at room temperature to yield a yellow solution which was stirred for 3 h at room temperature. Thereafter, the volatiles were removed under reduced pressure (cold trap condensation) and the residue was dissolved in hexane (10 mL) followed by filtration through a plug of diatomaceous earth. After washing with hexane ($2 \times 1 \text{ mL}$) the combined filtrate and washings were evaporated to dryness under reduced pressure. The resulting brownish yellow oil was dissolved in hexane (0.5 mL) and stored at -24 °C to afford crystals of 4a·0.5(hexane), which were separated from the supernatant by decantation and briefly dried under vacuum. Yield: 0.25 g (0.68 mmol, 34%). Elemental analysis indicates loss of solvent upon drying.

Anal. Found: C, 73.76; H, 9.62; N, 8.14. Calcd for $C_{20}H_{30}N_2S^{i}$ 0.1C₆H₁₄ (M_r = 335.169): C, 73.82; H, 9.44; N, 8.36. ¹H NMR (C₆D₆) 500 MHz): δ 0.27 (s, 6 H, SiCH₃), 1.15 (t, 6 H, 7.6 Hz, CH₂CH₃), 2.06 (s, 6 H, pyrrole 4 CH₃), 2.33 (s, 6 H, pyrrole 2 CH₃), 2.45 (q, 4 H, 7.6 Hz, CH₂CH₃), 5.52 (s, 2H C=CH₂). ¹³C{¹H} NMR (C₆D₆) 125 MHz): δ 2.25 (SiCH₃), 12.7 (pyrrole 4 CH₃), 12.8 (pyrrole 2 CH₃), 15.9 (CH₂CH₃), 18.3 (CH₂CH₃), 109.9 (C=CH₂), 118.1, 125.8, 127.4, 131.3, 132.3, (pyrrole ring atoms, methene C=CH₂ atom). ²⁹Si{¹H} NMR (C₆D₆, 99.4 MHz): δ -1.0.

4b,c were synthesized analogously to 4a.

Synthesis of 4b. A 2.0 mmol portion of 3 and 2.0 mmol of dichlorodiphenylsilane were used as starting materials. Yield: 0.35 g (0.78 mmol, 39%).

Anal. Found: C, 80.22; H, 7.64; N, 5.90. Calcd for $C_{30}H_{34}N_2Si$ (M_r = 450.690): C, 79.95; H, 7.60; N, 6.22. ¹H NMR (C_6D_6 , 500 MHz): δ 1.07 (t, 6 H, 7.6 Hz, CH₂CH₃), 1.85 (s, 6 H, pyrrole 4 CH₃), 2.37 (s, 6 H, pyrrole 2 CH₃), 2.38 (q, 4 H, 7.6 Hz, CH₂CH₃), 5.53 (s, 2H C= CH₂), 7.0 (m, 4 H, oPh) 7.08 (m, 2 H, pPh),7.60 (m, 4 H, mPh). ¹³C{¹H} NMR (C_6D_6 , 125 MHz): δ 12.6 (pyrrole 4 CH₃), 13.2 (pyrrole 2 CH₃), 15.8 (CH₂CH₃), 18.2 (CH₂CH₃), 110.5 (C=CH₂), 118.6, 127.2, 128.7, 131.2, 132.0, 132.2, 132.4, 135.8 (pyrrole ring atoms, methene C=CH₂ atom, phenyl ring atoms). ²⁹Si{¹H} NMR (C_6D_6 , 99.4 MHz): δ -25.1.

Synthesis of 4c. A 2.0 mmol portion of 3 and 2.0 mmol of 1,1dichlorosilacyclobutane were used as starting materials. Yield: 0.37 g (1.1 mmol, 55%).

Anal. Found: C, 74,62; H, 9.08; N, 8.08. Calcd for $C_{21}H_{30}N_2Si$ (M_r = 338.562): C, 74.50; H, 8.93; N, 8.27. ¹H NMR (C_6D_{61} 500 MHz): δ

1.14 (t, 6 H, 7.6 Hz, CH_2CH_3), 1.64 (m, 4H, $SiCH_2-$), 1.78 (m, 2 H, $SiCH_2CH_2$), 2.16 (s, 6 H, pyrrole 4 CH_3), 2.31 (s, 6 H, pyrrole 2 CH_3), 2.45 (q, 4 H, 7.6 Hz, CH_2CH_3), 5.51 (s, 2H C= CH_2). ¹³C{¹H} NMR (C₆D₆, 125 MHz): δ 11.6 (SiCH₂), 12.1 (pyrrole 4 CH_3), 12.6 (pyrrole 2 CH_3), 15.8 (CH_2CH_3), 18.2 (CH_2CH_3), 23.3 (SiCH₂ CH_2), 110.2 (C= CH_2), 118.5, 127.0, 127.7, 131.1, 131.9 (pyrrole ring atoms, methene C= CH_2 atom). ²⁹Si{¹H} NMR (C₆D₆, 99.4 MHz): δ -4.1.

Reactions of 4a–c with Phenols. To a precooled (0 °C) solution of **4a** prepared from 560 mg (2 mmol) of **3** and 260 mg (2 mmol) of dichlorodimethylsilane in toluene (15 mL) was added a solution of 280 mg (2 mmol) of *p*-nitrophenol in toluene (5 mL). After the mixture was warmed to room temperature (within 30 min), the solvent was removed under reduced pressure. The resulting dark residue was recrystallized from a mixture of toluene (0.2 mL) and hexane (0.5 mL). Crystals appeared after 1 day of standing at room temperature and appeared to be dimethylbis(*p*-nitrophenoxy)silane (**5**). This compound has been reported in the literature before (synthesized by reaction of *p*-nitrophenol with dialkoxydimethylsilanes).³³ For an efficient synthetic procedure toward dimethylbis(*p*-nitrophenoxy)silane (**5**) as well as NMR data see the Supporting Information.

Reactions of $4\mathbf{a}-\mathbf{c}$ with *p-tert*-butylphenol were carried out on a NMR scale: to the dissolved samples of $4\mathbf{a}-\mathbf{c}$ (0.1226 mmol) in benzene- d_6 (0.5 mL) was added the corresponding 1:1 stoichiometric amount of 4-*tert*-butylphenol as a 10% solution in benzene- d_6 (180 mg, 0.1226 mmol). Immediately, mixtures were mixed vigorously and subsequently subjected to NMR analysis.

4a: ²⁹Si{¹H} NMR (C₆D₆, 99.4 MHz) δ 0.8, -1.0 (starting material), -5.6 (Me₂Si(O-p^{tert}BuC₆H₄)₂).

4b: ²⁹Si{¹H} NMR (C_6D_6 , 99.4 MHz) δ -8.0, -11.0, -25.1 (starting material), -28.2.

4c: ²⁹Si{¹H} NMR (C_6D_6 , 99.4 MHz) δ -4.1 (starting material), -10.5, -21.1, -28.9, -38.4 (presumably an analogue of 6c').

Reaction of 4a with 2-Hydroxy-4-methoxybenzophenone. To a solution of $4a \cdot 0.5$ (hexane) (132 mg, 0.32 mmol) in C₆D₆ (0.4 mL) was added a solution of 2-hydroxy-4-methoxybenzophenone (72 mg, 0.32 mmol) in C_6D_6 (0.4 mL). The resulting mixture was stirred for 10 min at room temperature and subsequently subjected to NMR analysis. The signal in the ²⁹Si{¹H} NMR (C₆D₆, 99.4 MHz) spectrum at δ -1.0 confirmed the presence of 4a, and the ¹H NMR spectrum (C6D6, 500 MHz) revealed the signals of 4a and 2-hydroxy-4methoxybenzone. On reinvestigation after 1 day, in addition to the ²⁹Si{¹H} NMR signal at δ –1.0 (4a), a new peak at δ –3.9 was detected and assigned to Me₂Si(2-oxy-4-methoxybenzophenone)₂. In the ¹H NMR spectrum, which still showed signals of 4a and 2hydroxy-4-methoxybenzophenone, signals of the free ligand 2, a new signal of SiMe groups, and a new set of 2-oxy-4-methoxybenzophenone signals appeared. The identity of the reaction product as Me₂Si(2-oxy-4-methoxybenzophenone)₂ was finally confirmed by its deliberate synthesis from Me₂SiCl₂ (0.29 g, 2.25 mmol), 2-hydroxy-4methoxybenzophenone (oxybenzone; 0.92 g, 4.0 mmol), and triethylamine (0.45 g, 4.5 mmol) in THF (25 mL), at room temperature; removal of Et₃NHCl precipitate by filtration and washing with THF (15 mL) afforded 0.55 g (4.0 mmol) of Et₃NHCl. From the filtrate the solvent was removed under reduced pressure (cold trap condensation) and $^{29}\mathrm{Si}$ and $^{1}\mathrm{H}$ NMR spectroscopy was performed with a C₆D₆ solution of the oily residue. The signals observed in the ²⁹Si and ¹H NMR spectra correspond to those of the product formed in the reaction of 4a with oxybenzone.

Synthesis of 6c'. To a solution of 4c (0.78 g, 2.3 mmol) in toluene (10 mL) was added a solution of oxybenzone (0.52 g, 2.3 mmol) in toluene (3 mL), and the resulting clear solution was stirred for 3 h in the dark. After removal of all volatiles under reduced pressure the dark mixture was recrystallized from hexane. Yield: 0.42 g of an isolated solid that in addition to 6c' contained unreacted 4c and 2-hydroxy-4-methoxybenzophenone, as indicated by ¹H and ¹³C NMR.

Anal. Found: C, 73.97; H, 7.51; N, 5.90. Calcd for $C_{35}H_{42}N_2O_3Si^{-1}$ 0.54c ($M_r = 736.086$): C, 74.24; H, 7.81; N, 5,71. ¹H NMR (C_6D_6 , 500 MHz): δ 0.83 (t, 3 H, 7.3 Hz, CH₂CH₃), 1.07 (t, 3 H, 7.4 Hz, CH₂CH₃), 1.12 (s, 3 H CH₃), 1.46 (m, 2 H, CH₂ ring), 1.66 (m, 2 H, CH₂ ring), 1.84 (m, 2 H, CH₂ ring) 1.86 (s, 3H, CH₃), 2.15 (q (low resolution), 2 H, CH₂CH₃), 2.16 (s, 3 H, CH₃), 2.31 (s, 3 H, CH₃), 2.37 (q, 2 H, 7.6 Hz CH₂CH₃), 2.42 (s, 3 H, CH₃), 3.28 (s, 3 H, OCH₃), 5.66 (s, 1H), 6.42 (d, 1 H, 8.6 Hz), 7.05 (m, 1H), 7.14 (m, 2H), 7.47 (d, 1 H, 8.3 Hz), 7.90 (d, 2H, 7.2 Hz) (aromatic H atoms). ¹³C{¹H} NMR (C₆D₆, 125 MHz): δ 11.5, 11.8, 13.0, 14.3, 14.9, 16.0, 16.4, 18.1, 18.3, 19.8, 23.7, 37.7 (12 aliphatic C atoms), 54.9 (OCH₃), 69.7 (quat C atom), 95.6 (methene C atom), 102.9, 109.8, 114.8, 115.5, 123.1, 123.7, 128.1, 129.8, 131.8, 132.3, 134.1, 134.8, 140.7, 141.7, 151.2, 154.2, 163.8 (17 aromatic C atom), 195.1 (C=O). ²⁹Si{¹H</sup> NMR (C₆D₆, 99.4 MHz): δ –39.1.

ASSOCIATED CONTENT

S Supporting Information

Figures, tables, and CIF files giving details of the synthesis and characterization of compound 5 (¹H, ¹³C, and ²⁹Si NMR data), NMR spectra (¹H, ¹³C, ⁷Li) of compound 3, ¹H NMR spectrum of the reaction mixture obtained from 4a and 2hydroxy-4-methoxybenzophenone, atomic coordinates of the optimized molecular structures of compounds 2, 2', and 4a,b and model compounds $L^H SiMe_2^{singlet}$, $L^H SiMe_2^{triplet}$, $HL^{H}SiMe_{2}F$, electronic transitions calculated for compounds 2, 2', $4a,b, L^H SiMe_2^{singlet}$ and $HL^H SiMe_2F$ and color representations of the relevant MOs involved in these transitions, parameters of data collection and structure refinement for the crystal structure studies and crystallographic data of compounds 1.0.2H2O, 1', 2', 3, 4a.0.5(hexane), 4b, 4c (two modifications), 5, and 6c'. This material is available free of charge via the Internet at http://pubs.acs.org. The CCDC entries 957875 (1.0.2H₂O), 957874 (1'), 957876 (2'), 957877 (3), 957880 (4a·0.5(hexane)), 957882 (4b), 957873 (4c, modification in $P2_1$), 957878 (4c, modification in $P2_1/n$), 957881 (5), and 957879 (6c') contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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Notes

The authors declare no competing financial interest.

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