N,*N'*-Disilylated 1,4-Dihydropyrazines: Organosilyl Substitution Reactions, Structural Effects of Steric Hindrance, and Electron Exchange with C_{60}

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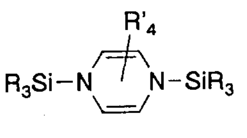
Organosilyl exchange reactions of the extremely electron-rich and formally "antiaromatic" 1,4-bis(trimethylsilyl)-substituted 1,4-dihydropyrazine **1** with Ph_3SiCl or Me_5Si_2Cl yielded the new compounds **2** and **3** with triarylsilyl and disilanyl substituents. At $\delta = 4.53$ in $CDCl_3$ compound **3** shows a particularly high-field shifted ^{1}H-NMR resonance for the 1,4-dihydropyrazine protons. In contrast to the planar ring arrangement of 1,4-bis(triisopropylsilyl)-1,4-dihydropyrazine **4**, the crystal structure determination of the 2,5-dimethylated analogue **5** as obtained by reductive silylation exhibits a pronounced boat conformation of the heterocycle due to steric repulsion between the substituents, the closest H...H (CH_3/CH) contact being 211 pm. Despite the sizeable structural differences between **4** and **5** both compounds are reversibly oxidized at very negative potentials, at -0.90 and -0.85 V vs. $Fc^{+/0}$, respectively. It appears that the electrochemical behavior of this class of compounds is determined primarily by the configuration at the nitrogen centers and less by the ring conformation. Compound **4** reacts with C_{60} under EPR-detectable electron exchange to afford $\mathbf{4}^{+\bullet}$ and $C_{60}^{-\bullet}$. The radical cation $\mathbf{4}^{+\bullet}$ generated separately via oxidation with iodine was characterized by low-temperature UV/Vis and ENDOR spectroscopy. An ENDOR spectrum revealing silylalkyl coupling was also obtained for the related radical cation of reversibly oxidizable 1,1'-bis(*tert*-butyldimethylsilyl)-1,1',4,4'-bipyridylidene (**8**).

The exceptional, i.e. very electron-rich[1a] and formally antiheteroaromatic[1b] ring system of 1,4-dihydropyrazine can be stabilized in its "genuine" form with a virtually planar six-membered ring and thus unimpaired 8π-electron conjugation by 1,4-trialkylsilyl and -germyl substitution at the nitrogen centers[1,2] (cf. compounds **1** and **4**). Although these compounds are very air-sensitive, their thermal stability induced us to explore their reactivity, substitutional variability, and structural response to such modifications.

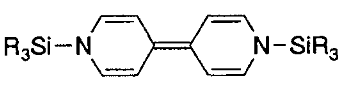
In this paper we report on the replacement of the Me_3Si groups in **1** by triphenylsilyl (**2**) and pentamethyldisilanyl[3,4] substituents (**3**) which reveal characteristics clearly different from those of trialkylsilyl ligands such as Me_3Si[2a,b,5], tBuMe$_2$Si ("TBDMS"[2d,6]) or iPr$_3$Si ("TIPS"[2c,7]).

Considering that the X-ray crystal structural analysis of 1,4-bis(triisopropylsilyl)-substituted 1,4-dihydropyrazine **4** still shows a planar heterocycle despite obviously nonbonded contacts between the pyrazine-H and the bulky TIPS substituents[2c], we now obtained crystals and an X-ray structural analysis of the corresponding 2,5-dimethyl derivative **5**. Previous studies of two 1,4-bis(trialkylsilyl)-2,3,5,6-tetramethyl-1,4-dihydropyrazines **6** and **7** have revealed bending into a boat conformation due to steric interference between substituents in these hexasubstituted derivatives[2b,8]. In this paper we investigate whether the size of two TIPS substituents can cause a similar bending in a 1,2,4,5 substitution pattern; MO calculations have shown a rather flat energy potential curve for the bending of the non-aromatic 1,4-dihydropyrazine system[9].

The relative stability of **4** due to steric shielding by the TIPS substituents[2c,7] may also be expected for its radical cation $\mathbf{4}^{+\bullet}$ which is formed in single-electron exchange reactions with acceptors such as TCNE or TCNQ[10]. In the following we investigate a similar reaction with the increasingly popular electron acceptor[11] C_{60} and study the radical products by EPR. For further characterization of the electronic structure of labile $\mathbf{4}^{+\bullet}$ we generated this species separately by oxidation with iodine and obtained low-temperature absorption and ENDOR spectra. It will finally be shown that bulky trialkylsilyl substituents can similarly stabilize oxidized (cationic) states of the related 1,1',4,4'-tetrahydro-4,4'-bipyridylidenes[2a,12] as evidenced by electro-



	R$_3$	R$_4$'
1	Me$_3$	H$_4$
2	Ph$_3$	H$_4$
3	Me$_2$SiMe$_3$	H$_4$
4	*i*Pr$_3$	H$_4$
5	*i*Pr$_3$	2,5-Me$_2$, 3,6-H
6	Me$_3$	Me$_4$
7	*t*BuMe$_2$	Me$_4$



	R$_3$
8	*t*BuMe$_2$
9	Me$_3$

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chemical and ENDOR results of the new 1,1′-bis(*tert*-butyldimethylsilyl)-substituted redox system **8**/**8**$^{+\bullet}$.

Results and Discussion

Syntheses, NMR Spectroscopy, and Structure Determination

Whereas the reductive silylation of pyrazine is the most convenient way of preparing trialkylsilyl-substituted 1,4-dihydropyrazines[1,2,5,8], application of this method to the preparation of compounds **2** and **3** failed because of coupling reactions between the organosilyl groups. We therefore resorted to thermal substitution of Me_3Si in **1** using the halides Ph_3SiCl and Me_5Si_2Cl in acetonitrile; a similar method involving the replacement of Me_3Si by dimesitylboryl substituents had been successful before[13].

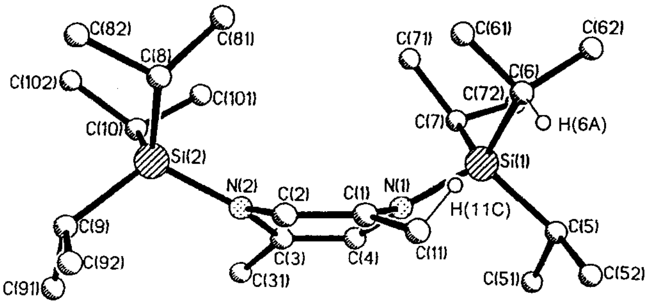
$$\mathbf{1} + 2\,X_3SiCl \xrightarrow[CH_3CN]{} 2\,Me_3SiCl + \mathbf{2} \text{ or } \mathbf{3} \qquad (1)$$

$$X_3 = Ph_3\ (\mathbf{2}) \quad \text{or} \quad Me_2SiMe_3\ (\mathbf{3})$$

The compounds **2** and **3** were characterized by ^1H and ^{13}C NMR as true 1,4-dihydropyrazines. However, the chemical shifts of the ring CH centers revealed slight differences. Whereas the slightly soluble **2** exhibits in C_6D_6 a small low-field shift of $\delta(CH) = 4.81$ because of the acceptor effect of Ph relative to Me, the replacement of one methyl group in $SiMe_3$ by a $SiMe_3$ group creates a Si–Si bond which is known to increase the donor character of the resulting pentamethyldisilanyl substituent[3]. Accordingly, the $\delta(CH)$ value of 4.53 (in $CDCl_3$) for **3** is still lower than the 4.64 reported for **1** and related *N,N′*-bis(trialkylsilyl) substituted 1,4-dihydropyrazines[1b,2]. Attempts to prepare the germanium and tin analogues of **2** in a similar fashion failed; the necessary high temperatures and long conversion times led to unidentified red product mixtures without olefinic ^1H-NMR signals.

The unexpected low-field shifted resonance $\delta(CH) = 4.78$ for the dihydropyrazine protons of the *yellow* TIPS-substituted derivative **4** was attributed to structurally detectable close contacts between those protons and CH(isopropyl) hydrogen atoms of the TIPS substituent[2c]. These close contacts result from a still planar ring conformation[2c]. This hypothesis prompted us now to prepare and study the *colorless* 2,5-dimethyl derivative **5**. Both NMR and UV-photoelectron spectroscopic investigations of the 2,5-dimethyl derivative of **1** revealed a diminished 8π-electron conjugation and thus suggested a non-planar ring structure[1,2a]. However, this material could not be crystallized. Compound **5** was synthesized via reductive silylation of 2,5-dimethylpyrazine as a solid which could be crystallized from benzene for X-ray structural determination. The crystal data are given in the Experimental[14]. Figure 1 shows a structure of the molecule with the atomic numbering, including two of the found and isotropically refined hydrogen positions.

Figure 1. Molecular structure of **5**; hydrogen atoms omitted for clarity, with the exception of H(11C) and H(6A) which are particularly close at 211 pm[a]



[a] Selected bond lengths [pm] and angles [°]: Si(1)–N(1) 175.6(1), N(1)–C(1) 143.1(2), N(1)–C(4) 143.2(2), C(1)–C(11) 149.4(2), C(1)–C(2) 133.0(2), C(2)–N(2) 143.1(2), N(2)–C(3) 142.9(2), N(2)–Si(2) 175.2(1), C(3)–C(31) 149.7(2), C(3)–C(4) 132.7(2); C(5)–Si(1)–N(1) 111.7(1), C(7)–Si(1)–N(1) 105.4(1), C(6)–Si(1)–N(1) 110.1(1), Si(1)–N(1)–C(1) 130.2(1), Si(1)–N(1)–C(4) 119.0(1), C(1)–N(1)–C(4) 110.7(1), N(1)–C(1)–C(11) 119.6(1), N(1)–C(1)–C(2) 119.0(1), C(11)–C(1)–C(2) 121.1(2), C(1)–C(2)–N(2) 122.4(1), C(2)–N(2)–C(3) 110.9(1), C(2)–N(2)–Si(2) 119.3(1), C(3)–N(2)–Si(2) 129.8(1), N(2)–C(3)–C(31) 119.3(1), N(2)–C(3)–C(4) 119.0(1), C(31)–C(3)–C(4) 121.4(1), N(1)–C(4)–C(3) 122.6(1), N(2)–Si(2)–C(8) 104.7(1), N(2)–Si(2)–C(9) 111.8(1), N(2)–Si(2)–C(10) 110.4(1).

As the lack of color suggests, the heterocyclic ring of **5** is no longer planar, thus disfavoring cyclic π electron conjugation. As in almost all other cases of non-planar dihydropyrazines, the ring conformation is that of a boat with the nitrogen centers at the bow positions[2b–d,8,15]. Yet the monosilyl-substituted nitrogen atoms in **5** have a completely planar configuration with a sum of corresponding bond angles $\Sigma\omega = 360 \pm 0.1°$, in contrast to the situation in *N,N′*-silylated 1,4-dihydro-2,3,5,6-tetramethylpyrazines **6** and **7**[2b,8] ($\Sigma\omega \approx 355°$) and in some other recently described silylamines with bulky substituents[16]. With 146.6°, the dihedral angle N(1)–C(1)–C(2)–N(2)/N(2)–C(3)–C(4)–N(1) is rather small, indicating significant repulsion effects between the ortho-substituents TIPS and CH_3(pyrazine). A detailed inspection of the interfering alkyl groups, including their crystallographically determined hydrogen positions, reveals that the main origin of this repulsion lies in very close contacts of 211 pm between H(6A) of a triisopropyl substituent of TIPS and H(11C) of the adjacent pyrazine methyl group (Figure 1). Another close distance is that between H(11C) and H(61C) at 238 pm which, however, is almost that of the normally assumed sum of 240 pm for the van der Waals radii of hydrogen atoms[17]. In contrast, the closest H...H contact between TIPS hydrogen atoms and CH(pyrazine) in **4** was established at 225 pm[2c]; apparently, this is still tolerable to accommodate the planar ring structure.

Structure and Electrochemical Behavior

While the planar configurations at the ring atoms, i.e. sp^2 carbon centers and silylated amine N centers, favor the planar ring conformation of 1,4-dihydropyrazines, the destabilizing effect of cyclic 8π-electron conjugation counteracts this preference. The result is a very flexible structural situation as evident from calculated shallow potential minima with respect to bending of the six-membered ring[9]. In contrast to **5**, 1,4-bis(*tert*-butyldimethylsilyl)-1,4-dihydro-

2,3,5,6-tetramethylpyrazine (**7**) exhibits slightly pyramidalized nitrogen centers[8]. The importance of this particular structural feature for the generally very low oxidation potentials is obvious from Table 1. Whereas $E^{0/+}$ is surprisingly little changed between planar **4** and boat-shaped **5** (Figure 2), there is a strong shift to a higher oxidation potential for compound **7** despite the presence of four electron-donating methyl substituents. Apparently, the ring conformation is less crucial for the ionization than the configuration at the nitrogen centers.

Figure 2. Cyclic voltammogram (5 cycles) for the oxidation of **5** in dichloromethane/0.1 M Bu_4NClO_4 (100 mV/s scan rate, potentials vs. $Fc^{+/0}$)

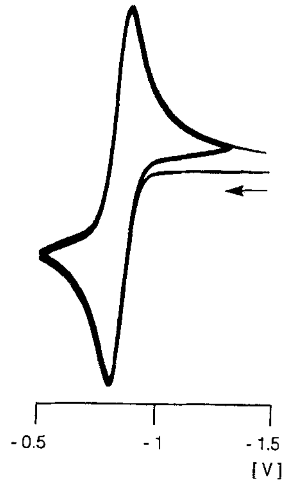


Table 1. Electrochemical potentials from cyclic voltammetry[a]

Compound	$E^{0/+}$	$E^{+/2+}$
3	−0.91(irr[b])	
4	−0.90(100)	+0.12(irr[b])
5	−0.85(80)	+0.01(irr[b])
7	−0.52(110)	−0.17(irr[b])
8	−1.10(115)	−0.66(70)

[a] Measured in CH_2Cl_2/0.1 M Bu_4NClO_4 at 100 mV/s scan rate. Potentials in V vs. ferrocene/ferrocenium, peak potential differences in mV (in parentheses). – [b] Irreversible process, anodic peak potential given.

The favorable electrochemical behavior (cf. Figure 2) of compounds with bulky triorganosilyl groups[2c,d,8] in contrast to simple trimethylsilyl derivatives[2c,18] or to the Si_2Me_5-substituted compound **3** described here (Table 1) may be attributed[19] to a diminished tendency for electrode adsorption. We were thus prompted to synthesize via reductive silylation the 1,1′-bis(*tert*-butyldimethylsilyl) derivative **8** of 1,1′,4,4′-tetrahydro-4,4′-bipyridylidene which, other than the bis(trimethylsilyl) analogue **9**[2a,12,20], showed two reversible oxidation waves and thus allowed us to calculate the stability constant K_c (Eq. 2) of the radical cation intermediate to be $2.8 \cdot 10^7$. This value is slightly higher than corresponding data of *N,N'*-dialkyl-substituted species[12] which can be attributed to smaller geometrical changes between the three forms of the two-step redox system $\mathbf{8}^{0/+\bullet/2+}$.

$$K_c = \frac{[M^{+\bullet}]^2}{[M] \cdot [M^{2+}]} = 10^{\Delta E/0.059\ \mathrm{V}} \qquad (2)$$

EPR/ENDOR and Absorption Spectroscopy of Radical Cations

Ease of formation and the high electrochemical stability constants of the radical cation intermediates in the silyl-substituted two-step redox systems $\mathbf{4}^{0/+/2+}$ and $\mathbf{8}^{0/+/2+}$ prompted us to study these states not only by EPR but also by ENDOR techniques[21]. ENDOR spectra should reveal particularly the small values of the proton coupling constants of the triorganosilyl substituents which receive their spin density only by indirect spin transfer mechanisms. Figure 3 shows the ENDOR spectra of $\mathbf{4}^{+\bullet}$ and $\mathbf{8}^{+\bullet}$, illustrating the typical[21,22] phenomenon of optimum detection of ^{14}N resonances at higher temperatures. Attempts to obtain useful EPR or ENDOR spectra of $\mathbf{2}^{+\bullet}$, $\mathbf{3}^{+\bullet}$ or $\mathbf{5}^{+\bullet}$ failed due to poor spectral resolution and rapid desilylation, producing the N–H-substituted dihydropyrazine radical cations[2a,23]. Previous studies had already shown that sterically strained organsilylamine radical cations can undergo facile R_3Si/H exchange reactions[24].

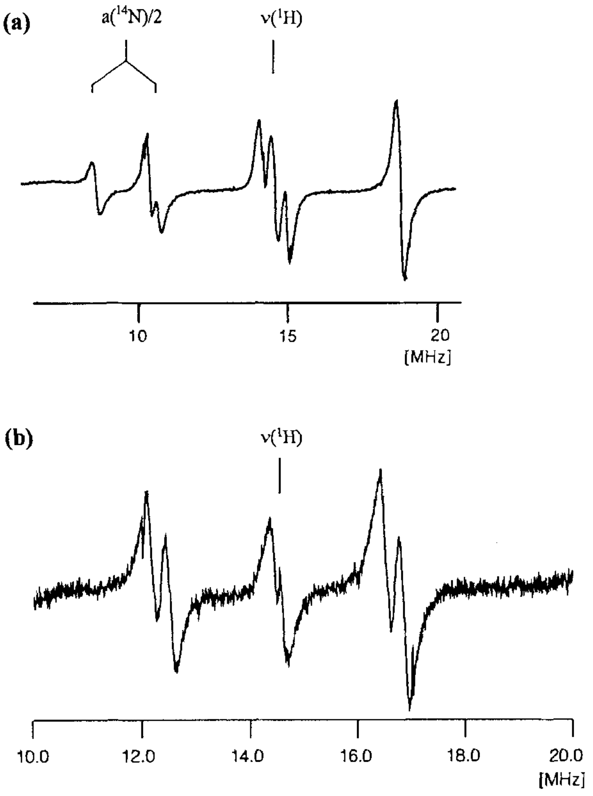
The EPR coupling constants reported for $\mathbf{4}^{+\bullet}$[2c] and for the bis(trimethylsilyl) analogue $\mathbf{9}^{+\bullet}$[20] of the radical cation $\mathbf{8}^{+\bullet}$ are in agreement with the values from ENDOR (Figure 3). In addition, this method yields now two small ^1H hyperfine splitting constants for $\mathbf{4}^{+\bullet}$ which are attributed to the Si–CH and Si–C–CH_3 protons, i.e. nuclei in γ and δ position to the spin-bearing π system of the heterocycle. For $\mathbf{8}^{+\bullet}$ we detected only one such small ^1H coupling constant, attributed to Si–CH_3 protons.

The recent observation[25] of weak but vibrationally structured long-wavelength UV/Vis absorption bands at about 600 nm for the electronic transition between the singly occupied (b_{1u}) and the lowest empty molecular orbital (a_u) of *N,N'*-dialkyl-1,4-dihydropyrazine radical cations led us to study $\mathbf{4}^{+\bullet}$, generated by oxidation with I_2 at low temperatures. In concentrated dichloromethane solution at −70 °C we could indeed observe the expected weak absorption band of the chromophore of $\mathbf{4}^{+\bullet}$ with a maximum at 685 nm. However, the broad band which is attributed to a $b_{1u} \rightarrow a_u$ transition exhibits no well-resolved fine structure.

Single Electron Transfer to C_{60}

The virtual coincidence of the oxidation potential of **4** (Table 1) and the reduction potential of C_{60} at −0.89 V vs. $Fc^{+/0}$ in dichloromethane solution[26a] prompted us to study the possibility of an (outer-sphere) electron exchange reaction between the two globular components. Such reactions, producing pairs of oppositely charge radical ions[10,11] from neutral precursors, should strongly depend on the ion-stabilizing capability of the solvent. In fact, there occurs no reaction between **4** and C_{60} in benzene or 1,2-dichlorobenzene

Figure 3. ENDOR spectra in CH_2Cl_2 solution (a) of $\mathbf{4}^{+\bullet}$ at 293 K, generated by oxidation with iodine and (b) of $\mathbf{8}^{+\bullet}$ at 210 K, generated by oxidation with $AlCl_3$; pairs of signals according to the ENDOR resonance condition $\nu = |\nu_X \pm a_X/2|$: (a) $a(^{14}N) = 0.664$, $a(^1H, NCH) = 0.317$, $a(^1H, SiCH) = 0.034$, $a(^1H, CH_3) \approx 0.01$ mT; (b) $a(^{14}N) = 0.315$, $a(^1H, NCH) = 0.168$, $a(^1H, NCCH) = 0.143$, $a(^1H, SiCH_3) = 0.058$ mT; 1 mT = 10 Gauss = 28 MHz



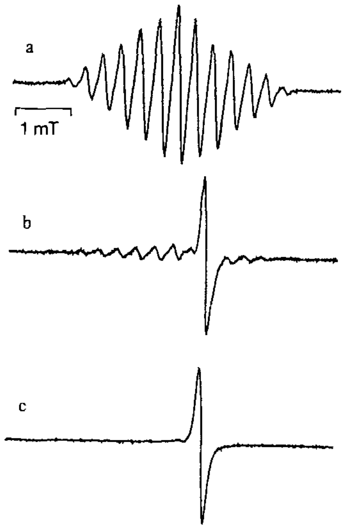
solution. In benzonitrile, the assumed electron exchange produced only $\mathbf{4}^{+\bullet}$ as EPR-detectable species, whereas THF and dichloromethane media at 200 K and 300 K showed the production of both $\mathbf{4}^{+\bullet}$ and $C_{60}^{-\bullet}$ albeit with poor EPR resolution. In terms of EPR resolution, the best results were observed when the reaction was carried out at 300 K in a 1:1 mixture of acetonitrile and benzene, benzene serving to solubilize C_{60} and acetonitrile ensuring a high dielectric constant for the separation of ion pairs (Figure 4).

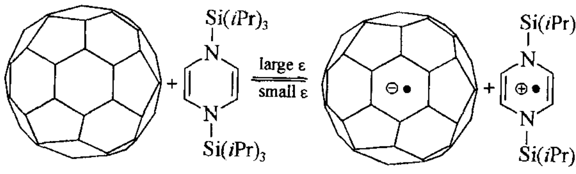
Initially, there is only the multiline spectrum of $\mathbf{4}^{+\bullet}$ visible with a center at $g = 2.0032$. After about half an hour, the single line of $C_{60}^{-\bullet}$ at $g = 1.9999$[26b] appears, whereas the signal of $\mathbf{4}^{+\bullet}$ slowly disappears (Figure 4). The EPR changes are eventually accompanied by precipitation of a brown solid. While the ability for electron exchange between **4** and C_{60} has thus been unambiguously demonstrated (Eq. 3), more detailed studies of this apparently complex electron transfer process will have to be carried out on a preparative scale and with controlled variation of the solvent.

Summary

In this report we have presented further examples of the typical reactivity of organosilyl-stabilized 1,4-dihydropyrazines. While the *electron exchange* with C_{60} illustrates once more the superb π electron donor capability of these extremely electron-rich molecules, as previously demonstrated similarly with TCNE and TCNQ as acceptors[10], the *substitution of N-silyl groups* requires high temperatures and long conversion times which limit this reaction to stable derivatives on the product side (**2**, **3**)[13]. A third type of reaction, the *insertion of heterocumulenes* such as O=C=O, O=C=S or O=C=NR into the N−Si bonds, will be described in forthcoming reports[27]. The structural results obtained for the derivative **5** reveal once more a delicate conformational situation as resulting from the shallow energy minimum[9], characterized here by the balance between the demands of hybridization and ring size (favoring planarity) versus the 8π-electron situation and the repulsion between the C−H "shells" of adjacent ring substituents which favor nonplanarity.

Figure 4. EPR spectra resulting from mixing equimolar amounts of **4** and C_{60} in C_6H_6/CH_3CN (1:1) at 300 K: (a) immediately after mixing, (b) after one hour, (c) after four hours





(3)

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Experimental

Instrumentation: EPR and ENDOR spectra were recorded in the X band with a Bruker System ESP 300 equipped with an ENI A500 RF amplifier, a Bruker ER033 field frequency lock, a Bruker ER035M gaussmeter, and a HP 3550B microwave counter. − ^1H NMR spectra were measured at room temperature with a Bruker AC 250 spectrometer. − UV/Vis absorption spectra were recorded with Shimadzu UV160 and Bruins Instruments Omega 10 spectrophotometers. − Cyclic voltammety was carried out in dichloromethane/0.1 M Bu_4NClO_4 by using a three-electrode configuration (glassy carbon electrode, Pt counter electrode, Ag/AgCl reference), and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium couple ($Fc^{+/0}$) served as internal reference. – Details of the crystal structure analysis are described below and in ref.[14].

Due to the lability of the products towards hydrolysis and oxidation all manipulations were carried out under dry argon. Syntheses and characterization of **1**[1,2a,b], **4**[2c], **7**[1,2a,b], **8**[8], and **9**[2a,12] were described previously.

1,4-Bis(triphenylsilyl)-1,4-dihydropyrazine (**2**): A mixture containing 2.61 g (11.5 mmol) of **1** and 7.0 g (23.7 mmol) of chlorotriphenylsilane in 60 ml of acetonitrile was heated to reflux for 12 hours. During the reaction a yellow solid formed from which the solvent was removed in vacuo. Recrystallization from 400 ml of THF and then several times from benzene yielded 2.65 g (39%) of very fine bright yellow needles which were dried at 80 °C in vacuo. The compound is virtually insoluble in dichloromethane, hexane or acetonitrile. M.p. >200 °C. – $C_{40}H_{34}N_2Si_2$ (598.9): calcd. C 80.22, H 5.72, N 4.68; found C 81.16, H 5.61, N 4.73. – ^1H NMR (C_6D_6): δ = 4.81 (s, 4H, CH), 6.97–7.27 (m, 30H, phenyl H).

1,4-Bis(pentamethyldisilanyl)-1,4-dihydropyrazine (**3**): To a solution of 1.35 g (6 mmol) of **1** in 50 ml of acetonitrile was slowly added 10 ml (8.6 g, 51 mmol) of chloropentamethyldisilane. The clear solution was heated to reflux for a total of 3 d, interrupted by short flushings with argon to remove Me_3SiCl. On cooling the mixture became turbid and eventually biphasic; removal of the solvent in vacuo and distillation of the residue at about 100 °C at 0.01 Torr gave 0.42 g (20%) of a yellow oil. Extreme air sensitivity and the oily consistency precluded an elemental analysis. – ^1H NMR ($CDCl_3$): δ = 0.05 (s, 18H, $SiMe_3$), 0.10 (s, 12H, $SiMe_2$), 4.53 (s, 4H, CH). – ^1H NMR (C_6D_6): δ = 0.05 (s, 18H, $SiMe_3$), 0.15 (s, 12H, $SiMe_2$), 4.67 (s, 4H, CH). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = −3.04 ($SiMe_3$), −1.86 ($SiMe_2$), 116.14 (CH). – ^{29}Si NMR (C_6D_6): δ = −23.01 ($SiMe_3$), 7.23 ($SiMe_2$).

2,5-Dimethyl-1,4-bis(triisopropylsilyl)-1,4-dihydropyrazine (**5**): A mixture of 0.50 g (4.6 mmol) of 2,5-dimethylpyrazine, 1.78 g (9.2 mmol) of chlorotriisopropylsilane, and 0.45 g (11.5 mmol) of potassium was stirred in 80 ml of THF for 2 d at ambient temp.; alternatively, the suspension could be immersed in an ultrasonic bath for 3–4 h. In any case, the yellowish solution was filtered to separate precipitated KCl, the solvent was removed by evaporation and the residue redissolved in warm benzene from which **4** crystallized in colorless form upon cooling in 43% yield (0.83 g). M.p. 131 °C. – $C_{24}H_{50}N_2Si_2$ (422.85): calcd. C 68.17, H 11.92, N 6.62; found C 67.08, H 11.84, N 6.70. – ^1H NMR (C_6D_6): δ = 1.19 (ps, 42H, *i*Pr), 1.66 [d, 6H, NCMe, ^4J(HH) = 1.0 Hz], 5.30 [q, 2H, NCH, ^4J(HH) = 1.0 Hz]. – $^{13}C\{H\}$ NMR ($CDCl_3$): δ = 13.4 (NC*Me*), 17.8 (CH*Me*), 18.4 (*C*HMe), 119.0 (N*C*Me), 127.5 (NCH).

1,1'-Bis(tert-butyldimethylsilyl)-1,1',4,4'-tetrahydro-4,4'-bipyridylidene (**8**): Addition of 1.70 g (11 mmol) of 4,4'-bipyridine to a mixture of 3.72 g (25 mmol) of *tert*-butylchlorodimethylsilane and 1.0 g (26 mmol) of potassium in 100 ml of THF produced a purple solution which was kept in an ultrasonic bath for 5 h for completion of the reaction. The dark red solution was filtered from bits of unreacted potassium, the solvent evaporated, the residue redissolved in benzene and the solution filtered again to remove KCl. Recrystallization from benzene gave 1.36 g (32%) of very air- and moisture-sensitive red platelets; an elemental analysis was thus not possible.

Oxidation of 1,4-Bis(triisopropylsilyl)-1,4-dihydropyrazine (**4**) *to* $\mathbf{4}^{+\bullet}$: A solution of 0.086 g (0.34 mmol) of iodine in 10 ml of dichloromethane was added to a solution of 0.27 g (0.68 mmol) of **4** in 30 ml of CH_2Cl_2. The color changed from yellow to reddish-brown and, after removal of most of the solvent and cooling to −70 °C, to green. Greenish crystals were growing which, however, decomposed on drying or warming.

Structure Determination: Suitable crystals of **5** were obtained by slow evaporation of the solvent from a benzene solution, separation under nujol and sealing in Lindemann capillaries. – *Crystal Data:* $C_{24}H_{50}N_2Si_2$, M = 422.8. Monoclinic, a = 1468.6(2), b = 1574.1(2), c = 1187.0(1) pm, β = 106.24(1)°, V = 2634.5(5) · 10^6 pm^3 (by least-squares refinement on diffractometer angles for 33 (20° ⩽ 2Θ ⩽ 28°) automatically centered reflections, λ = 0.71073 Å, space group $P2_1/c$ (ITC No. 14; automatic cell determination leads to $P2_1/a$ in which the mesurements of intensities were performed; after cell transformation the structure solution and refinements were carried out in the standardized space group $P2_1/c$.), Z = 4, D_x = 1.066 g cm^{-3}. Colorless plates with crystal dimensions 0.2 · 0.4 · 0.4 mm, μ (Mo-K_α) = 1.42 cm^{-1}, $F(000)$ = 944. – *Data Collection and Processing:* Syntex $P2_1$ diffractometer, ω-scans (Wyckoff), scan width 1.2°, scan speed variable (2–29°/min), graphite-monochromated Mo-K_α-radiation; 6568 reflections collected (3° ⩽ 2Θ ⩽ 55°; h = −19 to 18; k = −20 to 0; l = 0 to 15) of which 6060 independent and 4997 observed [$F > 4\sigma(F)$], two standard reflections monitored after every 98 measurements; Lorentz and polarization effects corrected. – *Structure Analysis and Refinement:* Direct methods followed by Fourier and difference-Fourier syntheses. Full-matrix least-squares; all non-hydrogen atoms with anisotropic and hydrogen atoms with isotropic thermal parameters [453 parameters refined, quantity minimized $\Sigma w(F_o - F_c)^2$]. Final R values are $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ = 0.038 and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$ = 0.043, weighting scheme $w = 1/[\sigma^2(F_o) + 0.0015\ F_o^2]$ with $\sigma(F_o)$ from counting statistics; $GooF = [w(|F_o| - |F_c|)^2/n - p]^{1/2}$ = 1.15; electron-density residuals for the last difference map 0.27 and −0.23 e · 10^{-6} pm^{-3}. Calculations and drawings performed with SHELXTL Plus package[30] on VAX-Station 3200.

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