Unexpected Basicity of a Hexacoordinate Silicon Compound, {2,6-Bis[(dimethylamino)methyl]phenyl}bis(1,2-benzenediolato)silicate

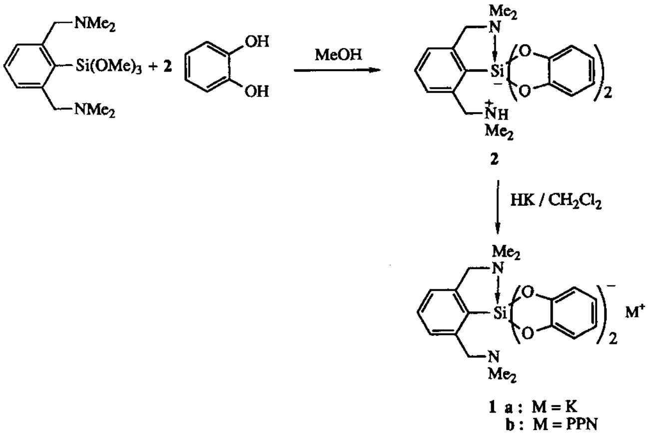
Claude Chuit, Robert J. P. Corriu*, Ahmad Mehdi and Catherine Reyé

Abstract: The high basicity of {2,6-bis[(dimethylamino)methyl]phenyl}bis(1,2-benzenediolato)silicate (**1**) was demonstrated by its quantitative protonation in methanol to give the zwitterion **2**. It was found that **1** is much more basic (pK_a in CH_2Cl_2 = 16.7) than the "proton sponge" 1,8-bis(dimethylamino)naphthalene (**3**) and also much more basic than {2,6-bis[(dimethylamino)methyl]phenyl}bis(1,2-benzenediolato)phosphorane (**4**). The stability of the zwitterion **2**, the geometry of which corresponds to a more perfect octahedron than **1**, can explain the high basicity of **1**. Dynamic NMR studies of **2** in solution show that at low temperature the hydrogen-bonding interaction with one oxygen atom observed in the solid state is maintained. On raising the temperature, firstly the hydrogen bond breaks, then dynamic coordination occurs, in which the NMe_2 groups displace each other in conjunction with transprotonation.

Keywords
basicity · hydrogen bonds · organosilicon compounds · zwitterions

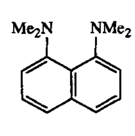
Introduction

In our investigation of hypercoordination at silicon,[1] we have already described the structure of the hexacoordinate silicate **1b**[2] originating from deprotonation of the zwitterionic λ^6 silicate **2**, itself obtained in an unexpected manner from the classical exchange reaction between catechol and {2,6-bis[(dimethylamino)methyl]phenyl}trimethoxysilane under basic conditions (Scheme 1). The X-ray structural analysis of **2**[3] has shown the hexacoordination of the silicon atom with an octahedral geometry, one NMe_2 group being coordinated to the silicon atom while the other is protonated. Furthermore, the proton attached to nitrogen is involved in an intramolecular hydrogen-bonding interaction with an oxygen atom. The recognition of this rather strong NH···O interaction prompted us to study thoroughly the formation of this zwitterion.



Scheme 1.

In this paper we report further data concerning the synthesis of **2**. The unusually high basic character of the silicate **1** is compared with that of the "proton sponge"[4] 1,8-bis(dimethylamino)naphthalene (**3**) and also with that of the corresponding phosphorus compound, {2,6-bis[(dimethylamino)methyl]phenyl}bis(1,2-benzenediolato)phosphorane (**4**). Finally dynamic NMR studies of **2** are reported which provide information concerning breaking of the hydrogen bond, intramolecular isomerization around the silicon atom and the dynamic N-Si-N coordination mode.



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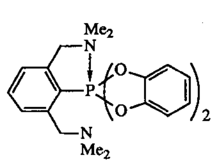

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Results and Discussion

Formation of the zwitterion 2: We have previously shown that the zwitterion **2** is obtained in methanol[3] according to Scheme 1. In that case it was prepared in 89% yield under the same conditions but without base. In order to find the limits for the formation of this compound we changed the experimental conditions and found that **2** is formed in methanol in the presence of one molar equivalent of Me_4NOH. It is also obtained in CH_2Cl_2 in the presence of one molar equivalent of MeOK and even in pyridine. Furthermore, treatment of 2,6-bis[(dimethylamino)methyl]phenylsilane (**5**) with 2 molar equivalents of catechol and one molar equivalent of MeOK in THF also affords **2**

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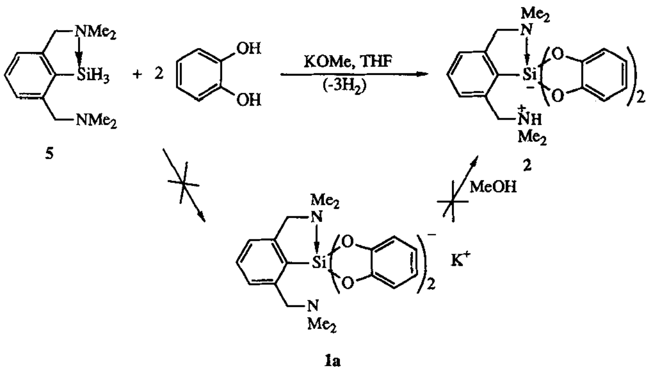

Scheme 2

immediately and quantitatively (Scheme 2). In this reaction, the formation of the potassium salt **1a** prior to the zwitterion **2** is unlikely since one molar equivalent of methanol in THF does not protonate **1a** under these conditions, and a stoicheiometric mixture of **5** and catechol affords **2** quantitatively. So we suggest that the protonation of one amino group that gives rise to the zwitterion **2** originates from the catechol (Scheme 3). The proximity of the lone pair of the nitrogen atom and of the remaining acidic proton of the catechol leads to the formation of the hydrogen bond.

Dynamic NMR studies: The ^{29}Si NMR chemical shift δ for **2** is -134.9 in solution (CD_2Cl_2) and -134.5 in ^{29}Si CP MAS NMR. In addition, the ^{29}Si NMR shift of **2** is temperature-independent in the temperature range studied (263–333 K in CD_3CN). These values indicate that **2** is also hexacoordinated in solution. In ^{1}H NMR at 243 K in solution (CD_3CN, Fig. 1 g, Table 1) the two NMe_2 groups are distinct and appear as four signals of equal intensity. The two doublets (δ = 2.62 and 2.98) were assigned to the protonated NMe_2 group. The nonequiva-

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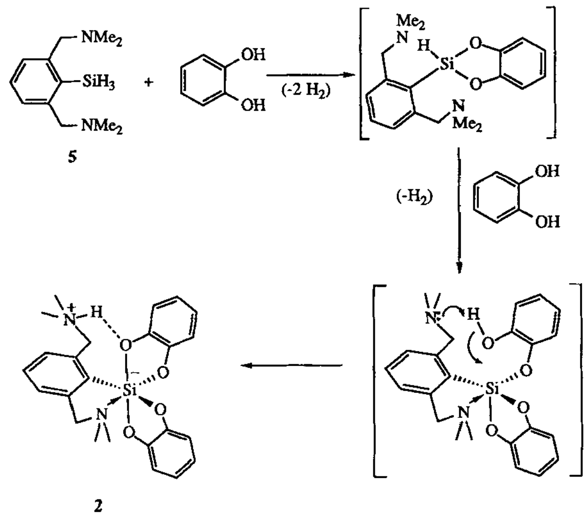
Robert Corriu, born in 1934 in Port-Vendres (France), obtained his degree of Docteur es Sciences Physiques in 1961 from the Université de Montpellier. He became Assistant Professor at the Université de Perpignan in 1963, Associate Professor at the Université de Poitiers in 1964 and Professor at the Université de Montpellier in 1969. His research interests involve organometallic chemistry: organosilicon, organogermanium and organophosphorus compounds, transition metal complexes and hypercoordinated silicon and phosphorus compounds. He is currently working on the chemistry of organometallic polymers as precursors to materials. He has received awards from the French Chemical Society (Prix Sue in 1969 and Prix Lebel in 1985), the CNRS (silver medal 1982) and the American Chemical Society (Kipping Award 1984). He was elected to the French Academy of Sciences in 1991 and obtained the Alexander von Humbold Research Award in 1992 and the Max Planck Research Award in 1993.



Scheme 3.

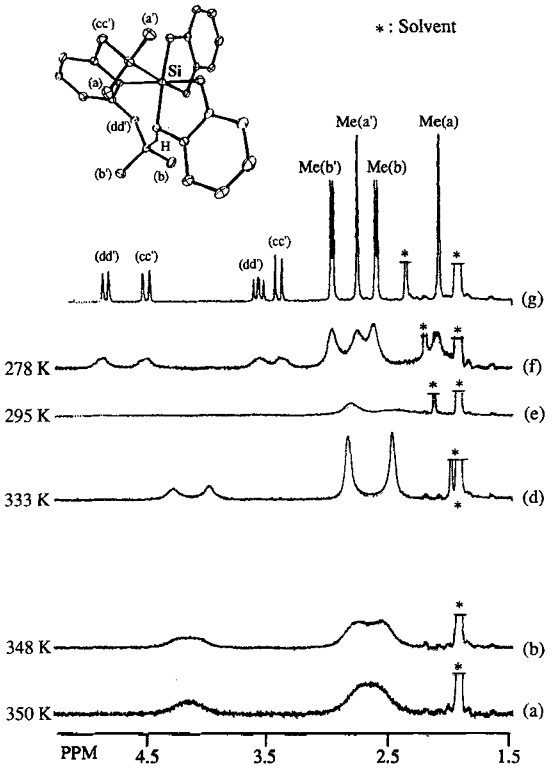


Fig. 1. 250 MHz ^{1}H NMR spectra of **2** in CD_3CN at different temperatures.

Table 1. ^{1}H NMR (250 MHz) data for NMe_2 and CH_2N groups of the zwitterionic silicate **2**.

T/K (solvent)	δ (NMe_2)	δ (CH_2N)
243 (CD_3CN)	2.09 (s, 3H)	3.42 (d, 1H, ^2J(H,H) = 13.8 Hz)
	2.62 (d, 3H, ^3J(H,H) = 4.6 Hz)	3.58 (dd, 1H, ^2J(H,H) = 12.0 Hz, ^3J(H,H) = 4.8 Hz)
	2.77 (s, 3H)	4.50 (d, 1H, ^2J(H,H) = 14.0 Hz)
	2.98 (d, 3H, ^3J(H,H) = 4.8 Hz)	4.84 (d, 1H, ^2J(H,H) = 12.0 Hz)
363 ($C_6D_5NO_2$)	2.54 (s, 12H)	4.00 (s, 4H)

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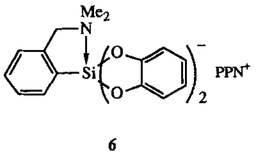


6

lence of the methyl groups indicates that free rotation is hindered by the NH $\cdots$ O interaction observed in the solid state and maintained in solution without internal or external proton exchange. The coupling with the NH proton confirms this interpretation. The two singlets at $\delta = 2.09$ and 2.77 were assigned to the other NMe$_2$ group coordinated to the silicon atom. The diastereotopy observed for the two NMe$_2$ groups results from the chirality of the silicon centre, chirality which indicates that there is no intramolecular nondissociative isomerization process around the silicon centre. In contrast the silicate **6**,[5] in which there is no intramolecular hydrogen bonding, undergoes this intramolecular isomerization process with a very low activation energy ($\Delta G^{\neq} < 28$ kJ mol^{-1}). This indicates that the isomerization process is hindered in **2** because of the hydrogen bonding. At 243 K the two methylene groups connected to the nitrogen atoms are also quite distinct (Fig. 1 g, Table 1). The signals were assigned by proton irradiation: the methylene protons of the coordinated CH$_2$NMe$_2$ group appear as an AX system owing to the chirality of the silicon centre. The methylene protons connected to the protonated amino group are different for the same reason. However, one appears as a doublet and the other as a doublet of doublets because of coupling with the ammonio proton. This also confirms the absence of any inter- or intramolecular proton exchange reaction at this temperature. As the temperature is raised (Fig. 1), a first coalescence of the N-methyl and methylene signals was observed at $T_c = 295$ K in [D$_3$]acetonitrile, giving rise to two broad signals for the NMe$_2$ groups and two others for the methylene protons at 333 K (Fig. 1 d). One methyl signal ($\delta = 2.87$) and one methylene signal ($\delta = 4.30$) were assigned to the free protonated CH$_2$NMe$_2$ unit while the other methyl ($\delta = 2.50$) and methylene ($\delta = 4.00$) signals were attributed to the CH$_2$NMe$_2$ unit coordinated to the silicon centre. These two sets of two signals for each CH$_2$NMe$_2$ group show that at this time the hydrogen bond breaks, allowing the intramolecular nondissociative isomerization process to occur as previously observed in **6**.[5] These two processes are synchronous. The $\Delta G^{\neq}$ calculated from the coalescence temperature of the N-methyl signals was found to be 64.2 kJ mol^{-1}. This value corresponds to the breaking of the hydrogen bond and not to the isomerization process, which requires little energy.[5] On further heating, a second coalescence of the N-methyl and the methylene signals was observed in [D$_3$]acetonitrile at 350 K (Fig. 1 a). Sharp singlets for the methylene protons and for the methyl groups are observed at 363 K in [D$_5$]nitrobenzene (Fig. 2 a). This pattern is indicative of the equivalence of the two CH$_2$NMe$_2$ units. This equivalence is consistent with a rapid coordination–decoordination process[7] involving the two NMe$_2$ groups along with transprotonation from one group to the other. The $\Delta G^{\neq}$ for this coordination–decoordination process has been estimated to be 73 kJ mol^{-1} from the coalescence temperature of N-methyl signals.

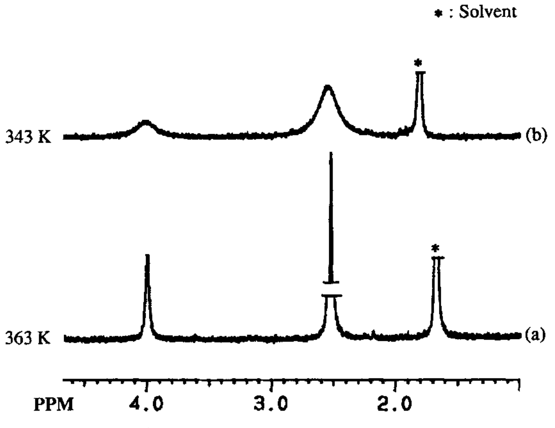
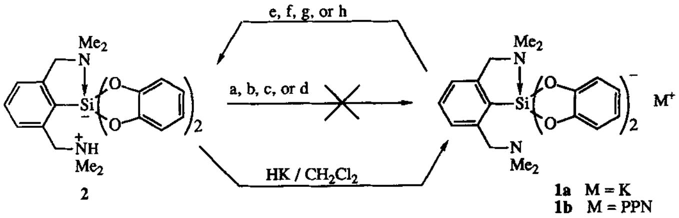
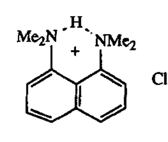


Fig. 2. 250 MHz ^{1}H NMR spectra of **2** in [D$_5$]nitrobenzene.



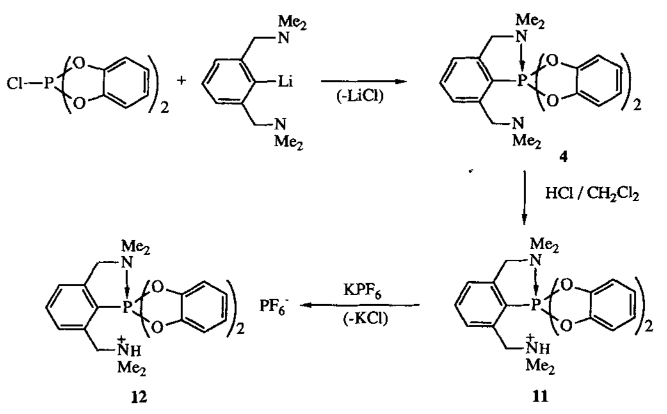
Scheme 4. Reactivity of **2** toward basic reagents and of **1** toward acidic reagents: a) pyridine (solvent); b) HNa (1 equiv) in CH$_2$Cl$_2$; c) KOMe (1 equiv) in CH$_2$Cl$_2$; d) **3** in CD$_2$Cl$_2$; e) MeOH (solvent), M = PPN; f) CH$_3$CO$_2$H (1 equiv) in CH$_2$Cl$_2$; g) MeOH (1 equiv) in CH$_2$Cl$_2$, 15 h, 25 °C, M = PPN; h) **7** in CD$_2$Cl$_2$, M = PPN.

Basic properties of the silicate 1: Abstraction of the proton from **2** is very difficult: **2** is deprotonated neither in pyridine nor with potassium methoxide or sodium hydride in CH$_2$Cl$_2$, nor even with 1,8 bis(dimethylamino)naphthalene (**3**, proton sponge), which is a strong but bulky base[4] (Scheme 4). **2** is quantitatively converted into **1a** only when treated with potassium hydride in CH$_2$Cl$_2$ (Scheme 4). Conversely the protonation of **1b**[8] is very easy. It occurs instantaneously in MeOH as a solvent or in the presence of one molar equivalent of CH$_3$CO$_2$H in CH$_2$Cl$_2$ and even in the presence of one molar equivalent of MeOH in CH$_2$Cl$_2$ but over a period of 15 hours. When **1b** is left in the air, atmospheric moisture induces its complete protonation over several days. Furthermore, in an equimolar mixture of **1b** and **7**, immediate and complete proton exchange takes place. This reaction was monitored by ^{1}H NMR spectroscopy (see Experimental Procedure). The spectrum of the mixture shows the signal of the ammonio proton of **2** ($\delta = 11.31$) and the disappearance of the N$\cdots$H$\cdots$N signal of **7** ($\delta = 18.32$). In addition, the spectrum shows a signal at $\delta = 2.73$ (NCH$_3$ of **3**) and the absence of a signal at $\delta = 3.17$ (NCH$_3$ of **7**). So the silicate **1b** is much more basic than the proton sponge **3**. The transprotonation equilibrium between **1a** and *t*BuOH (pK_a 16.54[9]) was studied in CD$_2$Cl$_2$ by NMR spectroscopy. After 30 hours at room temperature an equilibrium was established. By comparing the integration value for the CH$_2$N protons in **1a** ($\delta = 3.40$) with that for all the aromatic protons in the mixture, the **2**:**1a** ratio was estimated to be 28:22, giving a value of 16.7 for the pK_a of **1a**.

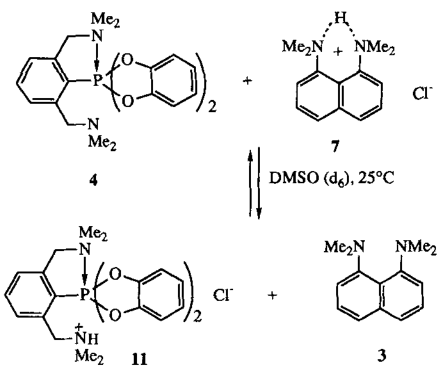


7

The basicity of the silicate **1b** has also been compared with that of the phosphorane **4**, prepared according to Scheme 5. Reaction of **4** with a molar equivalent of HCl in CH$_2$Cl$_2$ yielded the corresponding ammonium salt **11** quantitatively. Subsequent treatment of **11** with KPF$_6$ gave rise to the corresponding hexafluorophosphate **12**. When equimolar amounts of **4** and **7** were mixed in [D$_6$]DMSO, ^{1}H NMR analysis indicated an incomplete proton exchange reaction that led after 10 min to an equilibrium between the four species **4**, **7**, **11** and **3** (Scheme 6). Integration of the signals of the NMe$_2$ protons of **7** and **3** (**7**: $\delta = 3.17$; **3**: $\delta = 2.73$) indicates a **3**:**7** ratio of 13:8. Estimation



Scheme 5.



Scheme 6.

of the pK_a of **4** gave a value of 12.8; the pK_a value of **3** was 12.34.[10] In contrast, evidence for a complete and immediate proton exchange reaction was obtained in ^{1}H NMR spectroscopy by mixing an equimolecular amount of **1b** and the salt **12** in CD_3CN. Integration of the signals of the NMe_2 protons shows the disappearance of the protonated phosphorane **12** (δ = 2.46, 2.97 and 3.08) and of the NMe_2 signals of the phosphorane **4** (δ = 2.28). These experiments indicate that **4** has a basicity comparable to that of the 1,8-bis(dimethylamino)naphthalene but above all that the silicate **1b** is much more basic than the phosphorane **4**.

The unexpected basicity of the silicate **1** has both structural and electronic causes. The comparison of the X-ray structures of **1b**[2] and of **2**[3] (Fig. 3) shows that the geometry of the zwitterion **2** approximates more to the "quasi-perfect octahedron" than that of the silicate **1b**, which is favourable to the formation of **2**. Atoms N1 and O2, C1 and O3, O4 and O1 located on opposite sides of the central silicon atom give bond angles of 174.6, 168.8 and 175.9°, respectively, while O1-Si-N1, O4-Si-O2 and O3-Si-C1 angles on silicate **1b** are 170.4, 164.9 and 174.3°, respectively. In this hexacoordinate complex the negative charge is not centred on the silicon atom[11] but distributed around the oxygen atoms. That could explain the easy formation of the hydrogen-bonding interaction resulting in compound **2**. This interpretation is consistent with the high reactivity of anionic hypercoordinated silicon complexes toward nucleophilic reagents.[12, 13] It is to be noted that the ammonio proton on **2** is located in between the nitrogen atom and the oxygen O4 with an N–H distance of 1.16 Å and an H···O distance of 1.62 Å. This H···O distance represents a significant bonding interaction, much stronger than the H···O interactions observed on zwitterionic λ^5 spirosilicates such as **8**, **9** and **10**, whether the H···O interaction is intramolecular as in **8**[14] (2.042 Å) and **9**[15] (1.819 Å) or intermolecular as in **10**[15] (2.069 Å).

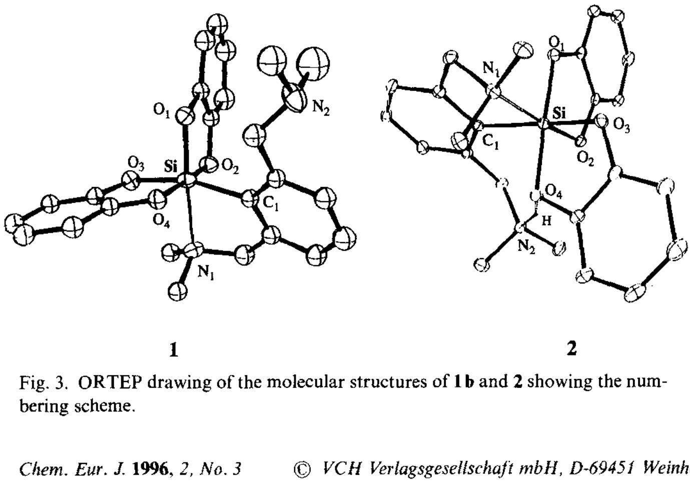
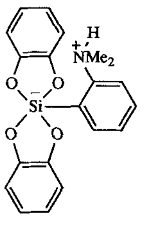


Fig. 3. ORTEP drawing of the molecular structures of **1b** and **2** showing the numbering scheme.



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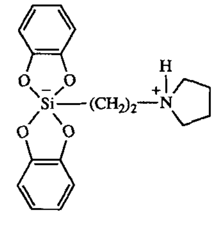

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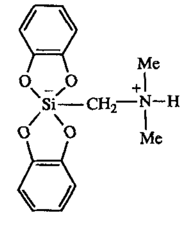

10

Conclusion

While several zwitterionic λ^5 spirosilicates have been reported,[16] few examples of zwitterionic λ^6 species are known.[3, 17] The zwitterion **2** is particularly stable because of the hydrogen bonding between one NMe_2 group and one oxygen atom. Such an interaction allows an appreciable modification of the arrangement of the atoms around the silicon leading to an octahedron more perfect than in the silicate **1b**. The stability of **2** explains the very easy protonation of the silicate **1b**. Conversely the very difficult abstraction of the proton from the zwitterion **2** results from the strength of the hydrogen bond and also to steric hindrance.

Experimental Procedure

All the reactions were performed under a dry nitrogen atmosphere by standard Schlenk techniques. ^{1}H, ^{13}C, ^{29}Si and ^{31}P NMR spectra were obtained with a Bruker WP-200-SY or a Bruker 250AC spectrometer. Solid-state NMR spectra were recorded on a Bruker AM-300 spectrometer. ^{1}H, ^{29}Si and ^{13}C chemical shifts are reported relative to Me_4Si, and ^{31}P chemical shifts relative to H_3PO_4. Elemental analyses were performed by the Centre de Microanalyse du CNRS.

{2,6-Bis[(dimethylamino)methyl]phenyl}silane (5): A solution of {2,6-bis[(dimethylamino)methyl]phenyl}trimethoxysilane [2] (8 g, 25 mmol) in ether (60 mL) was added dropwise at 0 °C to a suspension of $LiAlH_4$ (1.54 g, 40 mmol) in ether (60 mL). The mixture was stirred at room temperature for 2 d. The solvent was then removed under vacuum and the residue was taken up in pentane (40 mL). After filtration, the solution was concentrated and the oily residue was distilled to give 5.4 g of **5** (23.8 mmol, 95%); b.p. 45–50 °C/0.1 Torr; ^{29}Si NMR (39.76 MHz, $CDCl_3$): −81.4 (t, ^1J(Si,H) = 200 Hz); ^{15}N{^{1}H} NMR (20.28 MHz, $CDCl_3$, CH_3NO_2): −349 (s); ^{1}H NMR (250 MHz, $CDCl_3$): 2.11 (s, 12H, NCH_3), 3.47 (s, 4H, CH_2N), 4.05 (s, 3H, SiH_3), 7.0–7.24 (m, 3H, Ar); ^{13}C{^{1}H} NMR (62.89 MHz, $CDCl_3$,): 43.3 (NCH_3), 63.8 (CH_2N), 126.8, 127.8, 128.5, 132.8, 138.9, 147.9 (Ar); IR (CCl_4): 2099, 2122 and 2149 (SiH); MS (70 eV, EI) m/z (%): 222 (63) [M^+], 58 (100) [$H_2C{=}NMe_2^+$]; $C_{12}H_{22}N_2Si$ (222): calcd C 64.86, H 9.90, N 12.60; found C 63.98, H 9.20, N 12.60.

{2-[(Dimethylammonio)methyl]-6-[(dimethylamino)methyl]phenyl}bis(1,2-benzenediolato)silicate (2): A solution of {2,6-bis[(dimethylamino)methyl]phenyl}trimethoxysilane (2.25 g, 7.2 mmol) in ether (30 mL) was added dropwise at room temperature to a solution of catechol (1.58 g, 14.4 mmol). A white precipitate formed immediately. After half an hour of stirring, the precipitate was filtered and washed three times with ether. After drying under vacuum, 2.8 g (6.42 mmol, 89%) of **2** was obtained as a white solid; m.p. 219–221 °C; ^{29}Si NMR (39.76 MHz, CD_2Cl_2): −134.9 (s); ^{29}Si CP MAS NMR (59.62 MHz): −134.5 (s); ^{1}H NMR (80 MHz, CD_2Cl_2, 25 °C): 2.30 (br, 6H, NCH_3), 2.47 (br, 6H, NCH_3), 3.92 (br, 4H, CH_2N), 6.20–6.48 (2m, 8H, Ar), 6.70–7.03 (m, 3H, Ar), 11.3 (s, 1H, NH); ^{1}H NMR (250 MHz, CD_2Cl_2, −40 °C): 2.13 (s, 3H, NCH_3), 2.65 (d, 3H, ^{3}J(H,H) = 4.8 Hz, $NH(CH_3)$), 2.82 (s, 3H, NCH_3), 3.01 (d, 3H, ^{3}J(H,H) = 4.8 Hz, $NH(CH_3)$), 3.34 (d, 1H, ^{2}J(H,H) = 13.8 Hz, CH_2N), 3.40 (dd, 1H, ^{2}J(H,H) = 12 Hz, ^{3}J(H,H) = 4.8 Hz, CH_2N), 4.60 (d, 1H, ^{2}J(H,H) = 14 Hz, CH_2N), 4.96 (d, 1H, ^{2}J(H,H) = 12 Hz, CH_2N), 6.38–6.70 (2m, 8H, Ar), 6.9–7.15 (m, 3H, Ar), 11.29 (s, 1H, NH); (250 MHz, $C_6D_5NO_2$, 90 °C): 2.54 (s, 12H, NCH_3), 4.00 (s, 4H, CH_2N), 6.33–6.48 (2m, 8H, Ar), 6.70–6.81 (m, 3H, Ar), 11.39 (s, 1H, NH); MS (positive-ion FAB, NBA) *m/z* (%): 437 (100) [$(M+H)^+$]; MS (negative-ion FAB, NBA) *m/z* (%): 435 (100) [$(M-H)^-$]; $C_{24}H_{28}N_2O_4Si$ (436): calcd C 65.93, H 6.52, N 6.42; found C 66.05, H 6.42, N 6.42.

Preparation of 2 in MeOH: A solution of catechol (0.76 g, 6.92 mmol) in MeOH (10 mL) was added dropwise at room temperature to a solution of {2,6-bis[(dimethylamino)methyl]phenyl}trimethoxysilane (1.08 g, 3.46 mmol) in MeOH (10 mL). A white precipitate appeared immediately. After stirring for 10 min, the reaction mixture was cooled to 0 °C and 1.8 mL of a 20% Me_4NOH solution in MeOH was added. The reaction mixture was stirred for 1 h at room temperature, and the solvent was then removed under vacuum. Recrystallization of the residue from CH_3CN gave 1.1 g (2.52 mmol, 73%) of **2**; m.p. 221–222 °C; ^{29}Si NMR (39.76 MHz, $CDCl_3$): −134.4 (s).

Preparation of 2 in CH_2Cl_2: A solution of {2,6-bis[(dimethylamino)methyl]phenyl}trimethoxysilane (0.79 g, 25.3 mmol) in CH_2Cl_2 was added dropwise at room temperature to a mixture of catechol (0.56 g, 5.06 mmol) and KOMe (0.35 g, 5.06 mmol) in CH_2Cl_2 (60 mL). The reaction mixture was stirred at room temperature for 6 hours. After filtration to remove unreacted KOMe, half of the solvent was removed under vacuum. The concentrated solution was cooled overnight to give 0.74 g (1.69 mmol, 67%) of **2**; m.p. 218–220 °C; ^{29}Si NMR (39.76 MHz, $CDCl_3$): −134.3 (s).

Preparation of 2 in pyridine: A solution of {2,6-bis[(dimethylamino)methyl]phenyl}trimethoxysilane (1.15 g, 3.7 mmol) in pyridine (20 mL) was added dropwise at room temperature to a solution of catechol (0.8 g, 7.4 mmol) in pyridine (20 mL). A light precipitate appeared after one hour of stirring. The reaction mixture was refluxed for 2 h. The pyridine was then removed and the residue was washed three times with ether. 1.4 g (3.3 mmol, 87%) of **2** was obtained. M.p. 218–220 °C; ^{29}Si NMR (39.76 MHz, $CDCl_3$): −134.4 (s).

Preparation of 2 from 5: A solution of {2,6-bis[(dimethylamino)methyl]phenyl}silane **5** (0.6 g, 2.7 mmol) in THF (15 mL) was added dropwise at room temperature to a solution of catechol (0.6 g, 5.4 mmol) in THF (10 mL) in the presence of MeOK (0.19 g, 2.7 mmol). A white precipitate appeared immediately. The reaction mixture was stirred for 30 min at room temperature. The precipitate was then filtered and washed twice with ether (15 mL), giving 1.1 g (2.51 mmol, 93%) of **2**; m.p. 222–223 °C; ^{1}H NMR (80 MHz, CD_2Cl_2): 2.29 (br, 6H, NCH_3), 2.56 (br, 6H, NCH_3), 3.85 (br, 4H, CH_2N), 6.17–6.50 (m, 8H, Ar), 6.65–7.00 (m, 3H, Ar), 11.31 (s, 1H, NH).

Monoprotonated 1,8-bis(dimethylamino)naphthalene (7): A solution of HCl in ether (1.31 M, 7 mL) were added at 0 °C to a solution of 1,8-bis(dimethylamino)naphthalene (**3**) in ether (20 mL, 9.15 mmol). After half an hour of stirring, the precipitate formed was filtered off at room temperature, washed with ether and dried under vacuum to give 1.95 g (6.9 mmol, 85%) of **7** as a beige powder; m.p. 208–209 °C; ^{1}H NMR (250 MHz, [D_6]DMSO): 3.17 (d, 12H, ^{3}J(H,H) = 1.9 Hz, NCH_3), 7.71–8.15 (2m, 6H, Ar), 18.32 (s, 1H, NH).

Proton exchange reaction between the ammonium salt 7 and the silicate 1b: Compound **1b** (38 mg, 39 × 10^{-3} mmol) and salt **7** (9.8 mg, 39 × 10^{-3} mmol) were dissolved in CD_2Cl_2 (1 mL). The proton exchange reaction was monitored by ^{1}H NMR spectroscopy. It took place immediately. ^{1}H NMR (250 MHz, CD_2Cl_2, 25 °C): 2.48 (s, 6H, NCH_3 of **2**), 2.63 (s, 6H, NCH_3 of **2**), 2.69 (s, 12H, NCH_3 of **3**), 4.02 (br, 4H, CH_2N of **2**), 6.50–7.85 (3m, 47H, Ar), 11.31 (s, 1H, NH of **2**).

Proton exchange reaction between 1a and *t*BuOH: **1a** (42 mg, 94 × 10^{-3} mmol) was mixed with a solution of *t*BuOH (7.0 mg, 94 × 10^{-3} mmol) in CD_2Cl_2 (1.2 mL). The proton exchange reaction, which was monitored by ^{1}H NMR spectroscopy, occurred after 30 h at room temperature. ^{1}H NMR (250 MHz, CD_2Cl_2): 2.11 (s, 12H, NCH_3 of **1a**), 2.72 (br, 6H, NCH_3 of **2**), 2.96 (br, 6H, NCH_3 of **2**), 3.35 (br, 1H, CH_2N of **2**), 3.40 (s, 4H, CH_2N of **1a**), 3.62 (br, 1H, CH_2N of **2**), 4.65 (br, 1H, CH_2N of **2**), 5.04 (br, 1H, CH_2N of **2**), 6.45–7.29 (4m, 22H, Ar of **1a** and **2**), 11.51 (br, 1H, NH of **2**).

{2,6-Bis[(dimethylamino)methyl]phenyl}(benzene-1,2-diolato)phosphorane (4): A solution of 2,6-bis[(dimethylamino)methyl]phenyllithium (5.24 mmol) in ether (30 mL) was added dropwise at −30 °C to a suspension of chlorobis(1,2-benzenediolato)phosphorane [18] (1.48 g, 5.24 mmol) in ether (25 mL). The reaction mixture was stirred for 3 h at room temperature and the solvent was then removed under vacuum. The residue was taken up again with 20 mL of CH_2Cl_2. The precipitate of LiCl was filtered through Celite and the solvent was evaporated under vacuum to leave a foam which was washed with ether (30 mL). The resulting solid was recrystallized from toluene to yield **4** as white crystals (1.3 g, 57%); m.p. 186 °C (decomp.); ^{31}P{^{1}H} NMR (101.25 MHz, $CDCl_3$): −73.9 (s), (121.49 MHz, solid state): −77.0 (s); ^{1}H NMR (250 MHz, CD_3CN, 25 °C): 2.28 (s, 12H, NCH_3), 3.75 (br, 2H, CH_2N), 4.04 (br, 2H, CH_2N), 6.04–6.60 (2m, 8H, Ar), 7.05–7.30 (m, 3H, Ar); ^{1}H NMR (250 MHz, CD_2Cl_2, −60 °C): 2.22 (s, 6H, NCH_3), 2.38 (d, 3H, ^{3}J(P,H) = 5.6 Hz, NCH_3), 3.01 (s, 3H, NCH_3), 3.60 (dd, 1H, ^{2}J(H,H) = 13.9 Hz; ^{3}J(P,H) = 4.9 Hz, CH_2N), 3.75 (d, 1H, ^{2}J(H,H) = 15.9 Hz, CH_2N), 3.96 (d, 1H, ^{2}J(H,H) = 15.9 Hz, CH_2N), 4.82 (d, 1H, ^{2}J(H,H) = 15.8 Hz, CH_2N), 6.60–7.62 (5m, 11H, Ar); (250 MHz, C_6D_5N, 80 °C): 2.56 (d, 12H, ^{3}J(P,H) = 2.1 Hz, NCH_3), 4.3 (s, 4H, CH_2N), 6.75–6.95 (2m, 8H, Ar), 7.25–7.35 (m, 3H, Ar); ^{13}C{^{1}H} NMR (250 MHz, $CDCl_3$): 47.3 (NCH_3), 63.3; 63.4 (CH_2N), 110.0; 110.2; 120.3; 126.0; 126.3; 128.5; 128.6; 139.8; 143.6; 145.0; 145.1 (Ar); MS (positive-ion FAB, 2-nitrophenyloctylether) *m/z* (%): 439 (100) [$(M+H)^+$]; $C_{24}H_{27}N_2O_4P$ (438): calcd C 65.74, H 6.20, N 6.38; found C 65.92, H 6.30, N 6.41.

{2-[(dimethylammonio)methyl]-6-[(dimethylamino)methyl]phenyl}(benzene-1,2-diolato)phosphorane chloride (11): A solution of HCl (0.08 M, 20 mL, 1.6 mmol) in CH_2Cl_2 was added dropwise at 0 °C to a solution of **7** (0.72 g, 1.64 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred at room temperature for 1 h, then filtered off and the solvent removed under vacuum to leave 0.75 g (1.57 mmol, 96%) of a light violet solid; m.p. 221 °C. (decomp.); ^{31}P{^{1}H} NMR (101.25 MHz, $CDCl_3$): −78.6 (s); ^{31}P{^{1}H} CP MAS NMR (121.49 MHz): −82.4 (s); ^{1}H NMR (250 MHz, CD_3CN, 0 °C): 2.42 (d, 3H, ^{3}J(P,H) = 6.6 Hz, NCH_3), 2.78 (d, 3H, ^{3}J(H,H) = 4.8 Hz, NCH_3), 2.82 (d, 3H, ^{3}J(H,H) = 4.8 Hz, NCH_3), 3.05 (d, 3H, ^{3}J(P,H) = 3.7 Hz, NCH_3), 3.80 (dd, 1H, ^{2}J(H,H) = 14.8, ^{3}J(P,H) = 10.3 Hz, CH_2N), 4.43 (dd, 1H, ^{2}J(H,H) = 13.3 Hz, ^{3}J(P,H) = 5.2 Hz, CH_2N), 4.86 (dd, 1H, ^{2}J(H,H) = 14.8 Hz, ^{3}J(P,H) = 3.3 Hz, CH_2N), 5.10 (dd, 1H, ^{2}J(H,H) = 13.3 Hz, ^{3}J(P,H) = 7.0 Hz, CH_2N), 6.56–8.0 (3m, 11H, Ar), 11.35 (s, 1H, NH); (250 MHz, $CDBr_3$, 120 °C): 2.65 (s, 12H, $N(CH_3)_2$), 4.40 (br, 4H, CH_2N), 6.2–8.2 (3m, 11H, Ar), 11.40 (s, 1H, NH); MS (positive-ion FAB, NBA) *m/z* (%): 439 (100) [$(M-Cl)^+$].

{2-[(dimethylammonio)methyl]-6-[(dimethylamino)methyl]phenyl}(benzene-1,2-diolato)phosphorane hexafluorophosphate (12): A solution of KPF_6 (0.28 g, 1.51 mmol) in acetonitrile (7 mL) was added dropwise at room temperature to a solution of **11** (0.72 g, 1.51 mmol) in acetonitrile (10 mL). The resulting mixture was stirred for 18 h. The KCl precipitate was then filtered off and the solvent removed under vacuum. The resulting solid was recrystallized from CH_2Cl_2 to give 0.4 g (0.68 mmol, 45%) of light violet crystals of **12**; m.p. 219–220 °C; ^{31}P NMR (101.2 MHz, CD_3CN): −81.8 (s), −143.2 (sept, ^{1}J(P,F) = 706 Hz); ^{1}H NMR (250 MHz, CD_3CN, 25 °C): 2.46 (d, 3H, ^{3}J(P,H) = 4.9 Hz, NCH_3), 2.97 (s, 3H, NCH_3), 3.08 (s, 6H, NCH_3), 3.90 (t, 1H, J(H,H) = 12.4 Hz, CH_2N), 4.09 (d, 1H, ^{2}J(H,H) = 12.2 Hz, CH_2N), 4.86 (d, 1H, ^{2}J(H,H) = 14.1 Hz, CH_2N), 5.06 (d, 1H, ^{2}J(H,H) = 12.5 Hz, CH_2N), 6.77–6.96 (m, 8H, Ar), 7.30–7.49 (m, 3H, Ar); MS (positive-ion FAB, NBA) *m/z* (%): 439 (100) [$(M-PF_6)^+$]; MS (negative ion, NBA) *m/z* (%): 145 (100) [$(PF_6)^-$]; $C_{24}H_{28}F_6N_2O_4P_2$ (584): calcd C 49.31, H 4.79, N 4.79; found C 49.41, H 4.74, N 4.82.

Proton exchange reaction between 4 and 7: Phosphorane **4** (49 mg, 0.11 mmol) was added to a solution of **7** in [D_6]DMSO (1 mL). The proton exchange reaction was monitored by ^{1}H NMR. Equilibrium was reached after 10 min. ^{1}H NMR (250 MHz, [D_6]DMSO, 25 °C): 2.1–3.0 (br, 24H, NCH_3 of **4** and **11**), 2.73 (s, 12H, NCH_3 of **3**), 3.15 (s, 12H, NCH_3 of **7**), 3.65–5.05 (br, 8H, CH_2N of **4** and **8**), 6.57–8.13 (4m, 34H, Ar).

Proton exchange reaction between 1b and 12: Phosphorane **12** (10 mg, 1.7 × 10^{-2} mmol) was added to a solution of **1b** (16.5 mg, 1.7 × 10^{-2} mmol) in CD_3CN (1 mL). The transprotonation, monitored by ^{1}H NMR, was immediate. ^{1}H NMR (250 MHz, CD_3CN, 25 °C): 2.13 (br, 6H, NCH_3 of **2**), 2.29 (s, 12H, NCH_3 of **4**), 2.63 (br, 6H, NCH_3 of **2**), 3.75 (br, 2H, CH_2N of **4**), 4.05 (br, 2H, CH_2N of **4**), 3.10–4.87 (br, 4H, CH_2N of **2**), 6.26–7.47 (4m, 52H, Ar), 10.58 (s, 1H, NH of **2**).

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