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Intramolecular nitrogen ligand stabilization of phenyl-imidazolidine derived silicon species

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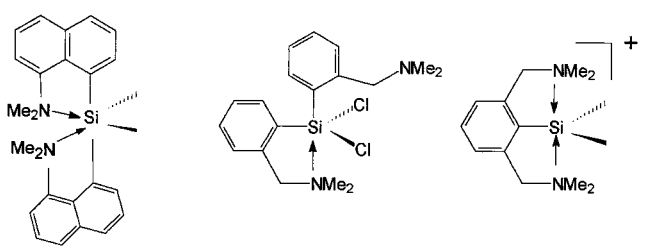
Abstract

The synthesis of some new functional aminoarylsilanes with the aromatic ring substituted in the *ortho*-position by a 2-(1,3-dimethyl)imidazolidine ligand is presented. The donating properties of the imidazolidine fragment, in which the two coordinating nitrogen atoms are located on the same side of the silicon center induce a specific chemical behavior of the organosilicon species. Thus, only one Si–H bond of $ArSiH_3$ was found to react with an excess of organic acids and heterocumulenes. NMR studies showed that, if in imidazolidinylphenyldihydrosilanes containing a strong electronegative substituent, the silicon center is pentacoordinated by forming one additional N→Si bond, only a small activation energy is sufficient to exchange the two donating nitrogen atoms. The reason for this easy exchange is probably the small distance between the two donor centers and the rigidity caused by the bridging ethylene unit. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Si-pentacoordination; 2-(1,3-Dimethylimidazolidine-2-yl)aryl ligand; Intramolecular nucleophilic activation

1. Introduction

There is continuing interest in the theoretical and mechanistic aspects of the nucleophilic catalyzed substitutions at silicon [1]. Hypercoordinated species with mono or bidentate aminoaryl ligands have been synthesized in order to mimic the different geometries of the possible intermediates involved in these reactions [2]. Among them, the fused bis(aminonaphthyl) derivatives **A**, with a formally hexacoordinated silicon atom, presented an unexpected chemical stability [3], whereas the bis(dimethylaminophenyl) compound **B** was shown to exist in solution as an equilibrium between pentacoordinated species [4].



A B C

More recently, we applied the approach of Van Koten [5] to obtain some new nitrogen bis chelating silicon species, starting from the 2,5-bis(dimethylamino)phenyl lithium. We isolated a series of stabilized siliconium ionic derivatives **C**, in which the two nitrogen atoms occupy the *trans*-diaxial positions of a trigonal bipyramidal geometric species [6]. The siliconium ionic compound was supposed to be formed [7] through the nucleophilic displacement of the halogen (as a good leaving group) by the second NMe_2 coordinating ligand at silicon (Chart 2).

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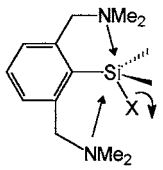
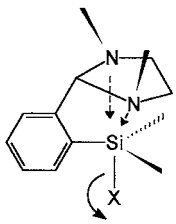
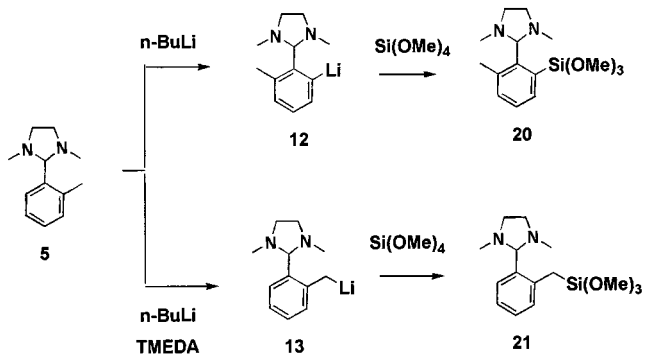
In this context, it was of interest to study the structure and the chemical behavior of compounds in which the two coordinating nitrogen centers are located on the same side of the silicon atom [8]. For this purpose, we choosed phenyl silanes substituted in *ortho*-position by a 2-(1,3-dimethyl)imidazolidine ligand.





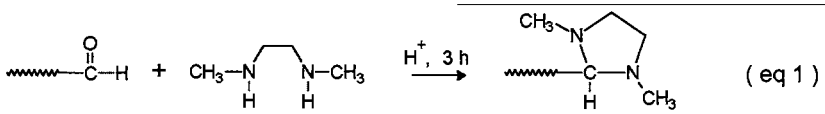


Scheme 1.

2. Results and discussion

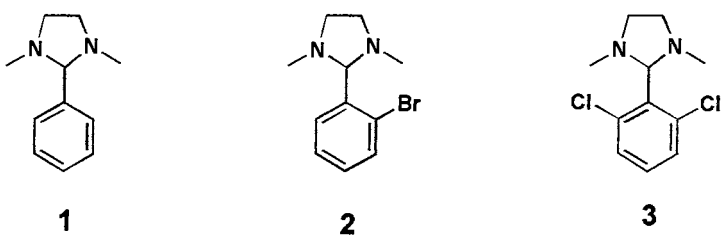
2.1. Synthesis and metalation of the ligands

The dimethylimidazolidine system can be easily built-up by reaction of an aromatic aldehyde with *N*,*N*′-dimethylethylenediamine in the presence of a catalytic amount of acid (Eq. 1) [9].

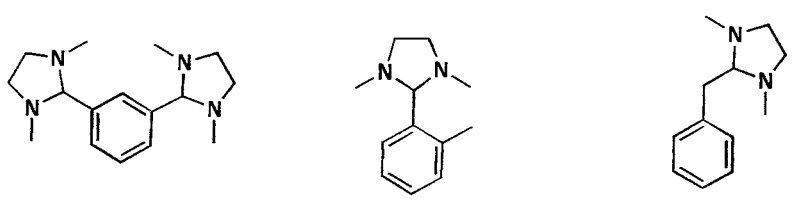


(eq 1)

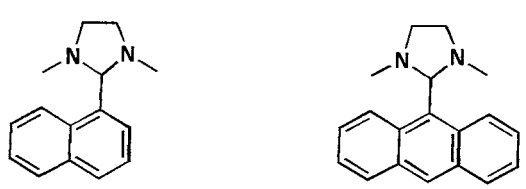
According to that method, we synthesized a series of aromatic imidazolidines. The heterocyclic compounds **1**–**8** (Chart 3) are available in high yields as very viscous colourless oils. To check the possibility of selective *ortho* (peri) lithiation for introducing a silicon side chain in these positions, the imidazolidines **1**–**8** were treated with one equivalent of *n*-butyl lithium in diethyl ether. After some hours, a colourless precipitation of the aryl lithium compound was observed, which was trapped after 12 h with a slight excess of tetramethoxysilane.



1 2 3



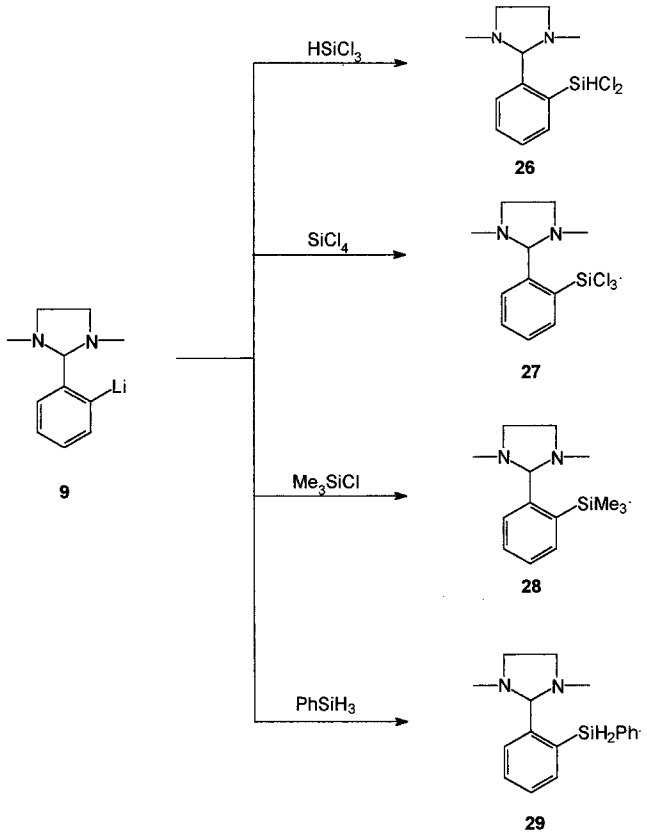
4 5 6



7 8

The isolated silanes showed that the phenyl derivatives **1**–**4** can be *ortho*-metalated selectively in good yields. Double metalation of the dichloro compound **3** was not possible, even when an excess of the lithiating agent was added. Compound **4** offered the possibility to introduce a silicon side chain in the 6-position between the two imidazolidine ligands. In fact, the metalation takes place only in the sterically less hindered 2-position, instead of the more activated 6-position. Surprisingly, deprotonation of the peri position of the naphthyl compound **7** presented some difficulties. Besides the peri silylated compound **25**, the *ortho* product **24** was formed simultaneously. A similar result was obtained by metalation of the *o*-tolyllimidazolidine **5** with *n*-butyl lithium, in Et_2O, followed by reaction with tetramethoxysilane. The reaction leads only to the *ortho* product **20**, and the compound **21** with the silyl group in benzylic position was not observed. However, such a metalation of the less favorable benzylic position in **5** is possible by complexing the *n*-butyl lithium with TMEDA (Scheme 1).

Deprotonation of the anthracenyl compound **8** failed completely. No silylated product was detectable after refluxing a mixture of **8** with *n*-butyl lithium in DME for several hours, followed by addition of $Si(OMe)_4$. The reason for this unusual behavior with compounds **5**, **7** is probably steric in origin.



Scheme 2.

2.2. Synthesis of imidazolidinylphenyl substituted silanes

Besides the trimethoxysilane **17**, both the chloro compounds **26** and **27** are available by reaction of the lithiated ligand **9** with one equivalent of the corresponding chlorosilane (Scheme 2). Compounds **26** and **27** are isolated as air and moisture sensitive powders, insoluble in apolar solvents like pentane or ether. Introduction of the trimethylsilyl group can be carried out by reaction of **9** with trimethylchlorosilane. Dihydrosilane **29**, bearing a second aryl substituent is directly available by reaction of phenyl silane with the lithiated ligand **9**.

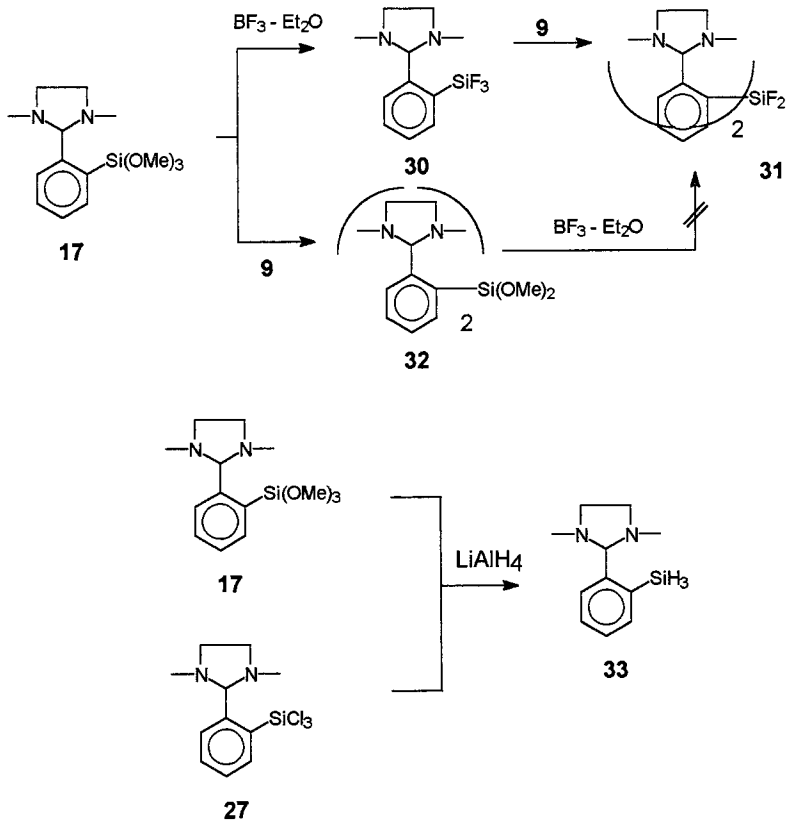
As already shown in the literature ([1]b, [2]c, [6–8]), aryltrimethoxy silanes are good precursors for the synthesis of other functionalized silanes. Thus, it should be possible to modify the substitution pattern in **17** and in **27** by standard reactions (Scheme 3). Correspondingly, treatment of **17** with boron trifluoride-diethyl ether complex at r.t. lead to the trifluorosilane **30**, isolated as a very air sensitive and highly viscous yellow liquid. The silane **33** was obtained as a colourless, air stable liquid, either by stirring of **17** with lithium aluminium hydride or by reduction of the trichlorosilyl derivative **27**. Compounds containing two imidazolidinyl-aryl ligands were available, for example, by reaction of tetramethoxysilane with two equivalents of the lithiated ligand **9,** which affords the dimethoxysilane **32**. The corresponding difluoro silane **31** is synthesized by reacting the aryl lithium compound **9** with the trifluorosilane **30**. Difluorosilane **31** is more stable to air than compound **30**, a situation which is certainly an effect of a better sterical protection of the SiF_2 unit by the second imidazolidinyl aryl system.

2.3. Reactions of imidazolidinylphenyl silane *33*

Corresponding to comparable known systems, the silane **33** itself should be also a good precursor for the synthesis of a wide range of aryl or alkyl substituted silanes by reaction with nucleophiles like alkyl or aryl lithium compounds ([1], [3]c, [6–8]).

Pentacoordinated organosilicon hydrides add to C=X double bonds (X = O, S, N) in heterocumulenes like carbodiimides, isocyanates, isothiocyanates, CO_2 and CS_2 [10–12]. In some instances, the intermediates are thermally unstable and decompose to products containing Si=X double bonds. Following that methodology, a silanethione has been isolated [13] in the case of dimethylaminomethylene naphthyl system (Scheme 4).

The imidazolidinylphenyl substituted silane **33** shows a chemical behavior different to that of the analogous arylmethyldimethylamino compounds (Scheme 5). In



Scheme 3.

33, only one hydrogen is activated and enabled to react, for example with organic acids or with heterocumulenes. Thus, the silane **33** reacts with acetic acid giving the silyl ester **36**. Bis- or tris-substituted products are not observed, even in the presence of an excess of acid. Only the corresponding formic ester **35** is formed with formic acid. Interestingly, this ester is also the only product obtained by adding the silane **33** to CO_2. Reaction of **33** with phenylisothiocyanate yields the thioamide **34**, which is characterized as a mixture of two isomers. Hydrogen–chlorine exchange in **33** is observed with PCl_5 [14].

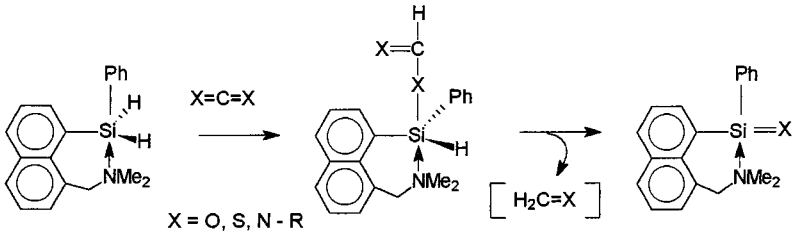
2.4. Intramolecular coordination at silicon

Extension of coordination around a silicon atom from four to five is normally accompanied by an upfield shift in the position of the ^{29}Si-NMR signal [6–8,15]. As expected, all the species described here show characteristic ^{29}Si-NmR upfield variations relative to their tetracoordinated analogues Table 1. Some 2-(dimethylaminomethyl)phenylsilanes and 2,6(bis-dimethylaminomethyl)phenylsilanes are also reported for comparisons. As already observed in previous studies previous studies [4,17], the smaller differences are noted in the case of methoxy derivatives **17**, **32** and trimethyl moiety **28**, which behave like tetravalent silanes.

Upfield shifts are obtained for the silanes **26**, **27**, **29**, **30**, **31**, **33**, and **34**–**37** which all contain electronegative substituents. The imidazolidine system is supposed to coordinate to the silicon center in these compounds, since the δ values correspond to those of the dimethylaminomethyl substituted derivatives (Table 1), for which extension of coordination is well demonstrated [4,6–8,17]. The question whether the silicon in the silanes containing an electronegative substituent is pentacoordinated or if the coordination sphere in these silanes is extended to six can be answered by the results of temperature dependent NMR spectroscopic investigations (Table 2), which were typically carried out for the silanes **30**, **33**, **36**, **37**.

The NMR data presented here prove that, in these compounds, the silicon center is only pentacoordinated, but the structure is highly dynamic. In other words, a fast exchange occurs from one nitrogen to the other for coordination to the central silicon, as shown in Scheme 6. This exchange can be stopped by cooling down the mixture to low temperature.

To better understand the fluxional behavior of our models, we have first carried out variable temperature ^{19}F-NMR investigation of compound **30**, in d_8-toluene. The ^{19}F-NMR spectrum presents at -90°C three triplets, two broad signals respectively at -125.75 ($J = 36$ Hz), -142.60 ppm ($J = 24$ Hz) and a better

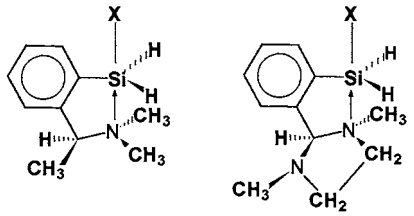


Scheme 4. Insertion and decomposition of heterocumulenes.

resolved system at -138.15 ppm ($J = 35.8$ Hz). When the temperature is raised, the signals coalesce at 213 K to give a single resonance at -135.55 ppm, allowing the free energy of activation for the whole process to be estimated as 8.7 kcal mol^{-1}, applying the Eyring equation [16]. The ^{29}Si-NMR spectrum gives a quartet at δ -101 ppm [$J(^{19}F-^{29}Si) = 232$ Hz], with no important modification of the shape from 223 to 343 K. Both, the upfield chemical shift and the lower Si–F coupling constant relative to $PhSiF_3$ are indicative of an hypercoordinated species. Temperature dependent ^{1}H-NMR investigations for the trifluoro silane **30** show that the N–Me groups are equivalent even at 203 K, whereas the quartets corresponding to the N–CH_2 groups (two types of protons) are maintained when the solution is cooled to 200 K. Such results can only be interpreted through a decoordinating process of the imidazolidine moiety, when the temperature is raised. The two *N*-methyl groups are equivalent through the fast exchange, whereas the methylenic hydrogens keep their different environment in the five-membered ring geometry with two hydrogen atoms in endo (exo) position relative to the silicon atom. An extension of coordination to six ligands around the central silicon, which could alternatively explain both the equivalence of the N–Me groups and maintain the AB system of the CH_2 groups, must be accompanied by the equivalence of only two of the fluorine atoms, which is not observed. The more reasonable explanation is fast decoordination, allowing free rotation of the non-coordinating substituents, before reclosure.

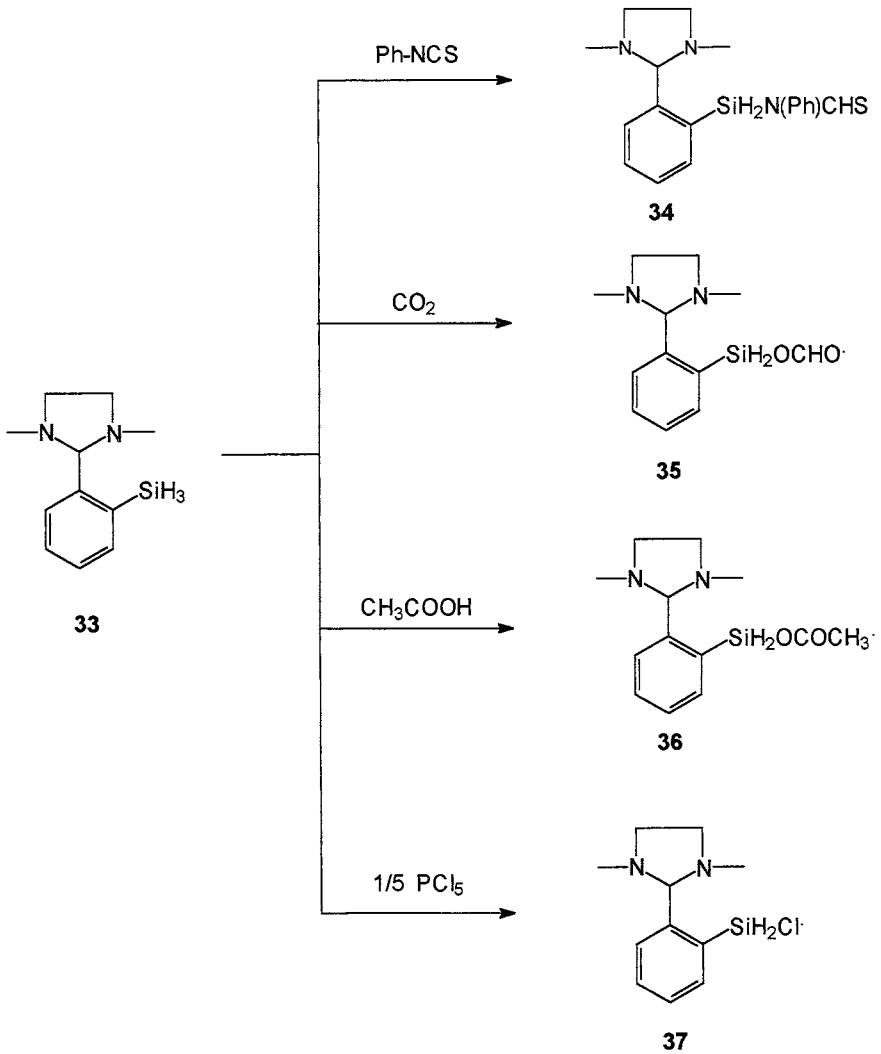
Table 2 shows the ^{1}H-NMR chemical shift values for compounds **33**, **35**, **36**, **37.** In the trihydrosilane **33**, signals corresponding to only one type of imidazolidine ring are observed at all temperatures from 183 K (in CD_2Cl_2) to 400 K (in $C_6D_5NO_2$). The ^{29}Si-NMR (d_8-toluene) spectrum gives a quartet of doublets at δ -70.45 ppm ($J_1 = 198.8$ Hz, $J_2 = 8.3$ Hz), with no important modification of the chemical shift and coupling constant from 223 to 343 K. Apparently, the nitrogen coordination is too weak and/or the nitrogen exchanges are too fast in the pentacordinated species to give rise to observable diastereotopy. Compounds **35**, **36** and **37** present a more interesting behavior in their ^{1}H-NMR spectra. At low temperature, the two N–CH_3 groups give differentiated signals, the N–CH_2 moieties give broad multiplets and the Si–H_2 protons appear as AB systems. At r.t., one signal is observed for the N–CH_3 groups, two quartets for the N–CH_2, and one singlet for the SiH_2 moiety. The more reasonable geometry of the stable form expected in pentacoordinated trifunctional silanes bearing two hydrogen ligands is this one in which the two hydrogen atoms occupy equatorial positions of a trigonal bipyramidal structure [17] with the third functional group and the nitrogen coordinating ligand in apical positions.

The results are interpreted by a fast exchange between the two nitrogen coordinating ligands. The values for the energy of activation calculated [16] for this process from the NMR data (Table 2) are lower than the 9–13 kcal mol^{-1} obtained [18] for the dissociative process of the corresponding 2-[1-(dimethylamino)ethyl]phenyl substituted analogues (Chart 4). Obviously, the nearness of the second nitrogen in the fused imidazolidine system facilitates a rapid change of these atoms in their coordination to the silicon center.



3. Conclusion

The synthetic and spectroscopic results presented here show that the imidazolidinyl-phenyl substituent bonded to a silicon center stretch out some unusual properties in the resulting compounds. Starting from the trimethoxy derivative **17**, a large number of silicon compounds with a wide range of different substituents at the silicon center is available. The donating properties of the imidazolidine fragment are suitable to compensate electron deficits at the silicon atom caused by a strong electronegative substituent, by forming a donor contact. The electronic properties also influence the chemical behavior of the silicon center. This is exemplified by the reactions of the silane **33**. Thus, only the



Scheme 5.

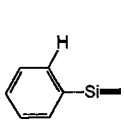
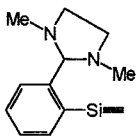
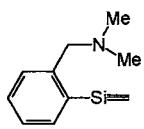
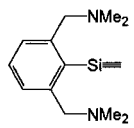
axial hydrogen was found to be activated enough to give reactions with organic acids and heterocumulenes.

NMR studies showed that, if in imidazolidinylphenyldihydrosilanes containing a strong electronegative substituent the silicon center is pentacoordinated by forming one additional N→Si bond, only a small activation energy is necessary to exchange the donating nitrogen atoms. The structure in solution is highly dynamic, but base-coordinated silyl cations are not evidenced ([6]c, [19]). The reason for this easy exchange is probably the small distance between the two donor centers and the rigidity caused by the bridging ethylene unit.

4. Experimental part

All reactions were carried out under an atmosphere of dry argon. Air-sensitive products and reagents were handled by standard Schlenk techniques. Diethyl ether was dried and distilled from a purple solution of sodium/benzophenone ketyl. Toluene was distilled from sodium under nitrogen. Chloroform and dichloromethane were dried with CaH_2 and distilled under nitrogen. Glassware was dried in an oven at 110–120°C prior to use. Commercially available chemicals were used as such without any further purification. For a concern of presentation, and since pertinent data are reported in the text (Tables 1 and 2), the NMR data of the new compounds have been placed in a supporting section. The mass spectra were obtained on a Delsi Nermag Automass [diphenyl (5%) dimethylsilicone as stationary phase, electron impact mode, 70 eV] or a JEOL JMS D100 apparatus by EI ionization at 30 or 70 eV. In some cases, positive FAB mass spectra in *m*-nitrobenzyl alcohol (NBA) were also recorded. Elemental analyses were carried out by the Service Central de Microanalyse du CNRS in Lyon or in the ENSC Montpellier.

Table 1
^{29}Si-NMR chemical shifts of some aminoaryl silanes versus tetravalent derivatives (coupling constants, in Hz, in parentheses)

Ar–SiF_3	−72.9 (267)	−101.0 (232)	−102.2 (233)	
Ar–SiH_3	−61.5 (200)	−70.45 (199)	−75.95 (198)	−80.0 (200)
Ar–$Si(OMe)_3$	−54.5	−54.0	−54.0	−53.8
Ar–$SiMe_3$	−4.1	−4.3	−4.9	−7.6
Ar–SiH_2Ph	−33.8 (200)	−44.4 (214)	−44.6 (210)	−51.5 (194)
Ar_2SiF_2	−29.1 (302)	−54.2 (269)	−53.9 (270)	
Ar_2SiH_2	−33.8 (200)		−45.01 (199)	
$Ar_2Si(OMe)_2$	−34.5	−29.4		

4.1. Substituted dimethylimidazolidines

Aryl substituted dimethylimidazolidines **1–8** have been prepared according to literature [9]. In a typical experiment, benzaldehyde (20 g, 0.19 mol) and *N*,*N*′-dimethylethylenediamine (18 g, 0.2 mol) are dissolved in 200 ml of toluene, with 0.5 ml of *p*-toluenesulfonic acid as catalyst, and the mixture is refluxed for 6 h with connection to a Dean–Stark trap in which water is collected. The solvent is then removed and the residue is distilled in vacuo. Colourless liquid, b.p. 65°C/0.1 mmHg:Yield 84%. The 1,3-dimethyl-2-phenylimidazolidine, **1**, has been identified by comparison of its characteristics with those of an authentic sample [9]. The other dimethylimidazolidines **2–8** have been prepared using the same procedure with the appropriate aldehyde.

1,3-Dimethyl-2(2-bromophenyl) imidazolidine, **2**: Colourless liquid. Yield 93%. b.p. 85°C/0.5 mmHg. Anal. Calc. for $C_{11}H_{15}$ Br N_2: C, 51.79; H, 5.93; N, 10.98. Found: C, 51.88; H, 6.18; N, 10.89. FAB MS; *m*/*e* (relative intensity%): 255 ($M^+ + H$), 253 (M^+-H), 99 ($Imid^+$).

1,3-Dimethyl-2(2,6 dichlorophenyl) imidazolidine, **3**: Colourless liquid. Yield 73%. bp. 104°C/0.5 mmHg. Anal. Calc. for $C_{11}H_{14}Cl_2N_2$: C, 53.89; H, 5.76; N, 11.43. Found: C, 54.05; H, 5.77; N, 11.29.

1,3-Bis(1,3-dimethyl imidazolidine-2-yl) benzene, **4**: Colourless oily liquid. Yield 74%. b.p. 110°C/5.10−2 Torr. Anal. Calc. for $C_{16}H_{26}N_4$: C, 70.03; H, 9.55; N, 20.41. Found: C, 70.25; H, 9.64; N, 20.81. FAB-MS (*m*/*e*, relative intensity ‰): 275 ($M^+ + H$, 25) 274 (M^+, 15), 273 (M^+-H, 60, 216 (M^+-$CH_3NCH_2CH_3$, 25), 175 (M^+-Imid-H, 30), 99 ($Imid^+$, 100).

1,3-Dimethyl-2-benzyl imidazolidine, **6**: 30.0 g (0.25 mol) of phenylacetaldehyde are mixed with 24.0 g (0.27 mol) of dimethylethylene diamine, plus a catalytic amount of *p*-toluene sulfonic acid, and refluxed in 300 ml of toluene. The water is collected in a Dean–Stark trap. After usual work-up, the compound **6** is distilled b.p. 106°C/1.6 mm Hg. Yield 21.7 g (46%). Anal. Calc. for $C_{12}H_{18}N_2$: C, 75.74; H, 9.53; N, 14.71. Found: C, 73.73; H, 9.39; N, 14.55. FAB-MS (*m*/*e*, relative intensity%): 191 ($M^+ +$ H, 95), 190 (M^+, 90), 146 (M^+-CH_3NCH_3, 50), 99 ($Imid^+$; 100) 190 (M^+, 90), 146 (M^+-CH_3NCH_3, 50), 99 ($Imid^+$, 100)

1,3-Dimethyl-2-(1-naphthyl)imidazolidine **7**: same procedure as above. Yield 73%. Colourless oily liquid. b.p. 110°C/0.01 mmHg. Anal. Calc. for $C_{15}H_{18}N_2$: C, 79.61; H, 8.02; N, 12.37. Found: C, 79.76; H, 7.97; N, 12.65. FAB-MS (*m*/*e*, relative intensity%): 226 (M^+, 35), 225 (M^+-H, 100), 182 (M^+-CH_3NCH_2, 15), 168 (M^+-$CH_3NCH_2CH_3$, 15), 99 ($imid^+$, 80).

1,3-Dimethyl [2-anthracen-9 yl] imidazolidine, **8**: same procedure as above. After removal of the solvent, the brown residue is crystallized in Et_2O/toluene (20/80). The solid is collected by filtration and washed with pentane. Yield 71%. m.p. 121°C. Yellow solid. Anal. Calc. for $C_{19}H_{20}N_2$: C, 82.57; H, 7.29; N, 10.13. Found: C, 82.44; H, 7.27; N, 10.13. FAB-MS (*m*/*e*, relative intensity%): 276 ($M^+ +$ H, 60), 275 (M^+-H, 40), 274 (M^+- H, 90), 232 (M^+-CH_2NCH_3,30), 218 (M^+-$CH_3NCH_2CH_3$, 28), 191 (M^+-$CH_3NCH_2CH_2NCH_3$, 20), 178 (M^+-imid, 15), 99 (imid. + -, 100).

2-(1,3-Dimethylimidazolidine-2-yl) phenyl trimethoxysilane **17**: 4.4 g (25.00 mmol) of 1,3-dimethyl-2-phenylimidazolidine are dissolved in 40 ml of anhydrous ether. The solution is treated with 10 ml of a 2.5 M solution of *n*-Bu Li in hexane (25.0 mmol). After stirring overnight, the mixture is added slowly to a solution of 5.7 g (27.5 mmol) of tetramethoxysilane in 40 ml of Et_2O at −10°C. The mixture is warmed to r.t. and stirred for additional 12 h. The solvent is removed in vacuo and hexane is added to precipitate MeOLi.

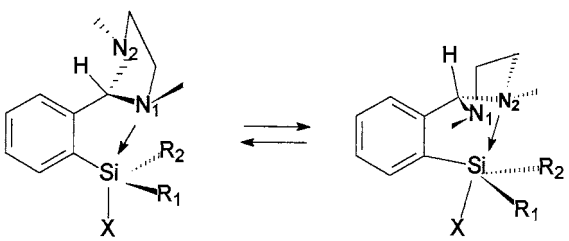
Table 2
Selected ^{1}H-NMR data of **29, 33, 35, 36, 37**

No	Formula	Conditions	N–CH_3	N–CH_2	N–CH	Si–H	$\Delta G^{\#}$ (kcal mol^{-1})
29	(Ip5)SiH_2Ph	25°C $CDCl_3$	2.04	2.47 3.35	3.42	4.91	<8.0
		−90°C CD_2Cl_2	2.10	2.57 3.35	3.48	4.80	T_c< −90°C
33	(Ip5) SiH_3	25°C $CDCl_3$	2.15	2.56 3.33	3.46	4.19	<7.5
		−100°C CD_2Cl_2	2.15	2.60 3.32	3.48	4.18	T_c< −100°C
35	(Ip5)SiH_2OCOH	25°C $CDCl_3$	2.31	2.73 3.50	3.76	4.82	10.1
		−80°C CD_2Cl_2	2.16 2.28	2.7 3.3–3.5	3.71	4.385 4.875	T_c −45°C
36	(Ip5)SiH_2OCOCH_3	25°C $CDCl_3$	2.27	2.69 3.47	3.71	4.78	9.9
		−90°C CD_2Cl_2	2.185 2.245	2.5 3.4–3.6	3.67	4.285 4.805	T_c −65°C
37	(Ip5)SiH_2Cl	25°C $CDCl_3$	2.28	2.72 3.45	3.78	5.18	11.0
		−80°C CD_2Cl_2	2.19 2.30	2.7 3.4–3.6	3.79	4.875 5.235	T_c −40°C

After filtration and concentration, the compound **17** is isolated by distillation, b.p. 95°C/5 × 10^{-2} mmHg. Yield 4.4 g (57%).

Anal. Calc. for $C_{14}H_{24}N_2SiO_3$: C, 56.73; H, 8.16; N, 9.45. Found: C, 56.55; H, 8.62; N, 9.90. FAB-MS (*m*/*e*, relative intensity%): 296 (M^+, 6) 175 (M^+-Si$(OCH_3)_3$, 25), 132 (M^+-Si (OCH)$_3$–CH_3 NCH_2, 20), 99 (imid.$^+$ 100).

3-Chloro-2 (1,3-dimethylimidazolidine-2-yl) phenyl trimethoxysilane, **18**: 20.4 ml of a 2.5 M solution of *n*-BuLi in hexane (48.8 mmol) are added dropwise to a solution of 3.0 g (12.2 mmol) of 2 (1,3-dichlorophenyl) 1,3-dimethylimidazolidine in 70 ml of ether. After 6 days the mixture is added to a solution of 8.0 g (52.6 mmol) of Si $(OMe)_4$, in 20 ml of ether. After 12 h, the solvent is removed and the residue is suspended in 50 ml of pentane. After filtration, the solvent is removed and the compound **18** is isolated by distillation in vacuo. b.p. 160°C/2 mmHg. Yield 2.3 g (58%). Anal. Calc..for $C_{14}H_{23}ClN_2SiO_3$: C, 50.81; H, 7.01; N, 8.47. Found: C, 51.54; H, 7.18; N, 8.48.



R_1, R_2 = H ; X = H (33), OAc (36), C(37)

R_1, R_2 = F ; X = F (30)

Scheme 6. Scheme 6

Bis [2-(1,3-dimethylimidazolidine-2-yl)-phenyl] dimethoxysilane **19:** using the same procedure as above, 20 ml of *n*-BuLi/hexane (2.5 M) were treated with 8.8 g (50 mmol) of 1,3 dimethyl-2-phenylimidazolidine; after 60 h, 3.8 g (25.2 mmol) of tetramethoxysilane were added. After usual work-up, distillation afforded 4.1 g (yield 36%) of pure dimethoxysilane **19** (b.p. 150°C/10^{-2} mmHg). Anal Calc.for $C_{24}H_{36}N_4SiO_2$: C, 65.43, H, 8.24; N, 12.50. Found: C, 64.95; H, 12.48. FAB-MS (*m*/*e*) 441 (M^+-H), 411 (M^+-OCH_3), 341 (M^+-Imid), 99 (Imid$^+$).

3-Methyl-2 (1,3-dimethylimidazolidine-2-yl) phenyltrimethoxysilane, **20**: In the same conditions as above, 9.5 g (50 mmol) of 1,3-dimethyl-2-*o*-tolylimidazolidine **11** are treated with *n*-BuLi (50 mmol) and then 10 g (65 mmol) of tetramethoxysilane, in anhydrous ether. After work-up, flash distillation of the crude material gave 2.7 g (17% yield) of compound **20**. Anal Calc. for $C_{15}H_{26}N_2SiO_3$: C, 58.03; H, 8.44; N, 9.02. Found: C, 58.67; H, 8.59; N, 8.81.

4.2. Miscellaneous reactions

Attempted synthesis of 2 (1,3-dimethylimidazolidine-2-yl) dichlorosilane, **26**. In 40 ml of Et_2O are mixed 4.4 g (25 mmol) of 1,3-dimethyl-2-phenyl-imidazolidine and 10 ml of *n*-BuLi (2.5 M) in hexane. After stirring for 12 h, silicochloroform is added at −40°C. The

mixture is warmed up and stirred for 12 h. The solvent is changed to hexane and the mixture is filtered. After removal of the solvent under vacuum, attempted distillation afforded an highly viscous residue.

$^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 41.03 (NCH_3), 52.75 (NCH_2), 91.35 (CH), 127.07, 129.86, 131.26, 133.62, 138.58, 143.71 (aromatics). ^{29}Si-NMR ($CDCl_3$): δ −54.3 (J(SiH): 352 Hz. Only broad signals were observed in the ^1H-NMR spectrum.

2-(1,3-Dimethylimidazolidine-2-yl) phenyltrichlorosilane **27**. To a solution of 5.0 g (19.6 mmol) of 1,3-dimethyl-2-(*o*-bromophenyl) imidazolidine in 100 ml of ether, was added a solution of 9.0 ml of *n*-butyl lithium (2.2 M) in hexane at −30°C. After coming to 0°C, the mixture was added to a solution of 4.0 g (23.5 mmol) of silicon tetrachloride at −60°C. The mixture allowed to come to r.t. and was stirred for 12 h. The solvent was removed in vacuo, and the yellow residue dissolved in 50 ml of methylene chloride. After filtration, removal of solvent left **27** as a yellow solid residue. Yield 91%. Anal. Calc..for $C_{11}H_{15}Cl_3N_2Si$: C, 42.68; H, 4.88; N, 9.04. Found: C, 42.65; H, 4.91; N, 8.88. MS [EI, 30 eV; *m*/*e* (relative intensity%)]: 175 (M^+-$SiCl_3$, 30, 132 (M^+-$SiCl_3$–CH_3NCH_2, 40) 99 ($Imid^+$, 100).

2-(1,3-Dimethylimidazolidine-21-yl) phenyl trimethylsilane, **28**: 5.0 g (19.6 mmol) of 2-(*o*-bromophenyl) 1,3-dimethylimidazolidine dissolved in 80 ml of anhydrous ether are metalated with 8.1 ml of a 2.4 M solution of *n*-butyllithium in *n*-hexane (19.6 mmol) at −20°C for 1.5 h. Then, 3.0 g (19.6 mmol) of trimethylchlorosilane are added. After coming to r.t., the mixture is stirred for 12 h. The solvent is removed and the residue is extracted with pentane. After removal of the volatile products, the compound **28** is purified by vacuum distillation. b.p. 102°C/1.5 mmHg. Yield: 4.10 g (84%). Anal. Calc. for $C_{14}H_{24}N_2Si$: C, 67.68; H, 9.74; N, 11.28. Found: C, 67.24; H, 10.03; N, 11.50. FAB-MS (*m*/*e*): 249 (M^+ + 1, 80), 2.48 (M^+, 50), 2.47 (M^+-1, 70). 233 (40), 217 (20), 204 (15), 190 (20), 176 (40), 99 (100).

2-(1,3-Dimethylimidazolidine-2-yl) phenylsilane, **29**: 3.1 g (17.6 mmol) of 1,3-dimethylimidazolidine are dissolved in 60 ml of ether. To the solution, 8 ml of a 2.5 M solution of *n*-BuLi in hexane (17.6 mmol) are added dropwise at r.t. and the mixture is stirred for three days. Then, 1.9 g (18.6 mmol) of phenylsilane is added. After 2 h, LiH is removed by filtration and the solvent is eliminated in vacuo. Distillation affords 3.02 g (10.7 mmol) of compound **29** as a pale yellow liquid, sensitive to air and moisture. Yield 61%. b.p. 116°C/0.02 mmHg. Anal. Calc. for $C_{17}H_{22}N_2Si$: C, 72.30; H, 7.85; N, 9.92. Found: C, 72.22; H, 7.79; N, 10.15 3. FAB-MS (*m*/*e*, relative intensity%): 282 (M^+, 15), 281 (M^+-1, 90), 265 (10), 224 (30), 205 (25), 175 (10), 148 (10), 99 (100).

2-(1,3-Dimethylimidazolidine-2-yl) trifluorosilane, **30**: 0.86 ml (7 mmol) of BF_3–Et_2O are added dropwise to a solution of 2.0 g (6.8 mmol) of 1,3-dimethyl imidazolidine-2-yl) trimethoxysilane, **17**, in 30 ml of anhydrous ether. After 3h, the solvent is removed in vacuo, and the compound **30** is isolated by distillation: b.p. 139°C/2 mmHg. Yield 59%. Anal. Calc..for $C_{11}H_{15}F_3N_2Si$: C, 50.76; H, 5.81; N, 10.76. Found: C, 51.06; H, 5.98; N, 10.74.

Bis [2-(1,3-dimethylimidazolidine-2-yl-phenyl] difluorosilane, **31**: 4.33 g (16.7 mmol) of 1,3-dimethyl-2-(2-bromophenyl) imidazolidine are dissolved in 70 ml of Et_2O. At −40°C, 6.7 ml (16.7 mmol) of *n*-butyl lithium in *n*-hexane (2.5 M) are added. After 1 h, the mixture is warmed up to 0°C and is added slowly to a solution of 2-(1,3-dimethylimidazolidine-2-yl) trifluorosilane, **30**, 4.33 g (16.7 mmol). The mixture is stirred for 3 h at r.t. After filtration and evaporation of the solvents, **31** is isolated by distillation in vacuo, 2.35 g (yield 34%). b.p. 160°C/0.2 mm Hg. Anal. Calc. for $C_{22}H_{30}F_2N_4Si$: C, 63.43; H, 7.26; N, 13.44: Found: C, 63.97; H, 7.18; N, 13.61.

Bis [2-(1,3-dimethylimidazolidine-2-yl) pheny] dimethoxysilane, **32**: 20.0 ml of a 2.5 M solution of *n*-butyllithium in *n*-hexane are added to a solution of 8.8 g (50 mmol) of 1,3-dimethyl-2-phenylimidazolidine, in 80 ml of Et_2O. After stirring for 48 h, 3.8 g (25 mmol) of tetramethoxysilane are added. The mixture is refluxed for 3 h and stirred overnight. After filtration, the solvents are removed and the oily residue is distilled in vacuo, giving 4.0 g of **32**. Yield 36%, b.p. 150°C, 0.05 mmHg. FAB-MS (*m*/*e* relative intensity%): 441 (M^+ + 1, 30), 411 (M^+-OCH_3, 15), 355 (M^+-CH_3NCH_2 CH_2CH_3, 10), 341 (M^+-Imid, 8) 250 (18), 209 (10), 174 (15) (6), 99 (100). Anal. Calc. for $C_{24}H_{36}N_4SiO_2$: C, 65.43; H, 8.24; N, 12.72. Found: C, 64.98; H, 8.19; N, 12.54.

Attempted fluoration of **32** with BF_3–Et_2O. In 15 ml of Et_2O were added dropwise 1.11 g (2.52 mmol) of **32** and 0.24 g (1.68 mmol) of BF_3–Et_2O, at r.t. A white precipitate formed immediately. After 3 h, the liquid phase was separated and the organic residue dried in vacuo. Distillation afforded an untractable material. No signal corresponding to **31** was observed, even if the BF_3-complex with **31** was observed in the wide material.

2-(1,3-Dimethylimidazolidine-2-yl)silane **33**: 2.0 g (6.76 mmol) of **17** in 10 ml of Et_2O is added to a suspension of 0.38 g (10.1 mmol) of $LiAlH_4$ in 20 ml of Et_2O at 0°C. The mixture is warmed up to r.t. and stirred for 15 h. After changing the solvent to hexane, the mixture is filtered and the solvent is removed. Distillation in vacuo yields 1.22 g (70%) b.p. 70°C/2 mmHg. Characteristics of **33**: Anal. Calc. for $C_{11}H_{18}N_2Si$: C, 64.01; H, 8.79; N, 13.57. Found: C, 62.92; H, 8.79; N, 14.09. FAB-MS (*m*/*e*, relative inten-

sity%): 206 (M+, 10), 205 (M^+- 1, 60) 148 (M^+-$CHNCH_2CH_2$), 25), 99 ($Imid^+$, 100).

4.3. Reactions of **33**

4.3.1. With PhNCS

In 20 ml of $CDCl_3$, 500 mg (2.43 mmol) of **33** are mixed with 328 mg (2.43 mol) of phenylisothiocyanate at −20°C. After warming up to r.t., the mixture is stirred for 3 h. Removal of the solvent affords an oily residue which is analyzed as such. The product identified as thioformyl phenylamido-2-(1,3-dimethylimidazolidine-2-yl) silane **34**. Anal. Calc. for $C_{18}H_{23}N_3SiS$: C, 63.33; H, 6.71, N, 12.31; S, 9.37. Found: C, 63.27; H, 6.81; N, 11.7; S, 9.24. MS (EI, 30 eV; *m/e*) 341 (M^+), 296 (M^+-CHS), 205 (M^+-CHSNPh) 137 (PhNCSH).

4.3.2. With CO_2 or HCOOH

A 290 mg (1.41 mmol) of **33** in 2.5 ml of $CDCl_3$ are treated with an excess of CO_2, under argon. CO_2 is dissolved immediately and the solution is stirred for additional 1 h. The crude mixture is concentrated to half-volume for spectroscopic measurements. ^{29}Si-NMR shows that only one product is formed, identified as 2-(1,3-dimethylimidazolide-2-yl) phenyl formyloxysilane, **35**. The same compound **35** is obtained quantitatively in the coupling reaction of 290 mg (1.4 mmol) of **33** with 64 mg (1.4 mmol) of formic acid in 2.5 ml of $CDCl_3$ at r.t. Characteristics of **35**, Anal. for $C_{12}H_{18}N_2SiO_2$ C, 57.59; H, 7.25; N, 11.19. Found C, 56.95; H, 7.29; N, 11.13.

4.3.3. With CH_3COOH

A total of 41.0 mg (0.68 mmol) of acetic acid are added to a solution of 140 mg (0.68 mmol) of 2-(1,3-dimethyl imidazolidine-2-yl) phenylsilane **33** in 2.5 ml of $CDCl_3$ at r.t. After 12 h, spectroscopic investigations show that only one product is obtained, identified as 2-(1,3-dimethylimidazolidine-2-yl) phenyl acetoxysilane, **36**.

Removal of the solvent left 179 mg of **36**. Characteristics of **36** Anal. Calc. for $C_{13}H_{20}N_2SiO_2$: C, 59.08; H, 7.63; N, 10.59. Found: C, 59.37; H, 7.49; N, 10.64. MS (EI, 30 eV; *m/e*, relative intensity%): 264 (M^+, 7), 263 (M^+-1, 28), 262 (M+ -2, 10), 221 (M^+-CH_3CO, 15), 205 (M^+-CH_3 COO, 42), 175 (M+-SiH_2OAc, 93), 99 (Imid.$^+$, 100). The same reaction was repeated with an excess of acetic acid. After work up, the only product was **36**, identified by ^{1}H-, ^{13}C- and ^{29}Si-NMR spectra.

4.3.4. With PCl_5

A total of 841 mg (4.08 mmol) of 2-(1,3-dimethylimidazolidine-2-yl) phenylsilane **33** are added to a suspension of 170 mg (0.82 mmol) of PCl_5 at −50°C, in 15 ml of dichloromethane (yellow solution). After the solution was warmed up to r.t., the solvent is removed in vacuo. The residue is washed with pentane: a yellow resinous solid is obtained which decomposes by heating. The characteristics correspond to 2-(1,3-dimethylimidazolidine-2-yl) phenylchlorosilane, **37**. Anal. Calc. for $C_{11}H_{17}N_2SiCl$: C, 54.87; H, 7.12; N, 11,63; Cl, 14.74. Found: C, 53.27; H, 7.01; N, 10.99; Cl, 13.86. MS (EI, 30 eV; *m/e*, relative intensity%) 240 (M+, 16), 239 (M+-1, 65), 205 (M+-Cl, 18), 182 (M+-$CH_3NCH_2CH_3$, 37), 99 (Imid+, 100).

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