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Modelling nucleophilic substitution at silicon using hypervalent silicon compounds based on di and tri halosilanes

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Abstract

The ^{29}Si- and ^{13}C-NMR spectral parameters of a range of *N*-(amidomethyl)-polyhalosilanes have been measured in solution and the extent of Si–O bond formation and pentacoordination determined. The larger the number of electronegative groups attached to the silicon the greater the extent of pentacoordination achievable by the silicon. Thus with trichlorosilanes a ‘tight’ pentacoordinate silicon is observed where the Si–O bond is almost fully formed. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Silicon; Pentacoordinate; NMR; Dichloro; Difluoro

1. Introduction

For a number of years we have been interested in the use of NMR spectroscopy to probe the structure of pentavalent silicon species and to map the reaction coordinate for substitution at silicon in solution [1–4]. We have prepared a number of series of structurally similar pentavalent silicon compounds and used them to demonstrate how the geometry around silicon changes as one bond to silicon is formed at the expense of another. By monitoring how the chemical shift of atoms attached to the nucleophilic atom changes, the extent of nucleophile–silicon bond formation can be determined, which reflects the Nu–Si bond length. Our previous studies have used *N*-(halodimethylsilylmethyl) pyridones and thiopyridones where the ^{13}C chemical shifts of the aromatic carbons change in a concerted fashion as the carbonyl oxygen becomes progressively coordinated to the silicon. The extent of pentacoordination at silicon reflects the location of the structure under study on the continuum between a tetracoordinated silicon and a fully pentacoordinate species and has been calculated from the ^{29}Si chemical shift. The NMR characteristics of the limiting tetracoordinate and pentacoordinate cases have been determined from model compounds. This anchors the scale to 0 and 100% and thus allows the extent of pentacoordination and nucleophile–silicon bond formation to be expressed as a percentage.

Our results suggest that for monohalodimethylsilanes, the extent of pentacoordination changes in a consistent fashion with the degree of nucleophile–silicon bond fomation irrespective of the nature of the nucleophile or leaving group. Pentacoordination increases with Si–O bond formation until it reaches a maximum at 50% Si–O bond formation after which the pentacoordination decreases. If these stable molecules can be used as models for transient species, this suggests that the pathway for substitution at silicon involves formation of the nucleophile–silicon bond at the expense of the leaving group via a genuine pentacoordinate species. A similar conclusion has been reached using X-ray crystallography [5–8].

We were interested in using our solution mapping technique to examine di and trihalosilanes. Previous X-ray crystallographic studies have shown that the presence of equatorial electronegative groups lead to more extensive axial coordination without subsequent cleavage of the other axial bond. For example, Table 1 gives key bond distances and angles for the *N*-(amidomethyl)-halosilanes **1**–**5** [9–11].

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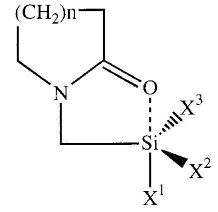


1, n = 2 , X^1 = Cl , X^2= Me , X^3 = Me
2, n = 2 , X^1 = Cl , X^2= Cl , X^3 =Me
3, n = 3 , X^1 = Cl , X^2= Me , X^3 = Me
4, n = 3 , X^1 = Cl , X^2= Cl , X^3 = Me
5, n = 3 , X^1 = Cl , X^2= Cl , X^3 = Cl

The data in Table 1 demonstrates that the presence of electron withdrawing groups in equatorial positions leads to shorter axial bonds. In terms of the % Si–O bond formation and extent of pentacoordination, this suggests that maximum pentacoordination does not have to occur at 50% Si–O bond formation and that the presence of more electronegative groups may shift the maximum pentacoordination to greater Si–O bond formation.

In this paper we use our mapping technique to examine how the relationship between the position of maximum pentacoordination and % Si–O bond formation in solution depends upon the number of equatorial electronegative groups.

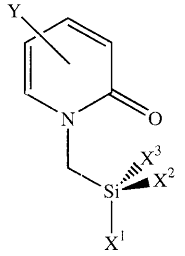
2. Results and discussion

We have synthesised a number of mono, di and trihalo pentacoordinated silicon compounds, **6**–**16**. The preparation of the monochloro derivatives have already been reported [3] and the di and trichloroderivatives were prepared using standard procedures from the chloromethyldichloromethylsilane or chloromethyltrichlorosilane. The difluoro derivatives were prepared from the corresponding dichloro compounds using antimony trifluoride [3–5].

The extent of Si–O bond formation was calculated as described for the corresponding monohalosilanes based on the ^{13}C chemical shifts of aromatic ring carbons where the nucleophile is either part of the aromatic system or adjacent to it. Since the chemical shifts of the model compounds representing 0 and 100% Si–O bond formation do not depend upon the nature of the silicon centre, the same model compounds were used for the di and trihalosilanes as for the monohalosilanes. The percentage Si–O bond formation of compounds **6**–**16** were calculated using the equation:

Percentage Si–O bond formation

$$= \frac{(\delta\,^{13}\mathrm{C})_{\mathrm{Cmpd}} - (\delta\,^{13}\mathrm{C})_{0\%}}{(\delta\,^{13}\mathrm{C})_{100\%} - (\delta\,^{13}\mathrm{C})_{0\%}} \times 100$$



6a Y = H, X^1 = F, X^2 = X^3 = Me
6b Y = H, X^1 = X^2 = F, X^3 = Me

7a Y = H, X^1 = Cl, X^2 = X^3 = Me
7b Y = H, X^1 = X^2 = Cl, X^3 = Me
7c Y = H, X^1 = X^2 = X^3 = Cl

8a Y = 3-MeO, X^1 = F, X^2 = X^3 = Me
8b Y = 3-MeO, X^1= X^2 = F, X^3 = Me

9a Y = 3-MeO, X^1 = Cl, X^2 = X^3 = Me
9b Y = 3-MeO, X^1= X^2 =Cl, X^3 = Me

10a Y = 5-Cl, X^1 = F, X^2 = X^3 = Me
10b Y = 5-Cl, X^1= X^2 = F, X^3 = Me

11a Y = 5-Cl, X^1 = Cl, X^2 = X^3 = Me
11b Y = 5-Cl, X^1= X^2 =Cl, X^3 = Me

12a Y = 6-Cl, X^1 = F, X^2 = X^3 = Me
12b Y = 6-Cl, X^1= X^2 = F, X^3 = Me

13a Y = 6-Cl, X^1 = Cl, X^2 = X^3 = Me
13b Y = 6-Cl, X^1= X^2 =Cl, X^3 = Me
13c Y = 6-Cl, X^1= X^2 = X^3 = Cl

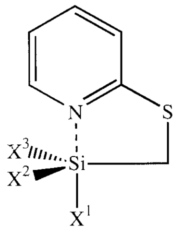
14a Y = Me, X^1 = Cl, X^2 = X^3 = Me
14b Y = Me, X^1= X^2 = X^3 = Cl

Where $(\delta\,^{13}\mathrm{C})_{\mathrm{Cmpd}}$ is the chemical shift of the particular ring carbon in the compound under study, $(\delta\,^{13}\mathrm{C})_{100\%}$ is the chemical shift of the particular ring carbon in the model compound for 100% Si–O bond formation and $(\delta\,^{13}\mathrm{C})_{0\%}$ is the chemical shift of the particular ring carbon in the model compound for 0% Si–O bond formation. These values are averaged over all the ring carbons and the results are shown in Table 2. The results confirm that the greater the number of electronegative groups, the larger the oxygen silicon interaction. For example, for the unsubstituted pyridone, on going from the mono (**7a**) to the di (**7b**) to the

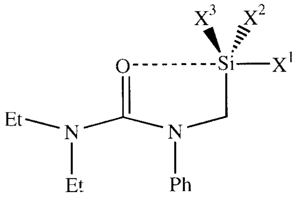
Table 1
Key bond distances and angles for the *N*-(amidomethyl)-halosilanes **1**–**5**

Compound	Si–O bond distanceo (Å)	Axial Si–X bond distance (Å)	Equatorial Si–X bond distance (Å)	Σ equatorial bond angles (°)	Ref.
1	1.954	2.307		359.7	[9]
2	1.852	2.207	2.047	359.7	[10]
3	1.958	2.294		359.8	[11]
4	1.907	2.256	2.051	358.8	[10]
5	1.865	2.213	2.058	359.5	[10]

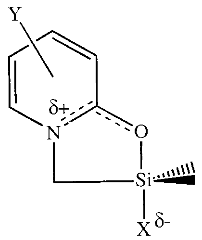
trichlorosilane (**7c**), the % Si–O bond formation increases from 50 to 65 to 70%. This trend is repeated in all the series including the thiopyridones (36% (**15a**), 51% (**15b**), 53% (**15c**)) and ureas (55% (**16a**), 68% (**16b**), 77% (**16c**)). Since fluorine is a poorer leaving group than chlorine the difluoro compounds exhibit a lower % Si–O bond formation than the dichloro compounds as observed with the monohalides. Within the pyridone series the extent of Si–O bond formation for the di and tri halosilanes depends upon the substituent on the pyridone ring with the order 3MeO < 5Cl < H < 6Cl < Me. This order is similar to that observed with the monohalides and reflects the ability of substituents to stabilise the build up of positive charge at the nitrogen on Si–O bond formation as shown in **17**.



15a $X^1 = Cl, X^2 = X^3 = Me$
15b $X^1 = X^2 = Cl, X^3 = Me$
15c $X^1 = X^2 = X^3 = Cl$



16a $X^1 = Cl, X^2 = X^3 = Me$
16b $X^1 = X^2 = Cl, X^3 = Me$
16c $X^1 = X^2 = X^3 = Cl$



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The extent of pentacoordination can be determined from the ^{29}Si chemical shift. For the monohalodimethylsilanes the inherent ^{29}Si chemical shift does not depend greatly on the halide. For example, the chloromethylchlorodimethylsilane has a ^{29}Si chemical shift of 23.0 ppm, whereas the chloromethylfluorodimethylsilane has a value of 24.7 and the chloromethylbromodimethylsilane a value of 27.0 ppm. Thus, a common value was used to anchor the scale to 0% Si–O bond formation. However, the presence of extra electronegative groups on the silicon can lead to a large change in the inherent chemical shift. The chloromethyldichloromethylsilane has a ^{29}Si chemical shift of 21.5 ppm, but the chloromethyltrichlorosilane has a ^{29}Si chemical shift of 1.0 ppm and the chloromethyldifluoromethylsilane and chloromethyltrifluoromethylsilane values of −9.0 and −71.5 ppm, respectively. Thus, to determine the extent of pentacoordination from the ^{29}Si chemical shift, the data for each type of pentacoordinate polyhalosilane needs to be anchored to its intrinsic chemical shift for 0% Si–O bond formation. This is achieved by subtracting the value for the corresponding chloromethylpolyhalosilane from the value for the pentacoordinate compound to give $\Delta^{29}Si$, as discussed by Kost and Kalikhman [12]. These values are shown in Table 2. For the monohalodimethylsilanes the % pentacoordination was determined from the ratio of $\Delta^{29}Si$ to the chemical shift change for 100% pentacoordination. However, Table 2 suggests there is no simple maximum that we can use for this value. This is demonstrated by the plot of % Si–O bond formation versus $\Delta^{29}Si$ given in Fig. 1, which also includes the data for the corresponding monobromo and monotriflato compounds [4]. The data suggests that whilst there is a clear maximum at about 50% Si–O bond formation and at about $\Delta^{29}Si = 68$ ppm for the monohalosilanes, the dihalosilanes have a higher maximum $\Delta^{29}Si$ value at a larger % Si–O bond formation. The lack of data for dihalo compounds at greater % Si–O bond formation means that the maximum is not distinct, although the values for the dichloro compounds seem to level off at about $\Delta^{29}Si = 74$ ppm. The trichlorocompounds have even higher $\Delta^{29}Si$ values without any sign of levelling off, even after 80% Si–O

Table 2
% Si–O bond formation together with selected chemical shift data for compounds **6**–**16**

Compound	X^1	X^2	X^3	% Si–O	^{29}Si	$\Delta^{29}Si$
6a	F	Me	Me	30	−22.3	47.0
6b	F	F	Me	45	−59.9	50.9
7a	Cl	Me	Me	50	−41.1	64.1
7b	Cl	Cl	Me	65	−52.5	74.0
7c	Cl	Cl	Cl	70	−77.7	78.7
8a	F	Me	Me	20	−13.5	38.2
8b	F	F	Me	40	−57.1	48.1
9a	Cl	Me	Me	45	−32.0	55.0
9b	Cl	Cl	Me	60	−50.0	71.5
10a	F	Me	Me	30	−14.6	39.3
10b	F	F	Me	45	−57.2	48.2
11a	Cl	Me	Me	65	−17.1	40.1
11b	Cl	Cl	Me	60	−50.2	71.7
12a	F	Me	Me	40	−26.0	50.7
12b	F	F	Me	50	−60.4	51.4
13a	Cl	Me	Me	50	−40.9	63.9
13b	Cl	Cl	Me	60	−52.3	73.8
13c	Cl	Cl	Cl	75	−85.6	86.6
14a	Cl	Me	Me	70	−24.7	47.7
14b	Cl	Cl	Cl	80	−89.7	90.7
15a	Cl	Me	Me	36	−19.4	42.4
15b	Cl	Cl	Me	51	−45.8	67.3
15c	Cl	Cl	Cl	53	−59.1	60.1
16a	Cl	Me	Me	55	−42.1	65.1
16b	Cl	Cl	Me	68	−52.3	73.8
16c	Cl	Cl	Cl	77	−87.9	88.9

bond formation. Since Δ^{29}Si is a measure of the extent of pentacoordination this again confirms that the presence of electronegative groups in the equatorial positions lead to a more pentacoordinate species with larger values of Δ^{29}Si. This is achieved by increasing the bond orders of both axial bonds, hence these high Δ^{29}Si values are associated with high values of the % Si–O bond formation. It also suggests that whilst we can define 100% pentacoordination for monohalosilanes that have similar equatorial groups this is not so straightforward with di and trihalosilanes.

In terms of the pathway for nucleophilic substitution at silicon in solution these results suggest that the intermediate/transition state becomes more pentacoordinate the greater the number of electronegative groups attached to the silicon. Such a passage via a tighter pentacoordinate species will have important consequences on the steric requirements of such reactions.

There is little ^{29}Si-NMR data for *N*-(amidomethyl)-polyhalosilanes in the literature. 1-(methyldifluorosilylmethyl)hexahydro-2-azepinone has a ^{29}Si chemical shift of -55.5 ppm and *N*-(methyldifluorosilylmethyl)-*N*-(1-phenylethyl)acetamide has a ^{29}Si chemical shift of -55.4 ppm [13]. These values are similar to those of **6b**, **8b**, **10b** and **12b**, suggesting that the extent of pentacoordination of difluorosilanes is not very susceptible to changes in the structure of the amide ligand. 1-(methyldichlorosilylmethyl)hexahydro-2-azepinone (**4**), has a ^{29}Si chemical shift of -46.8 ppm, again very similar to that of **7b**, **9b**, **11b** **13b** **15b** and **16b**, if anything towards the lower end of this range. The X-ray crystal structure of **4** gives a Si–O bond length of 1.907 Å which correlates with a % Si–O bond formation of about 68%. Plotting this on Fig. 1 with the value of Δ^{29}Si of 68.3 ppm, shows excellent correlation.

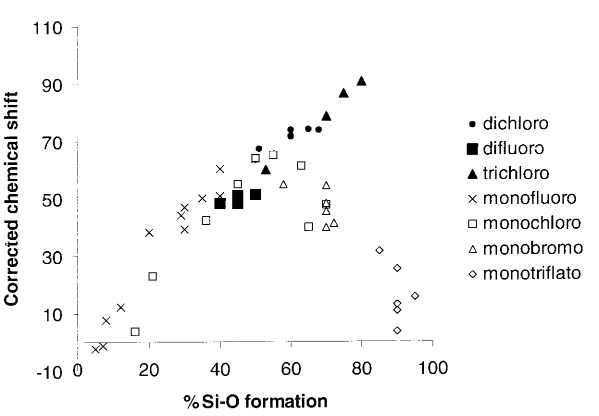

Fig. 1. Plot of Δ^{29}Si against Si–O bond formation for mono, di, and trihalosilanes.

3. Conclusions

NMR spectral parameters in solution can be used to determine the extent of Si–O bond formation for a range of pentacoordinate *N*-(amidomethyl)-polyhalosilanes. Whilst the percentage pentacoordination could not be determined, Δ^{29}Si values indicate that the larger the number of electronegative groups attached to the silicon the greater the extent of pentacordination achievable by the silicon. Thus with hypercoordinate polyhalosilanes a 'tight' pentacoordinate silicon is observed with a large Si–O coordination.

4. Experimental

Melting points were determined on a Buchi 510 melting point apparatus and are uncorrected. Infrared spectra were obtained as Nujol mulls or thin films using sodium chloride plates or as KBr discs on a Pye Unicam SP1050 or a Nicolet 205 FTIR spectrometer. NMR spectra were recorded as solutions in deuteriochloroform with tetramethylsilane as internal standard on a Jeol FX 90Q or a JEOL EX 400 NMR spectrometer (*J* values are given in Hz). Mass spectra were obtained using a Cresta MS 30 instrument or a VG20-250 quadrupole instrument.

4.1. General procedure for the synthesis of dichloromethylsilylmethylpyrid-2-ones

Chloromethyldichloromethylsilane (0.5 g, 3.1 mmol) in dry hexane was added slowly to a stirred solution of the 2-trimethylsiloxypyridine (3.1 mmol) in dry hexane under nitrogen. The reaction mixture was stirred for 7 h and the solid obtained was filtered under nitrogen and dried under vacuum.

The following dichloromethylsilylmethylpyrid-2-ones were obtained:

4.1.1. Dichloromethylsilylmethylpyrid-2-one (**7b**)

Complex **7b** (0.62 g, 88%), m.p. 107–111°C, δ_H (90 MHz, $CDCl_3 + CD_3CN$ (1:1), Me_4Si) 0.95 (3H, s, SiMe), 3.9 (2H, s, NCH_2) and 6.9–8.0 (4H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 11.9 (SiMe), 44.0 ($SiCH_2$), 113.9 (C5), 114.5 (C3), 139.0 (C4), 144.8 (C6) and 162.2 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) -52.5; *m*/*z* (EI). 221/223/225 (10:6:1, M^+), 220/222/224 (10:6:1, $M^+ - H$), 206/208/210 (10:6:1, $M^+ - Me$), 186/188 (3:1, $M^+ - Cl$) and 151 ($M^+ - 2Cl$) (Found: C, 37.95; H, 4.36; N, 6.31. $C_7H_9NOCl_2Si$ requires C, 37.85; H, 4.08; N, 6.31%).

4.1.2. Dichloromethylsilylmethyl-3-methoxypyrid-2-one (***9b***)

Complex **9b** (0.85 g, 90%), m.p. 108–111°C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.92 (3H, s, SiMe), 3.2 (2H, s, NCH_2), 3.9 (3H, s, OMe) and 6.9–7.6 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 12.2 (SiMe), 44.4 ($SiCH_2$), 56.8 (OMe), 112.8 (C5), 119.7 (C3), 128.7 (C6), 146.3 (C4) and 156.4 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) −50.0; *m*/*z* (EI) 251/253/255 (10:6:1, M^+), 236/238/240 (10:6:1, $M^+ - Cl$), 216/218 (3:1), 181 ($M^+ - 2Cl$). (Found: C, 37.57; H, 4.60; N, 5.40. $C_8H_{11}NO_2Cl_2Si$ requires C, 38.10; H, 4.40; N, 5.55%).

4.1.3. Dichloromethylsilylmethyl-5-chloropyrid-2-one (***11b***)

Complex **11b** (0.76g, 91%), m.p. 114–119°C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.97 (3H, s, SiMe), 3.8 (2H, s, NCH_2) and 6.9–7.9 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 10.0 (SiMe), 44.3 ($SiCH_2$), 115.6 (C5), 119.8 (C3), 136 (C6), 144.8 (C4) and 161.1 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) −50.2; *m*/*z* (EI) 255/257/259/261 (10:9.6:3:1, M^+), 240/242/244/246 (10:9.6:3:1, $M^+ - Me$), 220/222/224 (10:6:1, $M^+ - Cl$), 185/187 (3:1, $M^+ - 2Cl$). (C, 32.59; H, 3.40; N, 5.30. $C_7H_8NOCl_3Si$ requires C, 32.77; H, 3.14; N, 5.46%).

4.1.4. Dichloromethylsilylmethyl-6-chloropyrid-2-one (***13b***)

Complex **13b** (0.66 g, 90%), m.p. 115–117°C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.98 (3H, s, SiMe), 3.8 (2H, s, NCH_2) and 6.9–7.9 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 12.0 (SiMe), 43.1 ($SiCH_2$), 112.5(C5), 113.9 (C3), 140.3 (C4), 144.2 (C6) and 163.3 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) −52.3; (Found: C, 33.18; H, 3.39; N, 5.45. $C_7H_8NOC1_3Si$ requires C, 32.77; H, 3.14; N, 5.46%).

4.1.5. 2-(Dichloromethylsilylmethylmercapto)pyridine (***15b***)

To a solution of 2-(trimethylsilylmercapto)pyridine (0.50 g, 2.73 mmol) in benzene (4 cm^3) under a nitrogen atmosphere was added (chloromethyl)dichloromethylsilane (0.45 g, 2.75 mmol) and the solution stirred briefly. The title compound precipitated from the solution as a yellow crystalline material within 30 min. The compound was isolated by decanting off the solvent, washing the residue with benzene (2 × 5 cm^3) and drying it under high vacuum for 90 min (0.52 g, 80%). δ_H (90 MHz, $CDCl_3$, Me_4Si) 1.02 (3H, s, $SiCH_3$), 2.91 (2H, s, SCH_2), 7.29 (1H, m, H5), 7.39 (1H, d, $^3J_{H3–H4}$ 7.6, H3), 7.80 (1H, m, H4) and 8.67 (1H, d, $^3J_{H6–H5}$ 5.6, H6); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 12.0 ($SiCH_3$), 18.5 (SCH2), 120.5 (C5), 122.8 (C3), 139.9 (C4), 144.3 (C6) and 157.5 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) −45.8; *m*/*z* (EI) 237/239/241(9:6:1, M^+), 222/224/226 (9:6:1, $M^+ - Me$), 202/204 (3:1, $M^+ - Cl$), 124, 78. (Found: C, 34.98; H, 3.74; N, 5.64. $C_7H_9Cl_2NSSi$ requires C, 35.30; H, 3.81; N, 5.88%).

4.1.6. *N*,*N*-Diethyl-*N*′-(methyldichlorosilylmethyl)-*N*′-phenyl urea (***16b***)

N,*N*-Diethyl-*N*′-phenyl urea (1.1 g, 4.2 mmol) was dissolved in dry ether (5 ml) and (chloromethyl)-methyldichlorosilane (0.67 g, 4.2 mmol) was added. The flask was agitated briefly and the mixture left for 3 h, after which the solvent was removed to give *N*,*N*-diethyl-*N*′-(methyldichlorosilylmethyl)-*N*′-phenyl urea as a colourless liquid. ν_{max} 2974, 1600, 1510, 1446, 1256 and 850 cm^{-1}; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.98 (6H, t, ^3J 7.0, CH_3), 0.98 (3H, s, $SiCH_3$), 3.11 (4H, q, ^3J 7.0, NCH_2), 3.37 (2H, sbr, NCH_2Si) and 7.0–7.6 (5H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 12.0 (SiMe), 13.0 ($\mathit{C}H_3CH_2$), 44.2 ($SiCH_2$), 51.7 ($CH_3\mathit{C}H_2$), 125.5 (Ph), 128.1 (Ph), 130.4 (Ph), 142.7 (Ph) and 160.8 (C=O); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) −52.3; *m*/*z* (EI) 318 (M^+), 283 ($M^+ - Cl$). (Found, C, 49.44; H, 6.52; N, 8.70. $C_{13}H_{20}Cl_2N_2OSi$ requires C, 48.90; H, 6.31; N, 8.77%).

4.2. General procedure for the synthesis of difluoromethylsilylmethylpyrid-2-ones

The corresponding dichloromethylsilylmethylpyrid-2-one (3 mmol) was dissolved (or suspended) in 5 ml dry benzene under nitrogen. Antimony trifluoride (2 mmol) was added and the reaction mixture was stirred for 0.5 h. It was then diluted with water and extracted with chloroform (3 × 75 ml). The extract was dried over anhydrous magnesium sulphate and distilled and dried under vacuum to yield a colourless crystalline solid.

The following difluoromethylsilylmethylpyrid-2-ones were obtained:

4.2.1. Difluoromethylsilylmethylpyrid-2-one (***6b***)

Complex **6b** (0.43 g, 91%); m.p. 95–102°C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.39 (3H, t, $^3J_{HSiF}$ 5.1, SiMe), 3.3 (2H, s, NCH_2) and 6.7–7.8 (m, 4H, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 1.0 (t, $^2J_{CSiF}$ 20.7, SiMe), 37.3 (t, $^2J_{CSiF}$ 32.4, $SiCH_2$), 111.9 (C3), 115.6(C5), 138.9 (C4), 143.3 (C6) and 163.2 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) −59.9 (t, $^1J_{SiF}$ 253, SiF); *m*/*z* (EI) 189 (M^+), 188 ($M^+ - H$), 174 ($M^+ - Me$), 170 ($M^+ - F$) (Found: C, 44.22; H, 5.03. $C_7H_9NOF_2Si$ requires C, 44.43; H, 4.79%).

4.2.2. Difluoromethylsilylmethyl-3-methoxypyrid-2-one (***8b***)

Complex **8b** (0.51 g, 93%); m.p. 99–106°C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.47 (3H, t, $^3J_{HSiF}$ 5.3, SiMe), 3.3 (2H, s, NCH2), 3.9 (3H, s, OMe) and 6.5–7.4 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 0.86 (t, $^2J_{CF}$ 23.3, SiMe), 37.5 (t, $^2J_{CF}$ 33.7, $SiCH_2$), 56.4 (OMe), 110.4 (C3), 117.2 (C5), 128.3 (C4), 147.0 (C6) and 157.8 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) -57.1 (t, $^1J_{SiF}$ 256.8, SiF); m/z (EI) 219 (M^+), 218 ($M^+ - H$), 204 ($M^+ - Me$), 200 ($M^+ - F$), 188 ($M^+ - OMe$). (Found: C, 43.99; H, 5.20; N, 5.90. $C_8H_{11}NO_2F_2Si$ requires C, 43.82; H, 5.06; N, 6.39%).

4.2.3. *Difluoromethylsilylmethyl-5-chloropyrid-2-one* ***(11b)***

Complex **11b** (0.50 g, 89%); m.p. 102–105°C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.40 (3H, t, $^3J_{HSiF}$ 5.4, SiMe), 3.3 (2H, s, NCH2) and 6.7–7.8 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 0.63 (t, $^2J_{CSiF}$ 22.0, SiMe), 37.7 (t, $^2J_{CSiF}$ 32.4, $SiCH_2$), 116.5 (C3), 117.9 (C5), 136.3 (C4), 143.6 (C6) and 161.8 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) -57.2 (t, $^1J_{SiF}$ 255.9, SiF); m/z (EI) 223/225 (3:1, M^+), 222/224 (3:1, $M^+ - H$), 208/210 (3:1, $M^+ - Me$), 204/206 (3:1, $M^+ - F$), 188 ($M^+ - Cl$). (Found: C, 37.88; H, 3.86; N, 6.12. $C_7H_8NOClF_2Si$ requires C, 37.59; H, 3.60; N, 6.26%).

4.2.4. *Difluoromethyylsilylmethyl-6-chloropyrid-2-one* ***(12b)***

Complex **12b** (0.51 g, 91%); m.p. 102–104°C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.41 (3H, t, $^3J_{HSiF}$ 5.5, SiMe), 3.3 (2H, s, NCH2) and 6.8–7.7 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 0.75 (t, $^2J_{CSiF}$ 23.3, SiMe), 36.4 (t, $^2J_{CSiF}$ 35.0, $SiCH_2$), 111.9 (C5), 113.1 (C3), 140.6 (C4), 142.7 (C6) and 164.1 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) -60.4 (t, $^1J_{SiF}$ 253.9, SiF); m/z (EI) 223/225 (3:1, M^+), 222/224 (3:1, $M^+ - H$), 208/210 (3:1, $M^+ - Me$)), 188 ($M^+ - Cl$). (Found: C, 37.29; H, 3.87. $C_7H_8NOClF_2Si$ requires C, 37.59; H, 3.60%).

4.3. *General procedure for the synthesis of trichlorosilylmethylpyrid-2-ones*

Chloromethyltrichlorosilane (395 μl, 3.17 mmol) in dry hexane was added slowly into a stirred solution of 2-trimethylsiloxypyridine (0.53 g, 3.17 mmol) in dry hexane under nitrogen. The reaction mixture was stirred for overnight and the solid obtained was filtered under nitrogen and dried under vacuum.

The following trichlorosilylmethylpyrid-2-ones were obtained (the trichlorosilanes were very prone to hydrolysis thus it was not possible to obtain accurate elemental analyses):

4.3.1. *Trichlorosilylmethylpyrid-2-one* ***(7c)***

Complex **7c** (0.71 g, 92%); m.p. 125–130°C; δ_H (90 MHz, $CDCl_3 + CD_3CN$ (1:1), Me_4Si) 4.1 (2H, s, NCH2) and 7.0–8.1 (4H, m, arom); δ_C (22.5 MHz, $CDCl_3 + CD_3CN$ (1:1), Me_4Si) 44.2 ($SiCH_2$), 114.0 (C5), 115.4 C3), 140.0 (C4), 146.1 (C6) and 160.8 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) -77.7; m/z (EI) 241/243/245/247 (30:29:9:1, M^+), 206/208/210 (10:6:1, $M^+ - Cl$), 171/173 (3:1, $M^+ - 2Cl$), 136 ($M^+ - 3Cl$).

4.3.2. *Trichlorosilylmethyl-6-chloropyrid-2-one* ***(13c)***

Complex **13c** (0.62 g, 90%); m.p. 131–134°C; δ_H (90 MHz, $CDCl_3$, Me_4Si) 4.0 (2H, s, NCH_2) and 6.9–7.9 (3H, m, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 43.8 ($SiCH_2$), 111.9 (C5), 115.1 (C3), 140.6 (C4), 145.0 (C6) and 162.5 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) -85.6; m/z (EI) 275/277/279/281/283 (95:122:59:12:1, M^+), 240/242/244/246 (30:29:9:1, $M^+ - Cl$), 205/207/209 (10:6:1, $M^+ - 2Cl$)), 170/172 (3:1, $M^+ - 3Cl$)), 158/160 (3:1), 135 ($M^+ - 4Cl$).

4.3.3. *Trichlorosilylmethyl-6-methylpyrid-2-one* ***(14b)***

Complex **14b** (0.54g, 91%); m.p. 129–136°C; δ_H (90 MHz, CD_3CN, Me_4Si) 2.7 (3H, s, Me), 4.0 (2H, s, NCH2) and 6.9–8.2 (3H, m, arom); δ_C (22.5 MHz, CD_3CN, Me_4Si) 21.1 (Me), 39.0 ($SiCH_2$), 111.6 (C5), 117.4 (C3), 146.0 (C4), 152.0 (C6) and 162.1 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) -89.7; m/z (EI) 255/257/259/261 (30:29:9:1, M^+), 240/242/244/ 246 (30:29:9:1, $M^+ - Me$), 220/224/226 (10:6:1, $M^+ - Cl$), 185/187 (3:1, $M^+ - 2Cl$), 150 ($M^+ - 3Cl$).

4.4. *(Trichlorosilylmethylmercapto)pyridine* ***(15c)***

To a solution of 2-(trimethylsilylmercapto)pyridine (0.50 g, 2.73 mmol) in benzene (2 cm^3) under a nitrogen atmosphere was added (chloromethyl)trichlorosilane (0.51 g, 2.77 mmol) and the solution stirred briefly. The title compound, precipitated from the solution as a bright yellow crystalline material within 20 min. The compound was isolated by decanting off the solvent, washing the residue with benzene (2 × 3 cm^3) and drying it under a high vacuum for 90 min (0.61 g, 86%); δ_H (90 MHz, $CDCl_3$, Me_4Si) 3.13 (2H, s, SCH_2), 7.30 (1H, m, H5), 7.38 (1H, d, $^3J_{H_3H_4}$ 8.4, H3), 7.81 (1H, m, H4), and 8.68 (1H, d, $^3J_{H_6H_5}$ 6.0, H6); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 19.1 (SCH2), 120.5 (C5), 122.8 (C3), 140.5 (C4), 144.8 (C6), and 155.8 (C2); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) -59.1; m/z (EI) 257/259/261/263 (27:27:9:1, M +) (measured 256.9056 ($M^+ - {}^{35}C1_3$), requires 256.9056 for $C_6H_6^{35}C1_3NSSi$), 222/224/226 (9:6:1) ($M^+ - Cl$), 124, 78.

4.5. *N,N-Diethyl-N′-phenyl-N′-trichlorosilylmethyl urea* ***(16c)***

N,*N*-Diethyl-*N*′-phenyl-*N*′-trimethylsilyl urea (1.0 g, 3.8 mmol) was dissolved in dry ether (3 ml). (Chloromethyl)trichlorosilane (0.70 g, 3.8 mmol) was then added and the flask agitated briefly. After 3 h, the solvent was removed under vacuum to give *N*,*N*-diethyl-*N*′-phenyl-*N*′-(trichlorosilylmethyl) urea as a light brown liquid. ν_{max} 2976, 1638, 1499, 1445, 1255, 1098, 850 cm^{-1}; δ_H (90 MHz, $CDCl_3$, Me_4Si) 1.02 (6H, t, ^3J 7.0, CH_3), 3.14 (4H, q, ^3J 7.0, NCH_2), 3.13 (2H, s, NCH_2Si) and 7.2–7.4 (m, 5H, arom); δ_C (22.5 MHz, $CDCl_3$, Me_4Si) 13.4 (CH_3CH_2), 37.1 (CH_3CH_2), 43.0 ($SiCH_2$), 128.5 (Ph), 129.2 (Ph), 129.4 (Ph), 137.2 (Ph) and 160.6 (C=O); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) −87.9.

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