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Modelling nucleophilic substitution at silicon using hypervalent silicon compounds based on urea ligands

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Abstract

The X-ray crystal structure of a pentacoordinate silicon compound, **3**, with a urea ligand shows partial Si–O bond formation and Si–Cl cleavage. The solution NMR parameters for the related series of compounds with different leaving groups provides structural information and this can be used to model substitution at silicon. The corresponding thioureas exhibit N–Si bond formation with the silicon remaining tetracoordinate. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Silicon; Pentacoordination; Urea; Crystal structure; Substitution

1. Introduction

We are 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]. This involves preparing a series of structurally similar pentavalent silicon compounds that provide snapshots of how the geometry around silicon changes as the extent of formation of one bond to silicon increases at the expense of another. The extent of nucleophile–silicon bond formation is calculated from the chemical shift of other atoms attached to the nucleophilic atom. Our previous studies have focused on substituted pyridones and thiopyridones and have shown that the ^{13}C chemical shifts of the aromatic carbons change in a concerted fashion as the pyridone oxygen, nitrogen or sulfur becomes progressively coordinated to the silicon [3,4]. The extent of pentacoordination at silicon can be calculated from the ^{29}Si chemical shift. We have employed model compounds to define the NMR characteristics of the limiting tetracoordinate and pentacoordinate cases, enabling us to express the extent of pentacoordination and nucleophile–silicon bond formation as a percentage.

Our results suggest that irrespective of the nature of the nucleophile, the position of the adduct on the structural continuum between tetracoordinate silicon and pentacoordinate silicon changes in a consistent fashion with the degree of nucleophile–silicon bond formation. In terms of the trajectory for substitution at silicon, the nucleophile–silicon bond is formed at the expense of the leaving group forming a genuine pentacoordinate species followed by loss of the leaving group. A similar conclusion has been reached using X-ray crystallography [5–8]. It has been shown that in the solid state the tetrahedral reactants are converted into a trigonal bipyramidal structure with the non-participating groups equatorial. This is followed by reversion to a tetrahedral structure.

We were interested in examining the generality of our solution technique by applying it to more simple amides and ureas. In particular we have examined a series of simple ureas where the % Si–O bond formation can be calculated from the chemical shift of *N*-phenyl ring carbons. In such compounds the ^{13}C chemical shifts of the ring carbons should depend upon the extent of O–Si bond formation and, because of aromaticity, this effect should be efficiently relayed to the more distant

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carbons, less prone to other specific interactions at the reaction centre. However, we would expect smaller changes in the chemical shifts than in the pyridone system since the functional group is not part of the aromatic system.

Voronkov and coworkers have prepared *N*-(chlorodimethylsilylmethyl) ureas by reaction of the *N*-trimethylsilylurea with chloro(chloromethyl)dimethylsilane [9]. They found that transilylation occurred readily to give the *N*-chloromethyldimethylsilyl urea. Unlike the corresponding amides they did not rapidly rearrange to give the *N*-alkyl isomer. This was attributed to intermolecular hydrogen bonding between the NH proton of one urea and the carbonyl oxygen of another. The *N*-silyl derivative did rearrange to the desired *N*-chloromethyldimethylsilyl urea upon refluxing for 6 h.

In view of the possible problems associated with hydrogen bonding we chose to prepare and study the chelates arising from *N*,*N*′,*N*′-trialkyl-*N*-trimethylsilyl ureas.

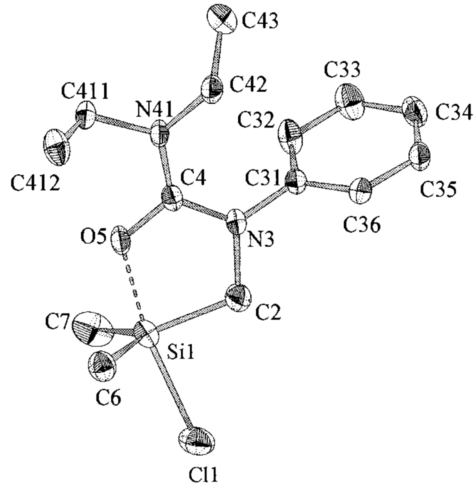


Fig. 1. Molecular structure of **3**. The thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) from the crystal structure of **3** [a]

Si1–Cl1	2.3163(11)	C6–Si1–C7	117.52(14)
Si11–Cl11	*2.3278(10)*	*C16–Si2–C17*	*120.24(13)*
Si1–O5	1.923(2)	C6–Si1–C2	123.16(12)
Si11–O3	*1.937(2)*	*C16–Si2–C12*	*120.10(12)*
O5–C4	1.282(3)	C7–Si1–C2	119.02(13)
O15–C14	*1.273(3)*	*C17–Si2–C12*	*119.38(12)*
C4–N3	1.338(3)	O5–Si1–Cl1	170.42(6)
C14–N13	*1.331(3)*	*O15–Si2–Cl11*	*171.12(6)*
N3–C2	1.346(3)	C2–Si1–O5	83.66(9)
N13–C12	*1.362(3)*	*C12–Si2–O15*	*83.31(9)*
C2–Si1	1.885(3)	C2–Si1–Cl1	86.96(8)
C12–Si2	*1.892(3)*	*C12–Si2–Cl11*	*87.80(8)*

[a] The data in italics belong to the second molecule in the lattice

2. Results and discussion

We have synthesised a number of pentacoordinated silicon compounds starting from *N*,*N*-diethyl-*N*′-phenyl-*N*′-trimethylsilyl urea (**1**). This was prepared by reaction of *N*,*N*-diethyltrimethylsilylamine with phenylisocyanate [10]. We found this to be a very convenient route to *N*,*N*′,*N*′-trialkyl-*N*-trimethylsilyl ureas with yields around 80%, and certainly more straightforward than trimethylsilylation of the corresponding *N*,*N*′,*N*′-trialkyl urea. Reaction of **1** with chloro(chloromethyl)dimethylsilane or (bromomethyl)-chlorodimethylsilane gave *N*-(chlorodimethylsilylmethyl)-*N*′,*N*′-diethyl-*N*-phenyl urea (**3**), and *N*-(bromodimethylsilylmethyl)-*N*′,*N*′-diethyl-*N*-phenyl urea (**4**), respectively. The fluoro derivative, **2**, and the triflato derivative, **5**, were prepared from **3** using antimony trifluoride and trimethylsilyltrifluoromethane sulfonate respectively.

Monitoring the reaction of **1** with chloro(chloromethyl)dimethylsilane or (bromomethyl)chlorodimethylsilane using NMR revealed that the reaction was complete in a matter of minutes with no sign of the corresponding transilylated or O–CH$_2$ intermediates. This suggests that *N*,*N*′,*N*′trialkyl-*N*-trimethylsilyl ureas are as reactive as amides and lactams, confirming Voronkov's conclusion that it is the presence of an N–H in the urea that leads to a reduced reactivity.

The structure of the *N*-(chlorodimethylsilylmethyl)-*N*′,*N*′-diethyl-*N*-phenyl urea was confirmed by X-ray crystallography. Fig. 1 shows an ORTEP image of one of the two crystallographically independant molecules **3** and Table 1 gives selected bond lengths and angles. In the subsequent discussion, values for the second molecule are in parentheses.

The geometry at the silicon is close to trigonal bipyramidal with the oxygen and the chlorine in the apical positions. The equatorial bond angles are between 117.52(14) and 123.16(12)° (119.38(12) and 120.24(13)°) and the sum of the equatorial angles is 359.70° (359.72°). The axial bond angles range between 83.31(9) and 83.66(9)°, the C2–Si1–O5 bond angle being limited by the five-membered ring. The Si–O bond lengths (1.923(2) and 1.937(2) Å) clearly show a high degree of bonding (standard Si–O covalent bond, 1.68 Å [6]). Similarly, the Si–Cl bond lengths (2.3163(11) and 2.3278(10) Å) show some bond breaking (standard Si–Cl covalent bond, 2.03 Å). The X-ray crystal structures of a variety of *N*-(halodimethylsilyl) ureas, amides and lactams have been published and Table 2 gives key bond length and bond angle data [6,11–17]. In this series of structurally similar pentacoordinate species, as the Si–O bond becomes stronger so the Si–Cl bond becomes weaker. Of the amides, the acyclic compound **6** has the smallest Si–O bond dis-

Table 2
Selected bond lengths (Å) and angles (°) from the crystal structure of **6–12**

Compound	Si–O bond length (Å)	Si–Cl bond length (Å)	O–Si–Cl bond angle (°)	Reference	^{29}Si chemical shift	Reference
6	1.918	2.348		[11]	−39.9	[3]
3	1.923	2.316	170.42		−42.5	
12	1.939	2.321	171.24	[12]	−38.4	[12]
11	1.950	2.315	171.70	[13]	−35	[20]
10	1.954	2.307	171.16	[14]	−38.5	[20]
8	1.975	2.306	170.8	[15]	−38.1	[15]
9	2.050	2.284		[16]	−5.7	[20]
8	2.077	2.229		[17]	−24.2	[21]

Table 3
% Pentacoordination and % Si–O bond formation together with selected chemical shift data for compounds **2**, **3**, **4** and **5**

Compound	^{29}Si	% Pent	^{13}C-*i*C	^{13}C-*o*C	^{13}C-*m*C	^{13}C-*p*C	% Si–O
13			148.6	124.5	129.2	124.3	0
2	−19.5	70	146.1	124.6	129.6	125.8	29
3	−42.5	103	143.7	125.0	130.0	127.2	55
4	−19.5	73	142.2	125.2	130.2	128.0	71
5	+16	26	141.7	125.5	130.5	128.9	87
14			141.4	125.9	130.7	129.4	100

tance. Inclusion of the amide in a lactam leads to slightly longer bond length depending upon the size of the ring [18,19]. Ureas and amides have similar basicity and, since chelate formation also involves coordination at the amide or urea oxygen, it is not surprising that the Si–O and Si–Cl bond lengths are very similar in the acyclic urea **3** and amide **6**. The O–Si–Cl bond angle has a value of around 171°, which varies little with the extent of bond formation/breaking. The ^{29}Si chemical shifts of the chelates are also given in Table 2. The pentacoordinate amides and ureas all have values around −40 ppm confirming that in this series of compounds amides and ureas have a similar nucleophilicity towards silicon.

Unfortunately we were unable to obtain crystal structures of the other urea derivatives **2**, **4** and **5**, and we thus used our solution mapping technique to examine the structures of these pentacoordinate species. Table 3 gives the relevant ^{29}Si and ^{13}C chemical shift data. As observed in other series the ^{29}Si chemical shift first becomes more negative on going from the fluoride to the chloride then more positive on going to the bromide and then the triflate. Our interpretation is that as the leaving group ability increases the silicon first becomes more pentacoordinate then reverts to a tetrahedral geometry. Very similar ^{29}Si chemical shifts are observed in the urea and amide series. For example, the corresponding piperidone compounds [20] have chemical shifts of −19.6 (F), −38.5 (Cl) and −22.6 (Br) and the pyridone series has chemical shifts of −22.3 (F), −41.1 (Cl), −18.4 (Br) and 32.3 (TfO). This again highlights the similarity between the amides and the ureas.

The % Si–O bond formation can be calculated by monitoring the chemical shift of atoms adjacent to the nucleophile and using model compounds to anchor the scale to 0 and 100% Si–O bond formation. The nuclei chosen need to have chemical shifts that are susceptible to the extent of coordination at oxygen, but not affected by other changes at the reaction centre. The ^{13}C chemical shifts of the aromatic ring carbons in **2**–**5** reveal a regular variation on going from fluoro to chloro to bromo to triflato and were thus used to determine the % Si–O bond formation. The model compound used to define 0% Si–O bond formation was the disiloxane, **13**, formed by hydrolysis of the chloro derivative. Titration of **13** with trimethylsilyl trifluoromethanesulfonate showed a regular variation of the ^{13}C chemical shift of the aromatic ring carbons, until 2 mol equivalent had been added. This led to the formation of the O-silylated adduct, **14**, which was used as the model for 100% Si–O formation. The ^{13}C chemical shift of the aromatic ring carbons of **13** and **14** are shown in Table 3. The % Si–O bond formation was calculated using the equation:

$$\text{Percentage Si–O bond formation} = \frac{(\delta\,^{13}\text{C})_{\text{cmpd}} - (\delta\,^{13}\text{C})_{0\%}}{(\delta\,^{13}\text{C})_{100\%} - (\delta\,^{13}\text{C})_{0\%}} \times 100$$

Where $(\delta\,^{13}\text{C})_{\text{cmpd}}$ is the chemical shift of the particular ring carbon in the compound under study, $(\delta\,^{13}\text{C})_{100\%}$ is the chemical shift of the particular ring carbon in the model compound for 100% Si–O bond formation, **14**, and $(\delta\,^{13}\text{C})_{0\%}$ is the chemical shift of the particular ring carbon in the model compound for 0% Si–O bond formation, **13**. For each compound this gave four values for the % Si–O bond formation (one for each carbon environment), thus, the values were averaged to give the values shown in Table 3. As expected the % Si–O bond formation increased with leaving group ability and had very similar values to the pentacoordinate silicon complexes formed with pyridone (30% (F), 50% (Cl), 70% (Br) and 90% (OTf)). This method gives an approximate bond order of 0.55 for the Si–O bond in **4**, which compares well with the Pauling Si–O bond order of 0.56 derived from the crystal structure [6,22].

A knowledge of the % Si–O bond formation enables the percentage pentacoordination to be determined, that is the relative position of the adduct on the structural continuum between a tetracoordinate tetrahedral silicon (0%) and a fully pentacoordinate trigonal bipyramidal silicon (100%). As with the pyridone series, if the compound exhibits a % Si–O bond formation between 0 and 50%, the extent of pentacoordination was calculated using ^{29}Si chemical shifts of $+28$ and -40 ppm for 0% and 100% pentacoordination respectively. The value of $+28$ ppm corresponds to that of a trimethylhalosilane (± 2 ppm) and the value of -40 ppm reflects that observed in many fully pentacoordinate silicon species [3]. For compounds that exhibited a % Si–O bond formation between 50 and 100%, the extent of pentacoordination was calculated using ^{29}Si chemical shifts of -40 and $+36$ ppm for 100% and 0% pentacoordination respectively. In this case, the value of $+36$ reflects that of a *O*-trimethylsilylated *N*-alkyl-2-hydroxypyridine [3]. The percentage pentacoordinations of compounds **2**–**5** are given in Table 3 and plotted against the % Si–O bond formation in Fig. 2. The data cover the full range of nucleophile–silicon bond formation and exhibit the same pattern as observed previously. As a model for the pathway for substitution at silicon it confirms that as the nucleophile approaches the silicon there is first formation of a pentavalent species followed by loss of the leaving group and reversion to the tetrahedral compound. Data for the pyridone series are also included in Fig. 1[3] and, within experimental error, the two sets of data overlap, suggesting that irrespective of the nature of the nucleophilic species, the extent of bond formation is the primary factor in determining the degree to which the adduct resembles a fully pentacoordinate silicon.

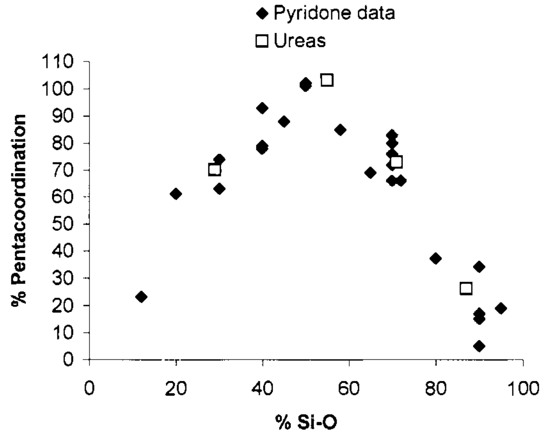


Fig. 2. Plot of % pentacoordination versus % Si–O bond formation.

We also prepared *N*-(chlorodimethylsilylmethyl)-*N*′,*N*′-dimethyl-*N*-phenylurea. This had a ^{29}Si chemical shift of -39.6 ppm corresponding to 99% pentacoordination. This suggests that changing the alkyl group on the nitrogen from ethyl to methyl has little effect on the extent of coordination. This is confirmed by the ^{13}C chemical shifts of the aromatic ring carbons (C1 143.7 ppm; C2 124.8 ppm; C3 130.2 ppm and C4 127.1 ppm) which correspond to 53% Si–O bond formation, extremely close to that of **3**.

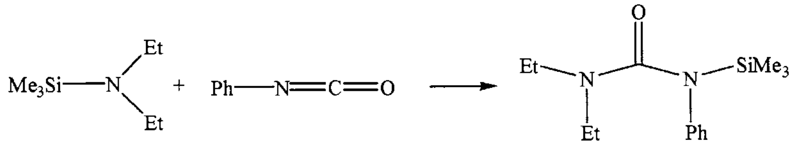
To extend the series of nucleophiles examined we tried to synthesise the corresponding thiourea derivatives. The parent *N*,*N*-diethyl-*N*′-methyl-*N*′-trimethylsilyl thiourea was prepared by the reaction of *N*,*N*-diethyltrimethylsilylamine with methyl isothiocyanate, however, in this case heating was required. NMR spectroscopy shows that the *N*-trimethylsilylated species predominates although a small amount of the *S*-trimethylsilylated species may be present. Unlike the corresponding urea derivative, the reaction of chloro(chloromethyl)dimethylsilane with *N*,*N*-diethyl-*N*′-methyl-*N*′-trimethylsilyl thiourea required heating at 50°C for 2 days. The spectra of the product revealed a S–CH$_2$ linkage, corresponding to structure **15**. The ^{29}Si chemical shift was at 41 ppm suggesting a completely tetrahedral silicon with little if any Si–Cl interaction. This was confirmed by reaction of the thiourea with bromo(bromomethyl)dimethylsilane which gave a product with almost identical spectra to that of **15**. An unusually high ^{29}Si chemical shift of 44 ppm was again obtained suggesting an essentially ionic structure.

The change in regiochemistry from O–Si to N–Si is not unexpected, the reaction of chloro(chloromethyl)-dimethylsilane with thiolactams leads to structures of the type **16** rather than the *N*-alkyl species [23,24]. Similarly, in the thiopyridone series we have observed that reaction of the thiopyridone with chloro(chloromethyl)dimethylsilane leads to compounds of the type **17** [4]. However, when a 6-methyl substituent is present in the thiopyridine, *N*-alkylation with S–Si coordination is observed as a result of steric factors. The ^{29}Si chemical shifts of **16** ($n = 1$) and **17** are -38.1 ppm and -19.4 ppm respectively, demonstrating substantial pentacoordination [23]. Extensive pentacoordination is also demonstrated in the X-ray crystal structure of **16** which shows it to be a distorted trigonal bipyramid where the Si–N and Si–Cl bond lengths are

1.95 and 2.42 Å respectively [24]. This suggests that the nitrogen in the thiourea is much more nucleophilic than that in the thiolactams and thiopyridones, since no Si–Cl coordination is observed in **15**. This is borne out by the extent of N–Si bond formation which appears to be 100% in **15** but only only 36% in **17**.

The crystal structures have been reported of a number of pentavalent alkylchlorosilicon compounds involving an sp^2 nitrogen as the donor atom in a five membered ring, **18** [25], **19** [26] and **20** [27]. Examination of the silicon–nitrogen bond lengths and the silicon–chlorine bond lengths suggests that an sp^2 nitrogen has a similar, if not greater, nucleophilicity than that of an sp^2 oxygen. For example, The Si–N and Si–Cl bond lengths in compound **18** are 1.90 and 2.60 Å respectively, whereas the Si–O and Si–Cl bond lengths in the 2-quinolinone analogue, **12**, are 1.94 and 2.32 Å respectively [25]. However, in all these cases pentacoordination is still observed with sp^2 nitrogens, unlike compound **15**. Kummer has reported the crystal structure of the aminopyridine derivative **21**, which involves coordination of an sp^2 nitrogen to a silicon. This is essentially ionic and has a ^{29}Si chemical shift of 19.0 ppm [28]. However, the crystal structure and variable temperature NMR studies suggest that hydrogen bonding between the chloride ions and the NH group play an important part in stabilising the ionic structure. No such stabilisation by hydrogen bonding is possible in **15**.

Structures



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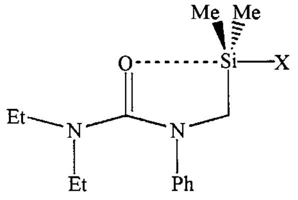
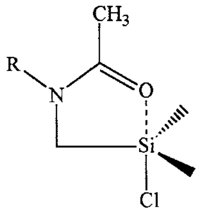
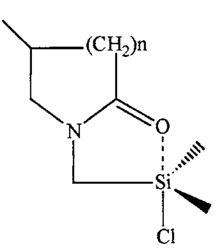


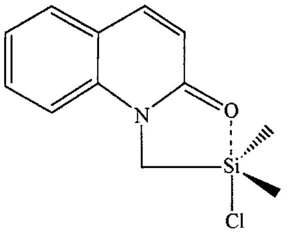
2, X = F
3, X = Cl
4, X = Br
5, X=OTf



6 R=CH$_2$SiMe$_2$Cl
7 R=CH$_3$CO
8 R=(S)-MePhCH



9 R=Ph, n=1
10 R=H, n=2
11 R=H, n=3



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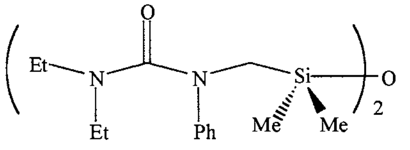

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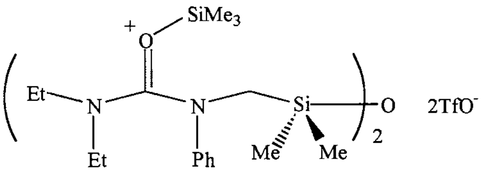

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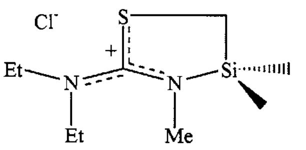
One possible explanation of this behaviour is that the donor nitrogen in **15** can easily convert from sp^2 to sp^3 hybridisation with concomitant formation of a full covalent Si–N bond and rotation of the alkyl group out of the plane of the urea, thus relieving steric strain between the methyl group and the adjacent ethyl group. The resulting charge is then largely delocalised between the sulfur and uncoordinated nitrogen. Such a conversion from sp^2 to sp^3 does not occur for the coordinating nitrogen in **18** since this would involve localisation of the charge onto only one electronegative centre. In **19** such a change would lead to loss of aromaticity. A conversion from sp^2 to sp^3 hybridisation is possible with **20** with delocalisation of the charge onto the adjacent two nitrogens, however, relief of steric strain is not so great with ring systems and the positive charge may not be stabilised as well by two nitrogens as by a sulfur and a nitrogen. Conversion of the oxygen to an sp^3 species in the series **2**–**5** is not favoured because the oxygen would no longer be available for delocalisation of the charge and there is no steric relief, the alkyl groups remaining in the plane of the urea.

3. Conclusions

Our results suggest that trisubstituted ureas readily form pentacoordinate silicon compounds involving Si–O coordination. The variation of structure with leaving group is similar to that obtained with the amide series, providing a consistent model for substitution at silicon. However, the thiourea derivatives involve N–Si bond formation with no pentacoordination at silicon. This is probably due to the donor nitrogen changing its coordination from sp^2 to sp^3 hybridisation.

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 FT-IR spectrometer. NMR spectra were recorded as solutions in deuteri-



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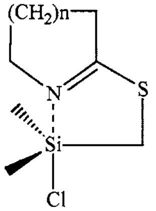

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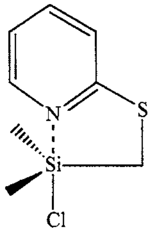

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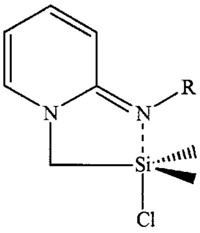

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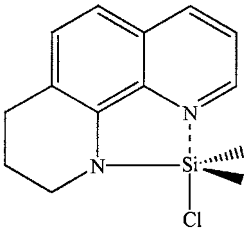

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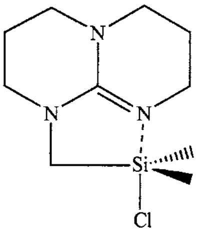

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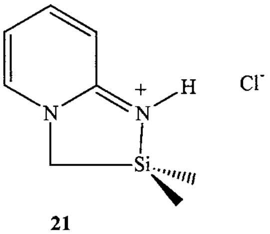

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ochloroform with tetramethylsilane as internal standard on a Jeol FX 90Q or a JEOL EX 400 NMR spectrometer (*J* values are given in Hz). Mass spectra were obtained using a Cresta MS 30 instrument or a VG20-250 quadrupole instrument.

*4.1. N,N-Diethyl-N′-phenyl-N′-trimethylsilyl urea (**1**)*

N,*N*-Diethyl trimethylsilylamine (2.9 g, 3.8 ml, 20 mmol) was cooled in an ice bath. Phenyl isocyanate (2.4 g, 2.2 ml, 20 mmol) was then added slowly over 5 min with vigorous stirring. The mixture was allowed to warm to room temperature and then stirred for 3 h. The yellow crude product was purified by distillation under reduced pressure to give 4.2 g (79%) of *N*,*N*-diethyl-*N*′-phenyl-*N*′-trimethylsilyl urea, as a colourless liquid; b.p. 100°C/0.1 mm Hg; ν_{max} (cm^{-1}) 2970, 1632, 1592, 1251 and 847; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.17 (9H, s, $Si(CH_3)_3$), 0.83 (6H, t, ^3J 7.1, CH_3), 3.10 (4H, q, ^3J 7.1, NCH_2) and 6.85–7.45 (5H, m, arom); δ_C (100 MHz, $CDCl_3$, Me_4Si) 0.4 ($Si(CH_3)_3$), 12.5 (CH_3), 42.0 (NCH_2), 124.5 (Ph), 127.3 (Ph), 128.8 (Ph), 144.2 (Ph) and 161.1 (C=O); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 9.5.

*4.2. N-(Chlorodimethylsilylmethyl)-N′,N′-diethyl -N-phenyl urea (**3**)*

N,*N*-Diethyl-*N*′-phenyl-*N*′-trimethylsilyl urea (1.0 g, 3.8 mmol) was placed in a dry flask under nitrogen. Dry ether (5 ml) was then added, followed by (chloromethyl)dimethylsilane (0.54 g, 3.8 mmol) and the flask was agitated to mix the reactants. After 2 h, the ether was removed gradually by placing the flask under vacuum until the product was observed to crystallise. The remaining ether was then removed via a syringe. The product was dried under vacuum and transferred to a dry box for storage; ν_{max} (cm^{-1}) 2975, 1570. 1510, 1255, 1229 and 848; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.67 (6H, s, $Si(CH_3)_2$), 0.95 (6H, t, ^3J 7.0, CH_3), 3.07 (4H, q, ^3J 7.0, NCH_2), 3.26 (2H, s, NCH_2Si) and 6.8–7.5 (5H, m, arom); δ_C (100 MHz, $CDCl_3$, Me_4Si), 7.4 ($Si(CH_3)_2$), 12.8 (CH_3), 43.6 (NCH_2), 50.2 (NCH_2Si), 125.0 (Ph), 127.2 (Ph), 130.0 (Ph), 143.7 (Ph) and 161.5 (C=O); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) −42.1; *m*/*z* (EI) 298 (M^+), 283 ($M^+ - Me$), 269 ($M^+ - Et$) and 263 ($M^+ - Cl$). Anal. Found: C 55.97, H 7.70, N 9.29. $C_{14}H_{23}N_2OSiCl$ requires: C 56.26, H 7.76, N 9.37%.

4.3. X-ray crystallographic study

Compound **3** was measured on a one-circle diffractometer equipped with an imaging plate system as detector (IPDS 2.75) [29]. Graphite monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å) was used. The data collection was performed in a ψ-rotation mode (50 kV, 40 mA, tube power 2.00 kW, temperature 120 K, detector distance 80 mm, resolution $3.8° < \theta < 56.3°$, ψ-rotation angle 220.8°, ψ-rotation increment 2.3°, frames 96, exposure 2.5 min/frame, duration 11 h, recorded reflections 23410/5243 (independent 5173, R_{merge} 0.1340). The raw intensity data were corrected for Lorentz and polarization effects, no attempts were made to correct for absorption. Structure solutions were searched and refined by direct methods [30] (SHELXS 97-2) and difference Fourier analyses (SHELXL 97-2) [30], respectivly based on F^2. Atom form factors for neutral atoms were taken from the literature [31]. Second and third row elements were allowed to refine anisotropically; hydrogen atoms were assumed in idealized positions riding on their pivot atoms.

*4.4. Structure analysis of **3***

$M_r = 365.4$, crystal dimensions $0.80 \times 0.60 \times 0.60$ mm^3, space group $P(2_1/n)$ (no.14), $a = 18.890(3)$, $b = 9.753(2)$, $c = 19.306(3)$ Å, $\alpha = 114.296(12)°$, $V = 3242.0(9)$ Å^3, $\rho_{calc} = 1.225$ g cm^{-3}, $Z = 8$, $F_{000} = 1280$, $\mu = 0.261$ mm^{-1}, 5243 reflections ($R_{int} = 0.000$), 344 parameter, ratio 15.24, $R_1 = 0.0530$, $wR_2 = 0.1492$ ($I > 2\sigma_I$), $R_1 = 0.0590$, $wR_2 = 0.1588$ (all data), GoF = 1.139; residual electron density 0.514 e Å^{-3} (max.).

*4.5. N-(Bromodimethylsilylmethyl)-N′,N′-diethyl-N-phenyl urea (**4**)*

N,*N*-Diethyl-*N*′-phenyl-*N*′-trimethylsilyl urea (1.0 g,3.8 mmol) was placed in a flask under nitrogen and dry ether (5 ml) was added. (Bromomethyl)dimethylchlorosilane (0.71 g, 3.8 mmol) was then added and the flask agitated briefly. After 2 h, a precipitate had formed. The ether was removed and the precipitate washed with further dry ether and then dried under vacuum. The *N*-(bromodimethylsilylmethyl)-*N*′,*N*′-diethyl-*N*-phenyl urea was then transferred to a dry box for storage; ν_{max} (cm^{-1}) 2975, 1576, 1506, 1255, 1228, 910 and.850; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.83 (6H, s, $Si(CH_3)_2$), 0.99 (6H, t, ^3J 7.1, CH_3), 3.13 (4H, q, ^3J 7.1, NCH_2), 3.52 (2H, s, NCH_2Si) and 7.0–7.5 (5H, m, arom); δ_C (100 MHz, $CDCl_3$, Me_4Si) 6.7 ($Si(CH_3)_2$), 12.8 (CH_3), 44.1 (NCH_2), 51.4 (NCH_2 Si), 125.2 (Ph), 128.0 (Ph), 130.2 (Ph), 142.2 (Ph) and 160.8 (C=O); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) −19.5; *m*/*z* (EI) 344 (M^+), 315 ($M^+ - Et$), 263 ($M^+ - Br$). Anal. Found: C 49.32, H 6.89, N 8.13. $C_{14}H_{23}N_2OSiBr$ requires: C 48.98, H 6.75, N 8.16%.

*4.6. N,N-Diethyl-N′-phenyl-N′-(trifluoromethylsulfonatodimethysilylmethyl) urea (**5**)*

To a solution of *N*,*N*-diethyl-*N*′-phenyl-*N*′-trimethylsilyl urea (0.5 g, 1.67 mmol) in dry ether (3 ml) was added trimethylsilyltrifluoromethylsulfonate (0.37 g, 1.67 mmol). A precipitate formed almost immediately. The solvent was removed and the precipitate washed with further dry ether, after which it was dried under vacuum and tranferred to a dry box; ν_{max} (cm^{-1}) 2975, 1577, 1509, 1235, 1030 and 845; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.60 (6H, s, $Si(CH_3)_2$), 0.95 (6H, t, ^3J 7.1, CH_3), 3.11 (4H, q, ^3J 7.1, NCH_2), 3.38 (2H, s, NCH_2Si) and 7.0–7.5 (5H, m, arom); δ_C (100 MHz, $CDCl_3$, Me_4Si) 0.0 ($Si(CH_3)_2$), 12.6 (CH_3), 44.6 (NCH_2), 47.9 (NCH_2Si), 120.5 (q, $^1J_{C-F}$ 319.2, CF_3), 125.5 (Ph), 128.9 (Ph), 130.5 (Ph), 141.7 (Ph) and 160.3 (C=O); δ_F (90 MHz, $CDCl_3$, Me_4Si) -80.1; δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 16.5; m/z (EI) 412 (M^+), 397 ($M^+ - Me$), 383 ($M^+ - Et$), 263 ($M^+ - OSO_2CF_3$). Anal. Found: C 43.20, H 5.49, N 6.78. $C_{15}H_{23}N_2O_4SSiF_3$ requires: C 43.67, H 5.62, N 6.79%.

*4.7. N,N-Diethyl-N-(fluorodimethylsilylmethyl)-N′-phenyl urea (**2**)*

N-(Chlorodimethylsilylmethyl)-*N′*,*N′*-diethyl-*N*-phenyl urea (0.5 g, 1.67 mmol) was dissolved in dry benzene (5 ml). Antimony trifluoride (0. 10g, 0.56 mmol) was then added and the mixture stirred for 3 h, during which time it became warm. Water (30 ml) was then added and the solution extracted with chloroform (3 × 50 ml). The combined organic extracts were dried over magnesium sulfate, filtered and the solvent removed to give the *N*,*N*-diethyl-*N′*-(fluorodimethylsilylmethyl)-*N′*-phenyl urea as a yellow liquid in a yield of 0.4 g (84%); ν_{max} (cm^{-1}) 2976, 1592, 1496, 1254, 1233 and 835; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.23 (6H, d, ^3J 7.8, $Si(CH_3)_2$), 0.82 (6H, t, ^3J 7.0, CH_3), 2.80 (2H, s, NCH_2Si), 2.93 (4H, q, ^3J 7.0, NCH_2) and 6.9, 7.3 (5H, m, arom); δ_C (100 MHz, $CDCl_3$, Me_4Si) 1.7 (d, $^2J_{C-Si-F}$ 24.8, $Si(CH_3)_2$), 12.8 (CH_3), 43.0 (NCH_2), 45.3 (d, ^4J 44.3, NCH_2Si), 124.6 (Ph), 125.8 (Ph), 129.6 (Ph), 146.1 (Ph) and 161.9 (C=O); δ_F (90 MHz, $CDCl_3$, Me_4Si) -120.5 (septet, ^3J 7.8); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) -19.5 (d, $^1J_{Si-F}$ 258.8); m/z (EI) 282 (M^+), 267 ($M^+ - Me$), 263 ($M^+ - F$), 253 ($M^+ - Et$). Anal. Found: C 59.21, H 8.01, N 9.98. $C_{14}H_{23}N_2OSiF$ requires: C 59.54, H 8.21, N 9.91%.

*4.8. 1,3-Bis(2,4-diaza-4,4-diethyl-3-oxo-2-phenylbutyl)-1,1,3,3-tetramethyldisiloxane (**13**)*

N-(Chlorodimethylsilylmethyl)-*N′*,*N′*-diethyl-*N*-phenyl urea (0.5 g, 1.67 mmol) was dissolved in chloroform (5 ml). Water (5 ml) was then added and the mixture stirred overnight. The organic layer was separated and the aqueous layer extracted with further chloroform (3 × 10 ml). The chloroform extracts were combined, dried over magnesium sulfate, filtered and the solvent removed to give the disiloxane; ν_{max} (cm^{-1}) 2971, 1634 1597, 1253, 1053 and 842; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.15 (6H, s, $Si(CH_3)_2$), 0.89 (6H, t, ^3J 7.1, CH_3), 3.07 (4H, q, ^3J 7.1, NCH_2), 3.07 (2H, s, NCH_2Si) and 6.9–7.3 (5H, m, arom); δ_C (100 MHz, $CDCl_3$, Me_4Si) 0.9 ($Si(CH_3)_2$), 12.8 (CH_3), 42.0 (NCH_2), 46.1 (NCH_2Si), 124.3 (Ph), 124.5 (Ph), 129.2 (Ph) and 148.6 (Ph); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 4.5; m/z (EI) 527 ($M^+ - Me$), 337 ($M^+ - Et_2NCONPhCH_2$) and 263 ($M^+ - Et_2NCONPhCH_2SiMe_2O$). Anal. Found: C 61.55, H 8.55, N 10.37. $C_{28}H_{46}N_4O_3Si_2$ requires: C 61.95, H 8.54, N 10.32%.

4.9. N-(Chlorodimethylsilylmethyl)-N′,N′-dimethyl-N-phenyl urea

N,*N*-Dimethyl-*N′*-phenyl urea (4.1 g, 25 mmol) and hexamethyldisilazane (1.6 g, 10 mmol) were dissolved in dry benzene (35 ml). Chloro(chloromethyl)-dimethylsilane (3.5 g, 25 mmol) was then added with stirring, and the reaction mixture was refluxed for 2 h. After cooling the resulting precipitate was removed by filtration, and removal of the solvent under vacuum gave *N*-(chlorodimethylsilyl) *N′*,*N′*-diethyl-*N*-phenyl urea in a yield of 5.5 g (81%), ν_{max} (cm^{-1}) 2986, 1600, 1518, 1415, 1257, 837, 720 and 697; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.60 (6H, s, $Si(CH_3)_2$), 2.63 (6H, s, NCH_3), 3.25 (2H, s, NCH_2) and 6.9–7.4 (5H, m, arom); δ_C (100 MHz, $CDCl_3$, Me_4Si) 7.8 ($Si(CH_3)_2$), 39.7 (NCH_3), 50.1 (NCH_2), 124.8 (Ph), 127.1 (Ph), 128.7 (Ph), 130.2 (Ph), 143.7 (Ph) and 161.9 (C=O); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) -39.6; m/z (EI) 270 (M^+), 255 ($M^+ - Me$), 235 ($M^+ - Cl$) and 198 ($M^+ - Me_2N-C{=}O$). Anal. Found: C 53.49, H 6.92, N 10.49. $C_{12}H_{19}N_2OSiCl$ requires: C 53.22, H 7.07, N 10.34%.

4.10. N,N-Diethyl-N′-methyl-N′-trimethylsilyl thiourea

Methyl isothiocyanate (0.73 g 10 mmol) was added to *N*,*N*-diethyltrimethylsilylamine (1.45 g, 10 mmol) and the mixture stirred at 100°C for 4 h. Vacuum distillation of the crude product gave *N*,*N*-diethyl-*N′*-methyl-*N′*-trimethylsilyl urea as a pale yellow liquid (1.95 g, 85.5%), b.p. 95°C/0 05 mm Hg; ν_{max} (cm^{-1}) 2971, 1482, 1408, 1315, 1258, 1126 and 847; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.32 (9H, s, $Si(CH_3)_3$), 1.20 (6H, t, ^3J 6.6, CH_3), 2.92 (3H, s, NCH_3) and 3.78 (4H, q, ^3J 6.6, NCH_2); δ_C (100 MHz, $CDCl_3$, Me_4Si) -0.4 ($Si(CH_3)_3$), 12.3 (CH_3), 37.9 (NCH_3), 46.1 (NCH_2) and 196.0 (C=S); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 11.6.

*4.11. S-(Chlorodimethylsilylmethyl)-N,N-diethyl-N′-methyl isothiourea (**15**)*

N,*N*-Diethyl-*N′*-methyl-*N′*-trimethylsilyl thiourea (0.50 g, 2.3 mmol) was dissolved in deuterated chloroform (2 ml) in a 10 mm NMR tube. Chloro(chloromethyl)dimethylsilane (0.33 g. 2.3 mmol) was added and the mixture kept at 50°C. Monitoring using ^{29}Si-NMR revealed that after 2 days reaction was complete. The solution was transferred to a flask and the solvent removed to give the product. ν_{max} (cm^{-1}) 2977, 1572,1360, 1261,929, 839 and 724; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.75 (6H, s, $Si(CH_3)_2$), 1.38 (6H, t, ^3J 6.5, CH_3), 2.65 (2H, s, SCH_2), 3.38 (3H, s, NCH_3) and 3.79 (4H, q, ^3J 6.5, NCH_2); δ_C (100 MHz, $CDCl_3$, Me_4Si) -0.8 ($Si(CH_3)_2$), 11.6 (CH_3), 13.6 (SCH_2), 35.9 (NCH_3), 48.7 (NCH_2) and 77.0 (C=S); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 41.4; m/z (EI) 255, 253 (MH^+) and 217 ($M^+ - Cl$). Anal. Found: C 42.52, H 8.20, N 10.79. $C_9H_{21}N_2SSi$ requires: C 42.78, H 8.38, N 11.08%.

4.12. *S-(Bromodimethylsilylmethyl)-N,N-diethyl-N′-methyl isothiourea*

N,*N*-Diethyl-*N′*-methyl-*N′*-trimethylsilyl thiourea (0.50 g, 2.3 mmol) was dissolved in deuterated chloroform (2 ml) in a 10 mm NMR tube. (bromomethyl)-chlorodimethylsilane (0.33 g. 2.3 mmol) was added and the mixture kept at 50°C. Monitoring using ^{29}Si-NMR revealed that after 3 h reaction was complete: ν_{max} (cm^{-1}) 2978, 2176, 1570, 1357, 1261, 924, 829 and 728; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.76 (3H, s, $Si(CH_3)_2$), 1.39 (6H, t, ^3J 7.1, CH_3), 2.67 (3H, s, SCH_2), 3.39 (311, s, NCH_3) and 3.81 (4H, q, ^3J 7.1, NCH_2); δ_C (100 MHz, $CDCl_3$, Me_4Si) -1.0 ($Si(CH_3)_2$), 11.5 (CH_3), 13.6 (SCH_2), 36.4 (NCH_3), 48.9 (NCH_2) and 177.3 (C=S); δ_{Si} (17.8 MHz, $CDCl_3$, Me_4Si) 44.4; m/z (EI) 299, 297 (MH^+) and 217 ($M^+ - Me$).

5. Supplementary material

The crystal structure of **3** has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 140097. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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