Hypervalent Silicon *via* Intramolecular Co-ordination in a Four-membered Ring System: Synthesis and Structure of $SiCl_2X[2\text{-}C(SiMe_3)_2C_5H_4N]$ (X = H or Me); *X*-Ray Structures of the Former Complex and of $SiCl_2Me(2\text{-}CPh_2C_5H_4N)$†

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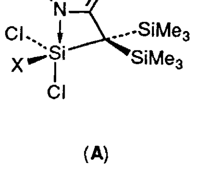
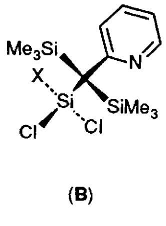
Reaction of $SiCl_3X$ (X = H or Me) with LiR [R = $2\text{-}C(SiMe_3)_2C_5H_4N$] yields the novel hypervalent five-co-ordinate compounds $SiRCl_2X$ which show strong intramolecular Si–N interactions in the four-membered chelate ring [Si–N 2.066(9) Å for X = H (*X*-ray)] which persists in solution; the related compounds, $SiR'Cl_2X$ (X = H or Me for R' = $2\text{-}CPh_2C_5H_4N$) have four-co-ordinate silicon (deduced from the ^{29}Si NMR spectra and, for X = Me, an *X*-ray structure).

Hypervalent, five-co-ordinate silicon is found in silicates (siliconates),[1] and in neutral compounds *via* intramolecular complexation of oxygen[2] or nitrogen[3—5] centres as part of five- or six-membered chelate ring systems. Such compounds are usually considered as model compounds for intermediates in nucleophilic substitution at four-co-ordinate silicon.[6]

We now show that five-co-ordinate silicon is accessible for a particular four-membered chelate ring (despite ring strain) not only in the solid state but also in solution even at room temperature. This feature is found in the compounds $SiRCl_2X$



(A)



(B)

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† No reprints available.

$$\mathrm{RH\ or\ R'H} \xrightarrow{\text{i, then ii}} \begin{array}{ll} \mathrm{SiRCl_2X} & \text{or}\ \mathrm{SiR'Cl_2X} \\ \mathrm{X = H}\,(\mathbf{1}) & \mathrm{X = H}\,(\mathbf{3}) \\ \mathrm{X = Me}\,(\mathbf{2}) & \mathrm{X = Me}\,(\mathbf{4}) \end{array}$$

Scheme 1. RH = 2-HC$(SiMe_3)_2C_5H_4N$, R'H = 2-$HCPh_2C_5H_4N$. *Reagents and conditions*: i, $LiBu^n$ (1.6 mol dm^{-3} in C_6H_{14}), tetrahydrofuran (thf), 0 °C; ii, solution derived from i added to $SiCl_3X$ in thf, −78 °C.

[X = H (**1**) or Me (**2**)],‡ where R is the bulky *N*-functionalised ligand 2-$C(SiMe_3)_2C_5H_4N$. We also find that analogous compounds (**3**) and (**4**),‡ based on the related ligand 2-$CPh_2C_5H_4N$ (R') with seemingly similar steric hindrance and ligand bite, are devoid of such Si–N bonding. Previously it was found that R readily forms chelate rings with certain main group elements which have stronger Lewis acid character; Mg^{II},[7] Al^{III} and Ga^{III};[8] and Sn^{II};[9] only recently has the main group chemistry of R' been initiated with the synthesis of a novel phosphacyclopropane [R'P(η^2-cyclo-octatetraene)], in which R' behaves as a unidentate *C*-centred ligand.[10]

The syntheses of the new silicon(IV) compounds, *via* the appropriate organolithium reagent based on R[7] and R',[11] are shown in Scheme 1.

The presence of two magnetically distinct trimethylsilyl groups (^{29}Si NMR spectra at ambient temperature) for (**1**) is consistent with it possessing the same stereochemically rigid structure as found in the crystal, *vide infra*; *i.e.* having the *N*-functionality apically bound to the Si, which is the locus of a distorted trigonal bipyramid with one $SiMe_3$ *cis* and the other *trans* with respect to the equatorial H and Cl, respectively (**A**, X = H).

By contrast, the ^{29}Si NMR chemical shifts for compound (**2**) in [$^2H_8$]toluene were found to be temperature-dependent, a limiting low-frequency value being observed for the central silicon at low temperature concomitantly with the development of two resonances for the $SiMe_3$ groups at low temperature (Table 1). These observations indicate that there is a rapid equilibrium between four- (**B**, X = Me) and five- (**A**, X = Me) co-ordinate species (203 K < T_C < 238 K; ΔG = 51.4 ± 3.5 kJ mol^{-1}) (*cf.*, ref. 11), the latter (**A**, X = Me) being dominant at low temperature, and presumably having the same stereochemistry as that established for (**1**).

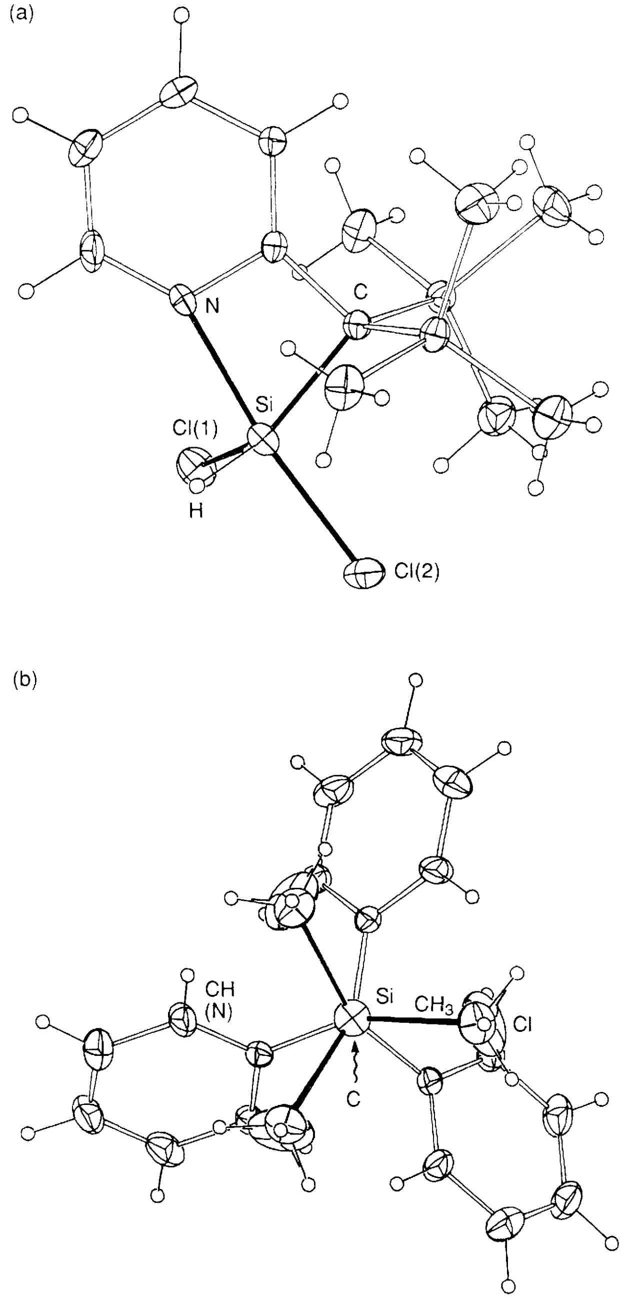

Figure 1. Projections of (a) (**1**), and (b) (**4**), down a 3-fold axis about which the molecule is disordered, showing 20% thermal ellipsoids for the non-hydrogen atoms, and arbitrary radii for hydrogen atoms. Selected bond distances (Å) and angles (°) for the central silicon atoms: compound (**1**): Si–Cl(1), –Cl(2) 2.077(3), 2.167(7), Si–N 2.066(9); Si–C 1.905(8); Si–H 1.57(6); Cl(1)–Si–Cl(2), –N, –C, –H 96.9(2), 92.0(3), 118.6(3), 113(2); Cl(2)–Si–N, –C, –H 170.4(3), 102.4(3), 91(3); N–Si–C, –H 70.0(3), 89(3); C–Si–H, 124(2). Compound (**4**): Si–C, –Cl, –'CH_3' 1.919(3), 1.993(2), 2.03(2); C–Si–Cl, –'CH_3' 113.3(1), 107.4(5), Cl–Si–'CH_3' 5.9; Cl–Si–Cl' 105.38(8).

It is noteworthy that the chemical shift differences ($\Delta\delta$ at 298 K) for the central ^{29}Si in $SiRCl_2H$ (**1**) and $SiR'Cl_2H$ (**3**) ($\Delta\delta$ −15.5 ppm), and $SiRCl_2Me$ (**2**) and $SiR'Cl_2Me$ (**4**) ($\Delta\delta$ −10.1 ppm) vary significantly. This is consistent with there being a change of co-ordination number between (**1**) and (**3**) but not (**3**) and (**4**) (*cf.*, ref. 4).

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‡ *Compound characterisation*: (**1**), colourless prisms, m.p. 120 °C (decomp.); yield 82%; ^1H NMR (250 MHz, C_6D_6): δ 0.25 (18H, s, $SiMe_3$), 6.26 (1H, s, Si–H, J_{Si-H} 1.2 Hz), 6.41, 6.79, 7.02, and 7.53 (4H, m, C_5H_4N); ^{13}C NMR (62.8 MHz, C_6D_6): δ 1.2 ($SiMe_3$), 40.9 (C–Si), 120.4, 139.2, 142.9, and 163.6 (C_5H_4N): ^{29}Si NMR (59.61 MHz, C_6D_6): δ −18.0 (Si–H)), −5.68, and −5.52 (SiMe); *m/z*: 336; IR ν(Si–H) 2190s cm^{-1}.

(**2**), colourless needles, m.p. 132 °C (decomp.), yield 66%; ^1H NMR (80 MHz, C_6D_6): δ 0.26 (18H, s, $SiMe_3$), 1.15 (3H, s, Si–Me), 6.38, 6.83, 7.96, and 7.52 (4H, m, C_5H_4N); ^{13}C NMR (20.1 MHz, C_6D_6): δ 2.2 ($SiMe_3$), 41.4 (CSiMe), 16.4 (ClSiMe), 120.3, 122.2, 138.6, 143.0, and 163.7 (C_5H_4N); ^{29}Si NMR (59.61 MHz, $CD_3C_6D_5$): δ −30.95 (Si–Cl) and 2.37 ($SiMe_3$); *m/z*: 350.

(**3**), colourless needles, m.p. 135 °C (decomp.), yield 66%; ^1H NMR (250 MHz, C_6D_6): δ 6.62 (1H, s, Si–H, J_{Si-H} 1.2 Hz), 6.45, 6.70, 6.87, and 7.90 (4H, m), and 7.0—7.4 (10H, m, Ph); ^{13}C NMR (62.8 MHz, C_6D_6): δ 65.0 (C–Ph), 123.5, 125.0, 129.0, 129.5, 132.0, 140.0, 143.0, 147.0, and 166.0 (ArC); ^{29}Si NMR (59.61 MHz, C_6D_6): δ −2.5; IR ν(Si–H): 2250s cm^{-1}; *m/z*: 244 ($M - SiCl_2H$)$^+$.

(**4**), colourless prisms, m.p. 153 °C (decomp.), yield 55%; ^1H NMR (250 MHz, C_6D_6): δ 6.30, 6.40, 6.75, and 7.85 (4H, m), and 6.8—7.1 (10H, m, Ph); ^{13}C NMR (62.8, MHz C_6D_6): δ 10.0 (Me), 64.0 (CPh), 122.0, 124.5, 128.0, 129.5, 131.5, 139.0, 143.5, 147.5, and 175.5 (ArC); ^{29}Si NMR (59.61 MHz, C_6D_6): δ −20.7; *m/z*: 244 ($M - SiCl_2Me$)$^+$.

Satisfactory elemental analyses were obtained for (**1**)—(**4**).

Table 1. Temperature dependence of the ^{29}Si NMR chemical shift (δ, rel. to $SiMe_4$ at 0.00 ppm) of SiR_2ClMe (**2**) [R = $2-C(SiMe_3)_2C_5H_4N$].

Temp. /°C	Central Si	$SiMe_3$
25	−30.9	2.4
−5	−34.1	2.3
−35	−37.5	2.4
−70	−41.5	0.4, 4.4

Results of the *X*-ray structure determination of (**1**) and (**4**)§ are shown in Figure 1. As in related structures[3,4] the N-donor in (**1**) is in an axial position of a distorted trigonal bipyramidal stereochemistry, although the distortion in (**1**) is more pronounced because of a smaller chelate ring system. The Si–N distance, 2.066(9) Å, is marginally longer than in the only other system involving sp^2 N, 2.028(7) Å which is in a less strained six-membered ring;[3] Si–sp^3-N donor groups distances are much longer, >2.44(1) Å.[4] In the solid state complex (**4**) consists of four-co-ordinate molecules disordered about the 3-fold axis so that the distinction between the Cl and Me groups, and the phenyl and pyridine groups, is lost. We believe that while electronic factors may be important the presence of Si–N interactions in compounds containing R arises from minimisation of steric buttressing between the proton attached to C(2) of the pyridine ring and the protons of adjacent silyl groups forcing the N-centre to be directed towards the central silicon. In compounds containing R′ the phenyl groups can orientate to avoid C(2)–phenyl proton interactions.

We thank the Australian Research Council for support of this work.

Received, 13th March 1990; Com. 0/01109F

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§ *Crystal data* (*T* 22 °C, Enraf-Nonius CAD-4 diffractometer): (**1**) $C_{12}H_{23}Cl_2NSi_3$, $M = 336.5$, orthorhombic, space group $Pna2_1$, $a = 13.878(4)$, $b = 12.229(9)$, $c = 10.454(4)$ Å, $U = 1774$ Å^3, $F(000) = 712$; $Z = 4$, $D_c = 1.26$ g cm^{-3}; μ (Mo-K_α) = 5.0 cm^{-1}, $A^* = 1.08$—1.14, specimen 0.18 × 0.32 × 0.70 mm, 1239 unique reflections, 940 with $I > 3\sigma(I)$ used in the refinement, $2\theta_{max.} = 45°$; $R = 0.037$, $R_w = 0.034$ (both chiralities).

(**4**) $C_{19}H_{17}Cl_2NSi$, $M = 358.3$, rhombohedral, space group $R\bar{3}$, $a = 9.712(4)$ Å, $\alpha = 95.43(3)°$, $U = 903.0$ Å^3, $F(000) = 372$, $Z = 2$, $D_c = 1.32$ g cm^{-3}, μ(Mo-K_α) = 3.7 cm^{-1} (no correction); specimen 0.37 × 0.40 × 0.42 mm, 1070 unique reflections, 566 with $I > 3\sigma(I)$ used in the refinement, $2\theta_{max.} = 50°$; $R = 0.043$, $R_w = 0.035$. The molecule was modelled as being rotationally disordered about the three-fold axis; independent C, N and C(H_3), Cl components being refinable.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.