

Synthesis and characterization of organosilicon(IV) complexes of nitrogen containing heteroaromatic carboxylic acids

Dr. Priya Duggal

Assistant Professor in Chemistry, D.A.V. College, Sector-10, Chandigarh, India

Email : priyadav1209@yahoo.com

Abstract- Some novel routes for the synthesis of some organosilicon (IV) complexes using nitrogen containing heteroaromatic carboxylic acids such as pyrazine-2-carboxylic acid and pyridine-2-carboxylic acid (picolinic acid) as ligands were explored. Pyrazine-2-carboxylic acid has three potential oxygen and nitrogen based coordination sites, but in most of the metal complexes it acts as a bidentate ligand via its (N,O) bonding moieties consisting of an oxygen atom of carboxylate ion and the adjacent hetero nitrogen atom. The present paper describes the synthesis of the compounds $C_7H_9N_2O_2SiCl$ (1), $C_8H_{10}NO_2SiCl$ (2), $C_{12}H_{12}N_4O_4 Si$ (3) and $C_{14}H_{14}N_2O_4 Si$ (4). These compounds were characterized by elemental analysis, IR Spectroscopy and (1H , ^{13}C , ^{29}Si) NMR Spectroscopy.

Index Terms- Hypercoordinated, organosilicon, dichlorodimethylsilane, pyrazine-2-carboxylic acid, pyridine-2-carboxylic acid

1. INTRODUCTION

The chemistry of silicon is largely that of four coordinated compounds but many stable compounds containing five and six coordinated silicon are known. Hypercoordinated silicon compounds attract interest from both the structural and reactivity point of view [1-3]. The isolation of such compounds allows detailed insight into mechanistic pathways of nucleophilic substitution at silicon [4]. On the other hand compounds based on such synthons exhibit interesting properties as electronic materials. Therefore much of the research efforts, recently have been directed towards their synthesis, reactivity and structural investigations [5].

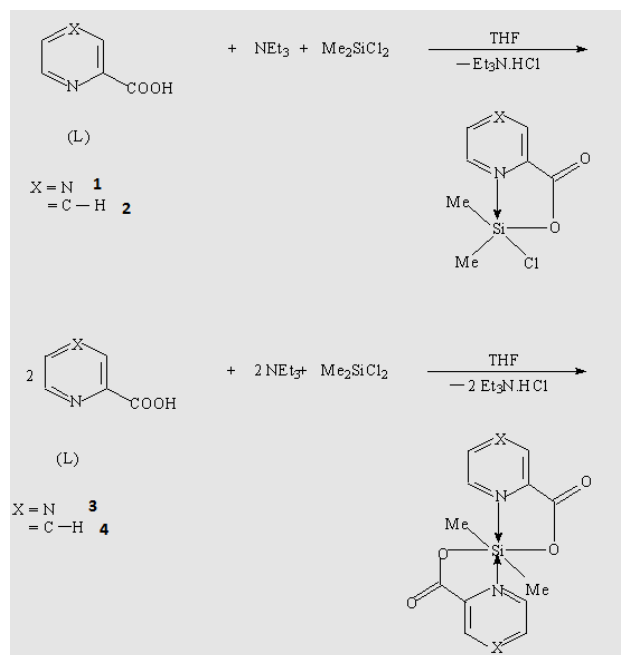
We have recently reported several studies of research on discrete spirobicyclic silicate anions and on hypercoordinated silicon compounds [6-13]. In continuation of our studies on such compounds I describe here the synthesis and characterization of some five and six coordinated organosilicon compounds.

2. RESULTS AND DISCUSSIONS

2.1 Synthesis

The reaction of pyrazine-2-carboxylic acid / pyridine-2-carboxylic acid with triethylamine and dichlorodimethylsilane in 1:1:1 molar ratio in anhydrous THF yield complexes $C_7H_9N_2O_2SiCl$ (1), $C_8H_{10}NO_2SiCl$ (2) and in 2:2:1 molar ratio yield complexes $C_{12}H_{12}N_4O_4 Si$ (3), $C_{14}H_{14}N_2O_4 Si$ (4)

(Scheme-1). The reaction proceeded smoothly with the precipitation of triethylamine hydrochloride. These complexes were white solids, stable at room temperature and insoluble in most of the common organic solvents except in DMSO and DMF. The molar conductivity of these complexes was low ($5-15 \Omega^{-1}cm^2mol^{-1}$) indicating their non-electrolytic nature. These complexes were characterized by their elemental analysis, infra-red, multinuclear (1H , ^{13}C , ^{29}Si) NMR spectroscopy. The complexes were purified by column chromatography and their purity was checked by TLC on silica gel. The complexes moved as a single spot indicating the presence of only one component.



Scheme -1

2.2 Spectroscopic Studies

2.2.1 Infra-red spectroscopy

In metal carboxylates, the carboxylate ions can show monodentate, bidentate bridging and chelating modes. In monodentate mode only one oxygen atom is coordinated to metal atom whereas in bidentate bridging and chelation mode both carbonyl oxygens are shared either by one or two metal ions which may be same or different. Therefore, in such cases the difference in the value of asymmetric and symmetric mode of vibrations ($\Delta\nu$) can serve as a measure of the mode of coordination. The infra-red spectra of the complexes $C_7H_9N_2O_2SiCl$ (1), $C_8H_{10}NO_2SiCl$ (2), $C_{12}H_{12}N_4O_4Si$ (3), $C_{14}H_{14}N_2O_4Si$ (4) showed $\nu_{as}(COO)$ in the range $1670-1700\text{ cm}^{-1}$ and $\nu_s(COO)$ in the range $1328-1340\text{ cm}^{-1}$. The value of ($\Delta\nu$) of approximately 340 cm^{-1} showed that the carboxylate ion function as monodentate ligand.

The $\nu(C=N)$ band in pyrazine-2-carboxylic acid and pyridine-2-carboxylic-acid (1662 and 1630 cm^{-1}) was shifted towards lower frequencies in the complexes $C_7H_9N_2O_2SiCl$ (1), $C_8H_{10}NO_2SiCl$ (2), $C_{12}H_{12}N_4O_4Si$ (3), $C_{14}H_{14}N_2O_4Si$ (4) ($1586-1595\text{ cm}^{-1}$). This showed the coordination of the N present in the heterocyclic ring to Si. During coordination, the $>C=N$ bond of the ring was weakened due to transfer to electron density from $N \rightarrow Si$ and as a result the stretching frequency was lowered. Other modes of vibrations viz $\nu Si-O$, $\nu Si-N$, and $\nu Si-Me$ were observed in the spectra of these complexes were found absent in the spectra of the ligands. Further the

stretching frequency corresponding to Si-Cl vibration was seen in the spectra of the complexes $C_7H_9N_2O_2SiCl$ (1) and $C_8H_{10}NO_2SiCl$ (2).

2.2.2 1H nmr spectroscopy

The proton (1H) NMR spectra of ligands showed a signal at δ 7.5 ppm due to carboxylic acid proton which disappeared in silicon complexes showing the coordination of oxygen of carboxylate ion after the deprotonation of this proton to silicon moiety. The signals in the range (0.8 – 1.1 ppm) in complexes $C_7H_9N_2O_2SiCl$ (1), $C_8H_{10}NO_2SiCl$ (2), $C_{12}H_{12}N_4O_4Si$ (3), $C_{14}H_{14}N_2O_4Si$ (4) indicated the attachment of methyl groups to the silicon atom.

2.2.3 ^{13}C nmr spectroscopy

The ^{13}C NMR spectral data for ligand and its metal complexes in $CDCl_3 + DMSO-d_6$ supports the coordination of the ligand through oxygen atom of COO^0 group. The shift in the position of carbon of carboxylate group / groups on complexation indicated bonding pattern in these complexes. The signals due to carbon atoms of the methyl groups attached to Si supports the involvement of methyl group in complexation.

2.2.4 ^{29}Si nmr spectroscopy

The ^{29}Si NMR spectra of these complexes $C_7H_9N_2O_2SiCl$ (1), $C_8H_{10}NO_2SiCl$ (2), $C_{12}H_{12}N_4O_4Si$ (3), $C_{14}H_{14}N_2O_4Si$ (4) were recorded in $CDCl_3 + DMSO-d_6$. A single sharp peak at δ -91.1 , -81.3 , -166.1 and -166.8 ppm for these complexes was obtained. These values suggested penta-coordination in complexes $C_7H_9N_2O_2SiCl$ (1) and $C_8H_{10}NO_2SiCl$ (2) and hexa-coordination in complexes $C_{12}H_{12}N_4O_4Si$ (3) and $C_{14}H_{14}N_2O_4Si$ (4)

3. MATERIALS AND METHODS

3.1 Apparatus

All experiments were performed in the absence of oxygen and moisture, in an all glass vacuum line connected to dry nitrogen gas supply. Nitrogen was made to pass separately through long columns of heated copper catalyst ($150-200^\circ C$), sodium hydroxide pellets, calcium chloride and phosphorus (V) oxide before use. Before each experiment the apparatus was cleaned, rinsed with acetone and kept in oven at $120^\circ C$ for about 3 hours. The vacuum assembly as well as glass apparatus were flame baked under reduced pressure and purged with dry nitrogen prior to use. During the removal of volatile fractions

under reduced pressure, traps were used to prevent back diffusion of moisture from the pump and passage of solvent vapors into the pump. Specially designed filtration units fitted with G-4 sintered glass crucible were used for filtration.

3.2 Purification of solvents

All solvents were purified and dried before use according to the standard methods. THF was distilled from sodium metal-benzophenone prior to use. Dimethylsulfoxide (DMSO) was kept over molecular sieves (4 Å) for one week. The decanted solvent was distilled under reduced pressure and the fraction distilling at 75-76°C / 12 mm Hg was collected. The fraction collected was further purified by partial freezing. The pure solvent was kept over molecular sieves in a stoppered flask.

3.3 Chemicals used

Triethylamine (Qualigens) was kept over potassium hydroxide pellets overnight and then refluxed for 5-6 Hours. The base was distilled at 55°C/ 760 mmHg before use. Dichlorodimethylsilane was purchased from Aldrich and used as received. Pyrazine-2-carboxylic acid (Aldrich) and Picolinic acid (Aldrich) were used as received.

3.4 Elemental analysis

Carbon, Hydrogen and Nitrogen contents of various samples were obtained by using Perkin Elmer (Model 2400) C,H,N elemental analyzer at Regional Sophisticated Instrumental Centre (RSIC), Panjab University, Chandigarh. Chlorine, Sulphur and Silicon content of the samples were estimated gravimetrically [14].

3.5 Molar conductance

Molar Conductance of the samples were determined for their millimolar concentrations in DMSO at 25± 5°C using Elico digital conductivity meter.

3.6 Infrared spectra

Infrared spectra were obtained as nujol mull on Perkin Elmer RX-I FT-IR spectrophotometer in the range 4000-200 cm⁻¹

3.7 Nmr spectra

All chemical shift values for ¹H, ¹³C, ²⁹Si NMR spectra were recorded with respect to tetramethylsilane (TMS) as internal standard. ¹H NMR spectra were recorded using Varian EM-360 (60 MHz), Bruker AC 400F (400 MHz) and JEOL AL-300 (300 MHz) FT NMR spectrometers. ¹³C NMR spectra were recorded on Bruker AC-

400F(400MHz) and JEOL AL-300(300 MHz) FT NMR spectrometers. ²⁹Si NMR spectra were recorded on JEOL FT NMR (AL-300 MHz) spectrometer.

4.0 SYNTHESIS OF COMPLEXES

4.1 Synthesis of complex C₇H₉N₂O₂SiCl (1)

In 25ml THF, pyrazine-2-carboxylic acid (1.2 gm, 9.5 mmoles) and triethylamine (1.32 ml, 9.5 mmoles) were stirred at room temperature when a clear transparent solution was obtained. The temperature was then lowered to 0°C and dichlorodimethylsilane (1.1 ml, 9.5 mmoles) was added dropwise and the resulting mixture was stirred at 0°C for 1 hour. The reaction mixture was then kept at room temperature overnight and the precipitated triethylamine hydrochloride was filtered off and washed with THF (3-4 times). The solvent was removed from the filtrate under vacuum and white colored solid was isolated from dry hexane (Yield : 1.1 gm, 53.6%).

Anal.(%) Calcd : C, 38.80; H,4.19; N,12.93; Si,12.96; Cl,16.36 .(**% Found** : C, 38.77 ; H, 4.12 ; N, 12.85 ; Si,12.92 ; Cl 16.27

IR (Nujol, cm⁻¹) : 1595 (ν C=N), 1670 (ν_{as} COO), 1340 (ν_s COO), 880 (ν Si-O), 700 (ν Si←N), 500 (ν Si-Cl), 1430, 1260 (ν Si-Me).

δ ¹H NMR (CDCl₃ + DMSO-d₆) : 0.9 (s, 6H, CH₃), 8.9 (d, 1H, C₃-H), 8.1 (d, 1H, C₅-H), 8.5 (d, 1H, C₆-H).

δ ¹³C NMR (CDCl₃ + DMSO-d₆) : 165.1(COO), 143.7(C₂), 145.5(C₃), 147.6(C₅), 144.5(C₆), 3.2 (Si-C).

δ ²⁹Si NMR (CDCl₃ + DMSO-d₆) : -91.1

4.2 Synthesis of complex C₈H₁₀NO₂SiCl (2)

To a stirred sol of pyridine-2-carboxylic acid (1.04gm, 8.5 mmoles) and triethylamine (1.18ml, 8.5 mmoles) in THF, dichlorodimethylsilane (1.03ml, 8.5 mmoles) was added dropwise. The contents were stirred at 0°C for 2 hours. The reaction mixture was then stored at room temperature overnight. The solid triethylamine hydrochloride was filtered off and washed with 10 ml of THF. The solvent was removed from the filtrate under vacuum and a white colored solid was obtained from dry hexane (20 ml). Yield (1.25gm, 68.6%) .

Anal.(%) Calcd : C, 44.54; H, 4.67; N, 6.49; Si, 13.02; Cl, 16.44 (**% Found** : C, 44.47; H, 4.63; N, 6.41; Si, 13.00 ; Cl, 16.00

IR (Nujol, cm⁻¹) : 1586(ν C=N), 1704 (ν_{as} COO), 1328 (ν_s COO), 820 (ν Si-O), 524 (ν Si←N), 506 (ν Si-Cl), 1446, 1258 (ν Si-Me).

δ ^1H NMR ($\text{CDCl}_3 + \text{DMSO-d}_6$): 0.9 (s, 6H, CH_3), 7.5-8.7 (m, 4H, py ring).

δ ^{13}C NMR ($\text{CDCl}_3 + \text{DMSO-d}_6$): 157.6 (COO), 142.1 (C_2), 127.1 (C_3), 139.4 (C_4), 125.1 (C_5), 149.4 (C_6), 2.1 (Si-C).

δ ^{29}Si NMR ($\text{CDCl}_3 + \text{DMSO-d}_6$): -81.3

4.3 Synthesis of complex $\text{C}_{12}\text{H}_{12}\text{N}_4\text{O}_4\text{Si}$ (3)

The above complex was prepared by the dropwise addition of addition of dichlorodimethylsilane (0.66ml, 5.5 mmoles) to a solution of pyrazine-2-carboxylic acid (1.36 gm, 11.0 mmoles) and triethylamine (1.5 ml, 11.0 mmoles) in dry THF at 0°C under dry nitrogen atmosphere. Rest of the procedure was analogous to the method given for complex $\text{C}_7\text{H}_9\text{N}_2\text{O}_2\text{SiCl}$ (1). Yield (0.9 gm, 54.8%)

Anal. (%) Calcd : C, 47.36 ; H, 3.97; N, 18.41; Si, 9.23. **(%) Found** : C, 47.30; H, 3.89; N, 18.39; Si, 9.20

IR (Nujol, cm^{-1}) : 1601 (v C=N), 1660 (ν_{as} COO), 1330 (ν_s COO), 890 (v Si-O), 676 (v Si \leftarrow N), 1435, 1273 (v Si-Me).

δ ^1H NMR ($\text{CDCl}_3 + \text{DMSO-d}_6$): 0.8 (s, 6H, CH_3), 8.3 (d, 1H, $\text{C}_5\text{-H}$), 8.7 (d, 1H, $\text{C}_6\text{-H}$).

δ ^{13}C NMR ($\text{CDCl}_3 + \text{DMSO-d}_6$): 169.4 (COO), 141.5 (C_2), 144.4 (C_3), 146.1 (C_5), 142.2 (C_6), 3.9 (Si-C)

δ ^{29}Si NMR ($\text{CDCl}_3 + \text{DMSO-d}_6$): -161.1

4.4 Synthesis of complex $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_4\text{Si}$ (4)

To a solution of pyridine-2-carboxylic acid (1.23gm, 10.0 mmoles) and triethylamine (1.4 ml, 10.0 mmloes) in dry THF, dichlorodimethylsilane (0.6 ml, 5.0 mmoles) was added dropwise at 0°C . Rest of the procedure was analogous to the method given for complex $\text{C}_8\text{H}_{10}\text{NO}_2\text{SiCl}$ (2). Yield (1.0 gm, 67.1%).

Anal. (%) Calcd : C, 55.61; H, 4.67; N, 9.26; Si, 9.29. **(%) Found** : C, 55.59; H, 4.60; N, 9.00; Si, 9.21

IR (Nujol, cm^{-1}) : 1587 (v C=N), 1708 (ν_{as} COO), 1336 (ν_s COO), 802 (v Si-O), 527 (v Si \leftarrow N), 1453, 1265 (v Si-Me).

δ ^1H NMR ($\text{CDCl}_3 + \text{DMSO-d}_6$): 1.1 (s, 6H, CH_3), 7.6 - 8.7 (m, 8H, py rings).

δ ^{13}C NMR ($\text{CDCl}_3 + \text{DMSO-d}_6$): 158.4 (COO), 142.5 (C_2), 128.1 (C_3), 139.2 (C_4), 127.3 (C_5), 149.5 (C_6), 2.5 (Si-C).

δ ^{29}Si NMR ($\text{CDCl}_3 + \text{DMSO-d}_6$): -166.8

5. CONCLUSIONS

Pentacoordinated silicon complexes of nitrogen containing heteroaromatic carboxylic acids were synthesized by the 1:1:1 stoichiometric reactions of triethylamine, dichlorodimethylsilane and pyrazine / pyridine-2-carboxylic acid under completely anhydrous conditions. The hexacoordinated silicon complexes were synthesized by the 2:2:1 stoichiometric reactions of triethylamine, pyrazine / pyridine-2-carboxylic acids and dichlorodimethylsilane under anhydrous conditions. The characterization of the complexes were done through elemental analysis, spectroscopic and chromatographic studies.

REFERENCES

- [1] R.R. Holmes, 'The stereochemistry of nucleophilic substitution of tetracoordinate silicon.' *Chem. Rev.* **90**(1990)17
- [2] R.R. Holmes, 'Comparison of Phosphorus and Silicon: Hypervalency, Stereochemistry, and Reactivity' *Chem. Rev.* **96** (1996) 927
- [3] C.Chuit, R.J.P. Corriu, C. Reye, J.C. Young, 'Reactivity of penta- and hexacoordinate silicon compounds and their role as reaction intermediates' *Chem. Rev.* **93**(1993)1371
- [4] A.R. Bassindale, P.G. Taylor, *The Chemistry of Organic Silicon Compounds*, ed. S. Patai, Z. Rappoport, Wiley, Chichester, 1989, p. 839.
- [5] M.F. Roll, J.W. Kampf, Y. Kim, E. Yi, R.M. Laine, 'Nano Building Blocks via Iodination of $[\text{PhSiO}_{1.5}]_n$, Forming $[p\text{-I-C}_6\text{H}_4\text{SiO}_{1.5}]_n$ ($n = 8, 10, 12$), and a New Route to High-Surface-Area, Thermally Stable, Microporous Materials via Thermal Elimination of I_2 ' *J. Am. Chem. Soc.* **132**(29) (2010)10171
- [6] J.K Puri, G. Singh, P. Duggal, 'Synthesis and characterization of Bis (2-aminobenzoato) Diphenylsilicate and Bis (2-aminothiophenoxy) Diphenylsilicate - New hexacoordinated silicates dianions with seven membered rings' *Main Group Met. Chem.* **30** (2007) 31
- [7] J.K Puri, G. Singh, P. Duggal, 'Synthesis, Characterization and Reactivity of a novel six-membered 1-isothiocyanato silatranes' *Phosphorus, Sulfur, Silicon Relat. Elem.* **183** (2008) 1853.
- [8] J. K Puri, R. Singh, V.K Chahal, 'Silatranes: a review on their synthesis, structure, reactivity and applications' *Chem. Soc. Rev.* **40** (2011) 1791
- [9] J.K. Puri, R. Singh, V.K. Chahal, R.P. Sharma, J. Wagler, E. Kroke, 'New silatranes possessing

- urea functionality: Synthesis, characterization and their structural aspects' *J. Organomet. Chem.* **696** (2011) 1341.
- [10] R. Singh, J.K. Puri, R. P. Sharma A.K. Malik, V. Ferretti, Synthesis, characterization and structural aspects of 3-azidopropylsilatrane *Journal of Molecular Structure.* **982** (2010) 107.
- [11] R Singh, JK Puri, VK Chahal, RP Sharma, P Venugopalan Synthesis and reactivity of novel 3-isothiocyanatopropylsilatrane derived from aminopropylsilatrane: X-ray crystal structure and theoretical studies *Journal of Organometallic Chemistry* **695** (2), 2010 , 183-188
- [12] J. K. Puri, R. Singh, V. K. Chahal, R.P. Sharma, Novel hexacoordinate organosilicon (IV) complexes of diethylenetriamine Schiff base with SiO₂N₃ skeleton *ARKIVOC XI* (2009) 247
- [13] J.K. Puri, R. Singh, V.K. Chahal, G.J.P. Singh, R.P. Sharma, Synthesis and characterization of penta-and hexa-coordinated silicon compounds with Schiff bases containing-NCS functionality *Main Group Met. Chem.* **32** (2009) 79.
- [14] A.I. Vogel, *A Text Book of Quantative Inorganic Analysis*, 3rded. Longmanns : London, 1961.