Mapana Journal of Sciences
2020, Vol. 19, No. 2, 11-19
ISSN 0975-3303 | https://doi.org/10.12723/mjs.53.2

Synthesis and Characterisation of Penta-coordinated 2- and 4-substituted Pyridine N-Oxide Silicon Complexes

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Abstract

NovelPenta-coordinated 2- and 4-substituted pyridine N-oxide silicon complexes were synthesised by the reaction of various 2- and 4-substituted pyridine N-oxides with silicon pinacolate. These complexes were characterised by ^{29}Si NMR, ^{1}H NMR and ^{13}C NMR spectroscopy. The objective of the present work is tothe study the influence of substitution at either 4 or 2-position of the pyridine *N*-oxide on the effect of the profile of pentacoordination.

Keywords: Silicon Pincolate, Pyridine N-oxides, Penta-coordination, ^{29}Si NMR

1. Introduction

The genesis of the present work comes from the empirical observation that poly 2-vinyl pyridine *N*-oxides were found to remove fine silica particles and were subsequently shown to promote the uptake of silica [1].The known chemistry of silica suggested activation for hydrolysis by pentacoordination involving pyridine *N*-oxide. The Si^{IV}-Si^{V} change has great significance since it transforms the inert silica to a reactive species that can participate in numerous reactions including the hydrolysis of silica to silicic acid. Interestingly, the pyridine *N*-oxide generated Si^{V} zwitterionic systems represent the closest approach of the counterions as reflected in their ^{29}Si NMR. Zwitterionic Si^{V} systems have great

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potential in organic synthesis because of the ease with which they could be prepared and their high reactivity compared to the tetravalent precursors [2].Perhaps the great utility of Si^V compounds is as transient intermediates to effect ligand displacement from tetracoordinated silicon [3].

The effective transformation of Si^{IV} to Si^V is not very easy due to various reasons. The vast literature available relating to hypervalent silicon systems [4-11] indicates the existence of a barrier in the transformation of Si^{IV} to Si^V that can be overcome most commonly by the use of spiro-silicon systems, which have severe tetrahedral distortion. This has been experimentally demonstrated by using ^{29}Si NMR. Thus, the spirosilicates exhibit a peak in the ^{29}Si NMR at –44.0 ppm, which is quite different from normal tetracoordination (-78.9 ppm). On pentacoordination,the normal value of around 110.0 ppm is seen.

Pyridine *N*-oxide is a weak base (p*Ka* = 0.79) [12]. The limitations were found from the fact that the Si^V compound arising from pyridine *N*-oxide and silicon pinacolate (**1**) (^{29}Si NMR: -108.5 ppm) on standing underwent a total reversal. Therefore in the preliminary experiments reported earlier[13], the basicity of pyridine *N*-oxide was enhanced by electron-donating substituents.Structural analysis of these led to a novel zwitterionic pentacovalent silicon assembly by the reaction of pyridine *N*-oxide and silicon pinacolate. Preliminarily experiments confirmed the ability of pyridine *N*-oxide to solubilize silica possibly by pentacoordination.

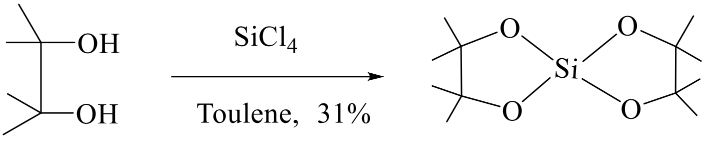
2. Present Study

The present work relates to a novel approach to the synthesis of 2- and 4-N-substituted pyridine *N*-oxides because of their possible involvement in the enhancement of solubilisation of silica.Suitable changes in the pyridine *N*-oxide design has been introduced that would permit demonstration of several novel properties such as tandem formation of Si^V systems generated from tethered pyridine *N*-oxide, the crafting of pyridine *N*-oxides that could form multiple pentacoordinated systems, the synthesis of pyridine *N*-oxide Si^V systems that can harbour metal ions, and the factors that influence the stability and reactivity of the systems.The objectives of the present work areto study the influence of substitution at either 4 or 2-position of the pyridine *N*-oxide on the effect of the profile of pentacoordination.

3. Experimental Methods

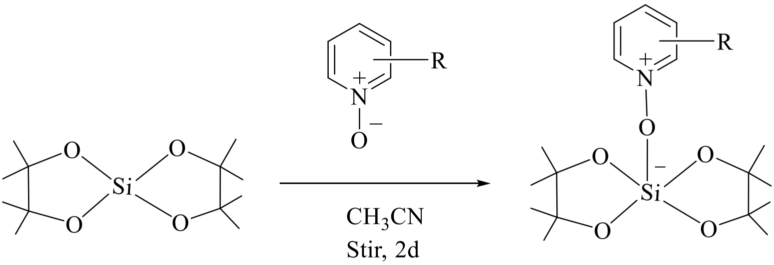
Silicon pinacolate1 was readily prepared by reaction of pinacol with $SiCl_4$ (Scheme 1).The zwitterionic Si^V complexes from pyridine *N*-oxides were mostly prepared by a general procedure involving the mixing of equivalent amounts of acetonitrile solutions, leaving stirred for 2 days and evaporation of the solvents in *vacuo* below 40 ˚C. The structural assignment for the compounds is supported by ^{29}Si NMR, ^1H NMR and ^{13}C NMR.

As mentioned before the synthesis of the novel pyridine *N*-oxide complexes described in the present work were designed with a purpose. They are prepared mostly by the general procedure as shown in Scheme 2.



1

Scheme 1



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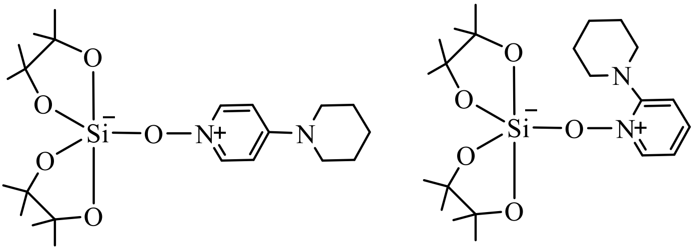
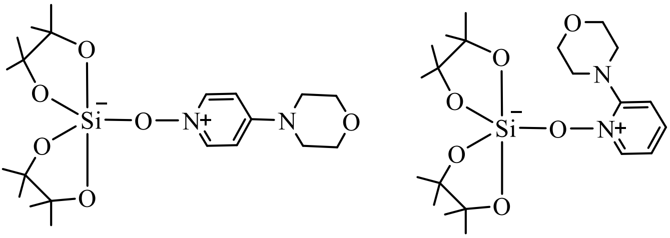
2.1 - 2.6

Scheme 2



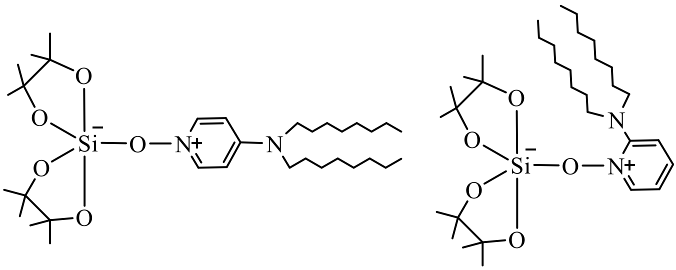
2.1 (76%, -105.9 ppm) **2.2** (80%, -106.0 ppm)

Figure 1



2.3 (75%, -110.4 ppm) **2.4** (84%, -106.2 ppm)

Figure 2



2.5 (67%, -107.5 ppm) **2.6** (81%, -106.7 ppm)

Figure 3

The melting points were recorded on a Fischer – John's apparatus and are uncorrected. ^{1}H, ^{13}C NMR and ^{29} Si NMR spectra were recorded on a Varian Gemini-200, Bruker-Avance-300, Varian UNITY-400 MHz NMR spectrometers. All the reactions were performed under nitrogen atmosphere. The organic solvents used were dried and purified according to standard procedures, stored under nitrogen and distilled before reactions. Evaporations were generally carried out under reduced pressure on Büchi rotary evaporator at below 40°C.

Given the tendency of Si^V compounds to undergo reversal, the purity of these compounds has been established by standard 1D-proton decoupled ^{13}C NMR spectrum as well as a well resolved high field ^1H NMR spectrum, which are also accepted criteria.

4. Results and Discussion

The structural assignments for compounds **2.1** and **2.2** are supported by ^{29}Si, ^1H NMR and ^{13}C NMR.The spectral data of **2.1** and **2.2** showed no discernable difference in the ^1H NMR in the placement of the piperidine ring either at 2 or 4-positions. The ^{29}Si NMR signal was sharper in the case of **2.2** and both of them exhibited weak peaks around –95 ppm possibly because of the presence of minor conformations.

The Si^V structure for **2.3** and **2.4** is supported by ^{29}Si NMR, ^1H NMR and ^{13}C NMR. Also in the case of **2.4** the ^{29}Si peak at –106.3 and the satellite peak at –94.7 ppm were sharper and were downshifted by about 4 ppm compared to **2.3**.

Compounds **2.5** and **2.6** were designed to test the coordination of 4-*N*- and 2-*N*-substituted pyridine *N*-oxides harbouring long chains to form zwitterionic complexes with Si^{IV} systems. The objective was that in the event the results are positive, the corresponding pyridine *N*-oxides could be integrated into reverse micellar systems, with a surfactant, like AOT, harbouring water pools in a hydrophobic solvent like isooctane [14]. Thus, it is planned to test the ability of the uptake of silica into the water pools of such reverse micellar systems, thereby demonstrating the transfer of insoluble silica from a hydrophobic system to a polar one. The structural assignment for **2.5** and **2.6** were supported by ^{29}Si, ^{13}C and ^1H NMR and showed a similar profile.

The work described so far has widened the scope of pyridine *N*-oxide complexed Si^V systems. It has provided novel observations and has opened up several avenues for new investigations. It has provided proof for the interaction of up-take of silica by poly 2-vinyl pyridine *N*-oxide.

5. Experimental Study

5.1. Preparation of Silicon Pinacolate (1)

To a stirred solution of water-free pinacol [15] (24g, 0.2 mol) in 100 mL of dry toluene was added silicon tetrachloride (17g, 0.1mol) in 30 mL dry toluene slowly, through a pressure-equalizing dropping funnel and the mixture warmed to 35-40 °C with control of the evolution of HCl, refluxed for 4 h, toluene removed in *vacuo* and residue sublimed at 115-118 °C at 5mm pressure to afford highly crystalline and hygroscopic silicon pinacolate.

Yield: 8.2 g (31.3%); M.p. 112-113 °C (lit. [16]: 112 °C); ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.33 (m, 24 H, pinacol CH_3's).

5.2. 4-Piperidino *N*-oxy pyridinium siliconate, 2.1:

Acetonitrile solutions of silicon pinacolate (0.260g, 1 mmol, 5mL) and 4-piperidino pyridine *N*-oxide (0.178g, 1 mmol, 5mL) were admixed and stirred for 2d. Solvents were evaporated below 40 °C in *vacuo*, washed with dry hexane (2x5 mL) and dried to yield 0.335g (76%) of **2.1** as a brown thick liquid.

^{29}Si NMR (400 MHz, $CDCl_3$): -105.900 ppm; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.17, 1.24 (s, s, 18H), 1.37 (s, 6H) (pinacol H), 1.72 (m, 6H, piperidine *bcb* H), 3.48 (m, 4H, piperidine *a* H), 6.77 (d, 2H, *J* = 7.35 Hz, aromatic β), 8.12 (d, 2H, *J* = 7.35 Hz, α); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 23.4, 24.5, 24.8 (pinacol $\underline{C}$, piperidine *c*, *b*$\underline{C}$), 47.5 (piperidine *a*$\underline{C}$), 74.5 (t-C-O), 108.0 (β), 139.0 (α), 152.1 (γ).

5.3. 2-Piperidino *N*-oxy pyridinium siliconate, 2.2:

Acetonitrile solutions of silicon pinacolate (0.260g, 1 mmol, 5mL) and 2-piperidino pyridine *N*-oxide (0.178g, 1 mmol, 5mL) were admixed and stirred for 2d. Solvents were evaporated below 40 °C in *vacuo*, washed with dry hexane (2x5 mL) and dried to yield 0.350g (80%) of 2.2 as a low melting solid.

^{29}Si NMR (400 MHz, $CDCl_3$): -106.001 ppm; ^{1}H NMR (300 MHz, $CDCl_3$,): δ 1.20, 1.23 (s, s 18H), 1.40 (s, 6H) (pinacol H), 1.66 (m, 2H, piperidine *c* H), 1.78 (m, 4H, piperidine *b* H), 3.33 (m, 4H, piperidine *a* H), 6.84 (m, 2H, aromatic β, β'), 7.21 (app t, 1H, *J* = 8.49 Hz, γ), 8.17 (d, 1H, *J*= 6.42 Hz, α); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 24.2, 24.4, 24.7 (pinacol $\underline{C}$, piperidine *c*$\underline{C}$), 25.4 (piperidine *b*$\underline{C}$), 49.1 (piperidine *a*$\underline{C}$), 75.0 (t-C-O), 115.1 (β), 117.1 (β'), 127.7 (γ), 140.5 (α), 155.1 (α').

5.4. 4-Morpholino *N*-oxy pyridinium siliconate, 2.3:

Acetonitrile solutions of silicon pinacolate (0.260g, 1 mmol, 5mL) and 4-morpholino pyridine *N*-oxide (0.180g, 1 mmol, 5mL) were admixed and stirred for 2d. Solvents were evaporated below 40 °C in *vacuo*, washed with dry hexane (2x5 mL) and dried to yield 0.330g (75%) of 2.3 as a solid with m.p. 253 - 254 ˚C.

^{29}Si NMR (400 MHz, Solid): -110.500 ppm; ^{1}H NMR (200 MHz, DMSO-d_6): δ 1.0 (s, 18H), 1.30 (s, 6H) (pinacol H), 3.20 (br, 4H, N-$C\underline{H_2}$), 3.70 (s, 4H, O-$C\underline{H_2}$), 6.80 (d, 2H, *J* = 8.0 Hz, aromatic β), 7.90 (d, 2H, *J* = 8.0 Hz, α); ^{13}C NMR (50 MHz, DMSO-d_6): δ 25.2 (pinacol $\underline{C}$), 46.2 (N-$\underline{C}$), 65.6 (O-$\underline{C}$), 73.5 (t-C-O), 110.2 (β), 138.4 (α), 148.0 (γ).

5.5. 2-Morpholino *N*-oxy pyridinium siliconate, 2.4

Acetonitrile solutions of silicon pinacolate (0.204g, 0.78 mmol, 5mL) and 2-morpholino pyridine *N*-oxide (0.141g, 0.78 mmol, 5mL) were admixed and stirred for 2d. Solvents were evaporated below 40 °C in *vacuo*, washed with dry hexane (2x5 mL) and dried to yield 0.290g (84%) of **2.4** as a low melting solid.

^{29}Si NMR (400 MHz, $CDCl_3$): -106.289 ppm; ^{1}H NMR (200 MHz, $CDCl_3$,): δ 1.19, 1.23 (s, s, 18H), 1.40 (s, 6H) (pinacol H), 3.42 (m, 4H, N-$C\underline{H_2}$), 3.93 (m, 4H, O-$C\underline{H_2}$), 6.88 (m, 2H, aromatic β, β'), 7.26 (app t, 1H, *J* = 7.61 Hz, γ), 8.20 (d, 1H, *J* = 6.25 Hz, α); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 24.3, 24.7 (pinacol $\underline{C}$), 48.0 (N-$\underline{C}$), 66.4 (O-$\underline{C}$), 74.9 (t-C-O), 114.6 (β), 118.0 (β'), 127.9 (γ), 140.6 (α), 154.0 (α').

5.6. 4-Di-n-octylamino *N*-oxy pyridinium siliconate, 2.5:

Acetonitrile solutions of silicon pinacolate (0.260g, 1 mmol, 5mL) and 4-di-n-octylamino pyridine *N*-oxide (0.334g, 1 mmol, 5mL) were admixed and stirred for 2d. Solvents were evaporated below 40 °C in *vacuo*, washed with dry hexane (2x5 mL) and dried to yield 0.400g (67%) of **2.5** as a pale yellow thick liquid.

^{29}Si NMR (400 MHz, $CDCl_3$): - 107.560 ppm; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.84 – 0.90 (m, 6H, aliphatic CH_3), 1.24 – 1.29 (br, 44H, pinacol H & aliphatic CH_2), 1.87 (br, 4H, N-CH_2-C$\underline{H_2}$), 2.85 - 2.93 (m, 4H, N-C$\underline{H_2}$), 7.27 (d, 2H, *J* = 7.34 Hz, aromatic β), 8.13 (d, 2H, *J* = 7.34 Hz, α).

5.7. 2-Di n-octylamino*N*-oxy pyridinium siliconate, 2.6:

Acetonitrile solutions of silicon pinacolate (0.190g, 0.73 mmol, 5mL) and 2-di-n-octylamino pyridine *N*-oxide (0.243g, 0.73 mmol, 5mL) were admixed and stirred for 2d. Solvents were evaporated below 40 °C in *vacuo*, washed with dry hexane (2x5 mL) and dried to yield 0.350g (81%) of **2.6** as a dark brown thick liquid.

^{29}Si NMR (400 MHz, $CDCl_3$): -106.750 ppm; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (s, 6H, aliphatic CH_3), 1.18, 1.24, 1.39 (s, s, s, 44H, pinacol H, aliphatic CH_2), 1.59 (m, 4H, aliphatic, N-CH_2-C$\underline{H_2}$), 3.47 (m, 4H, N-C$\underline{H_2}$), 6.78 (m, 1H, aromatic β), 6.88 (d, 1H, *J*= 8.12 Hz, β'), 7.36 (app t, 1H, *J*= 8.12 Hz, γ), 8.22 (app t, 1H, *J*= 8.3 Hz, α); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 14.0, 22.7, 24.3, 24.7, 26.9, 29.0, 29.2 (aliphatic & pinacol $\underline{C}$), 31.7 (N-C-$\underline{C}$), 51.0 (N-$\underline{C}$), 74.9 (t-C-O), 115.6 (β), 116.2 (β'), 127.2 (γ), 140.9 (α), 153.0 (α').

6. Conclusion

Six novel penta coordinated silicon complexes were prepared by the reaction of various 2- and 4-substituted pyridine N-oxides and silicon pinacolate and well characterised by ^{29}Si, ^{13}C and ^{1}H NMR spectroscopy. As a result, the present work has given rise to several novel leads that hopefully would be examined resulting in a better understanding of these new class of compounds.

References

[1] D. W. Parry,Ann. Bot. 1975, 39, 815.
[2] R. R. Holmes,Chem. Rev. 1996, 96, 927.
[3] C. Chuit, R. J. P. Corriu, C. Reye and J. C. Young, Chem. Rev. 1993, 93, 1371.
[4] R. R. Holmes, Chem. Rev. 1990, 90, 17.
[5] V. Jitchum, S. Chivin, S. Wongkasemjit and H. Ishida, Tetrahedron, 2001, 57, 3997.

[6] C. L. Frye, J. Am. Chem. Soc. 1970, 92, 1205.

[7] K. C. Kumara Swamy, V. Chandrasekhar, J. J. Harland, J. M. Holmes, R. O. Day and R. R. Holmes, J. Am. Chem. Soc. 1990, 112, 3241.

[8] R. M. Laine, K. Y. Blohowiak, T. R. Robinson, M. L. Hoppe, P.Nardi, J. Kampfand J. Uhm, Nature, 1991, 353, 642.

[9] B. Herreros, S. W. CarrandJ. Klinowski, Science, 1994, 263, 1585.

[10] K. Y. Blohowiak, D. R. Treadwell, B. L. Muller, M. L. Hoppe, S.Jouppi, P. Kansal, K. W. Chew, C. L. S. Scotto, F. Babonneau, J. Kampf and R. M. Laine, Chem. Mater., 1994, 6, 2177.

[11] R. Tacke, M. PulmandB. Wagner, Adv. In Organomet. Chem. 1999, 44, 221.

[12] H. H. Jaffe andG. O. Doak, J. Am. Chem. Soc. 1955, 77, 4441.

[13] S. Ranganathan, CH. C. Rao, S. D. Vudayagiri, Y. B. R. D. Rajeshand B. Jagadeesh, J. Chem. Sci.2004, 116(3), 169.

[14] D. Ranganathan, G. P. SinghandS. Ranganathan, J. Am. Chem. Soc.1989, 111, 1144.

[15] A. I. Vogel, Practical Organic Chemistry, 5th ed. Wiley, New York, 1989, p528.

[16] R. MullerandL. Heinrich, Chem. Ber. 1961, 94, 1943.