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SYNTHESIS AND SPECTROSCOPIC STUDY OF ORGANOSILICON (IV) DERIVATIVES OF N,N'-O-PHENYLENEBIS(SALICYLIDENEIMINE)

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ABSTRACT

Some tri- di-and monoorganosilicon(IV) derivatives of N,N'-o-phenylenebis(salisilideneimine) synthesised by the reactions of the corresponding tri, di- and monoorganosilicon (IV) chlorides with the sodium salt of N,N'-o-phenylenebis(salisilideneimine) in different molar ratios. These derivatives have been characterized by elemental analyses, molecular weights, conductivity measurements and spectral data such as (IR, ^{1}H, ^{13}C and ^{29}Si NMR studies).

Keywords: **N,N'-o-phenylenebis(salisilideneimine); monoorganosilicon (IV) chlorides; ^{29}Si NMR studies.**

INTRODUCTION

Organosilicon complexes with N,O and N,S donar ligands have been reported[1-3],and are widely used in medicinal and pharmaceutical chemistry[4-5]. Certain organosilicon compounds have been extensively used in chemical vapour deposition and deoxygenation reactions in organic transformations[7]. Moreover, they are valuable synthons for a wide variety of useful chemicals. Thus in view of peculiar behavior and pharmacological importance of the ligand[8] and in continuation of our studies in organosilicon(IV) derivatives[9-11].We report here the synthesis and characterization of some new complexes of organosilicon (IV) with N,N'-o- phenylenebis(salisilideneimine).

EXPERIMENTAL

Due to the highly hygroscopic nature of the metal alkoxides stringent precautions were taken to exclude moisture throughout the experiments, using glassware with the interchangeable joints. All the reactions were carried out under strictly anhydrous conditions and analytical grade chemicals were used for all experiments. The Schiff base have been synthesized by the condensation of salicyldehyde and o-phenylenediamine in 2:1 molar ratio in benzene as reaction medium. Thus solution was refluxed for 3-4 h and then allowed to cool to room temperature. The products so obtained were recrystallised from pet.ether-benzene mixture.Silicon was determined as siliconoxide gravimetrically and nitrogen was determined by Kjeldahl's method. Infrared spectra were recorded on a perkin-Elmer model 377 spectrophotometer in the range 4000-400 cm^{-1}. The ^{1}H NMR spectra were recorded on a jeol FX -90 using tetramethylsilane as an external standard.

Reaction between triphenylsilicon(IV)chloride and sodium salt of N,N'-o-phenylenebis(salisilideneimine) in a 1:1 molar ratio:

0.09g of sodium metal and 15 ml of isopropanol were taken in a round bottom flask (fitted with a dried and a cooled water condenser and guard tube) and refluxed for about half an hour till a clear solution of sodium isopropoxide was obtained. After cooling 1.29g(3mmole) of N,N'-o- phenylenebis(salisilideneimine) was added and the mixture was for two hours again. 1.20g(3mmole) of triphenylsiliconchoride was added and mixture was further refluxed for two hours to ensure the completion of the reaction. The desired product

(80%) was isolated by evaporation of the solvent under reduced pressure, after filtering of the precipitated sodium chloride. The product was further purified by crystallization using a benzene-petrolium ether (40^o-60^o) mixture.

All other organosilicon(IV) derivatives of N, N'-o- phenyleneis(salisilideneimine) were synthesized analogously. The pertinent data for this compound and other derivatives are listed bellow.

Compound 1: $C_{38}H_{30}N_2O_2Si$ Yield 79%; Mol.Wt.[F(C)]: 574.74 (574.74); yellow solid; M.P.103-105^{o}c. Analysis:C,79.41 (79.41);H,5.26 (5.26) ;N,4.87 (4.87); O,5.57(5.57); Si,4.89 (4.89) IR(cm^{-1}):υC= O,1680; υ C= N,1605; υ Si-O-C,1095, 670cm^{-1}PMR(ppm):8.65(s,2H,CH=N),7.46-7.65(m,12H,Ar).^{13}CNMR(ppm):166.23,160.65, 154.34, 142.46,133.42,132.48,127.63,119.42,119.12,118.86,116.43; MS (El, 70Ev): m/z 342 (M$^+$,26),314,298,282,208,192,77.

Compound 2: $C_{32}H_{42}N_2O_2Si$ Yield 86%; Mol.Wt.[F(C)]: 514.70 (514.70);yellow solid; M.P.104-106^{o}c. Analysis[%F(C)]: C, 74.66(74.66) ;H,8.22 (8.22);N,(5.44) O, 6.22(6.22) Si,5.46 (5.46) IR(cm^{-1}):υC= O,1685; υ C= N,1600; υ Si-O-C,1090, cm^{-1} ^{1}PMR(ppm):8.70 (s,2H,CH=N), 7.507.69(m,12H,Ar) ^{13}CNMR(ppm):166.35, 161.00, 154.45, 142.50,133.50,133.00,127.70,119.50,119.17,117.10, 116.52; MS (El, 70Ev): m/z 342 (M$^+$,26),316,297,284,209,193,79.

Compound 3: $C_{28}H_{32}ClN_2O_2Si$ Yield 86%; Mol.Wt.[F(C)]: 493.11 (493.11);yellow solid; M.P.104-106^{o}C. Analysis [%F(C)] : C, 68.20 (68.20) ;H, 6.75 (6.75); Cl N, 5.68 (5.68)O, 6.49 (6.49) Si,55.70 (5.70) IR(cm^{-1}):υC= O,1685; υ C= N,1600; υ Si-O-C,1090, cm^{-1} PMR(ppm): 8.70(s,2H,CH=N),7.507.69(m,12H,Ar) ^{13}CNMR(ppm):166.35, 161.00, 154.45, 142.50,133.50,133.00,127.70,119.50,119.17,117.90,116.52; MS (El, 70Ev): m/z 342 (M$^+$,26),316,297,284,209,193,79.

Compound 4: $C_{54}H_{66}N_4O_4Si$ Yield 88%; Mol.Wt.[F(C)]: 863.21(863.21);yellow solid; M.P.109-110^{o}C.Analysis[%F(C)]: = C, 75.11 (75.11) H, 7.71 (7.71) N, 6.49 (6.49) O, 7.41 (7.41) Si,3.25 (3.25) IR(cm^{-1}):υC= O,1687; υ C= N,1608; υ Si-O-C,1092 cm^{-1}. PMR(ppm): 8.70(s,2H,CH=N),7.50-7.69(m,12H,Ar). ^{48} Si NMR(ppm): -180.20 ^{13}CNMR(ppm):166.35,161.00,154.45,142.50,133.50,133.00,127.70,119.50,119.17,114.90,116.52; MS (El, 70Ev): m/z 342 (M$^+$,26),314,298,284,209,193,79.

Compound 5: $C_{22}H_{21}ClN_2O_2Si$ Yield 89%; Mol.Wt.[F(C)]: 408.95 (408.95);yellow solid; M.P.110-114^{o}c. Analysis[%F(C)]: C, 64.61 (64.61) ;H, 5.18 (5.18) Cl, 8.67(8.67);N, 6.85 (6.85);O,7.82 (7.82);Si, 6.87 (6.87) IR(cm^{-1}):υC= O,1685; υ C= N,1600; υ Si-O-C,1092, cm^{-1} PMR(ppm): 8.70(s,2H,CH=N),7.50-7.69(m,12H,Ar). ^{48} Si NMR(ppm): -126.52 : ^{13}CNMR(ppm):166.35,161.00,154.45,142.50,133.50,133.00,127.70,119.50, 119.17, 113.90,116.52; MS (El, 70Ev): m/z 342 (M$^+$,26),315,299,284,209,191,79.

Compound 6: $C_{48}H_{54}N_4O_4Si$ Yield 87%; Mol.Wt.[F(C)]: 779.05 (779.05);yellow solid; M.P.104-106^{o}c. Analysis[%F(C)]: C,74.00 (74.00), H,6.99(6.99);N.7.19(7.19); O,8.21(8.21), Si,3.61(3.61) IR(cm^{-1}):υC= O,1685; υ C= N,1600; υ Si-O-C,1089cm^{-1}. PMR(ppm): 8.70(s,2H,CH=N),7.50-7.69(m,12H,Ar)., ^{48} Si NMR(ppm): -118.6 ^{13}CNMR(ppm):166.35,161.00,154.45,142.50,133.50,133.00,127.70,119.50,119.17,115.90,116.52; MS (El, 70Ev): m/z 342 (M$^+$,26),316,297,284,209,193,79.

Compound 7: $C_{21}H_{18}Cl_2N_2O_2Si$ Yield 86%; Mol.Wt.[F(C)]: 414.32(414.33)yellow solid; M.P.104-106^{o}c. Analysis[%F(C)]: C, 58.74 (58.74) ;H,4.23(4.23) ;N, 6.52 (6.52) ;O,7.46(7.45) ;Si,6.54 (6.54) IR(cm^{-1}):υC= O,1685; υ C= N,1600; υ Si-O-C,1095 cm^{-1} PMR(ppm):8.70(s,2H,CH=N),7.50-7.69(m,12H,Ar).

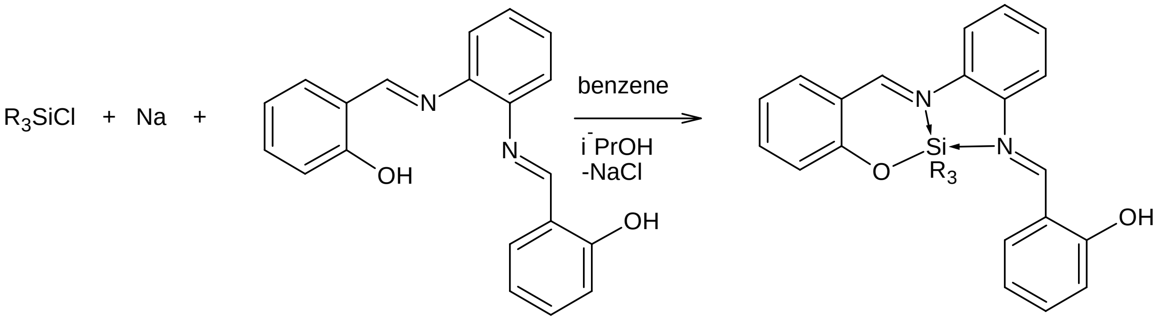
^{13}CNMR(ppm):166.35,161.00, 154.45, 142.50,133.50,133.00,127.70,119.50,119.17,115.90,116.52; MS (El, 70Ev): m/z 342 (M$^+$,26),316,299,281,209,192,79.

Compound 8: $C_{41}H_{33}ClN_4O_4Si$ Yield 89%; Mol.Wt.[F(C)]: 709.26 (709.26);yellow solid; M.P.104-106^{o}c. Analysis[%F(C)]:Si,3.95 (3.96),H,4.68(4.69);N.7.89(7.90); O,9.01(9.02) C, 69.43 (69.43) IR(cm^{-1}):υC= O,1685; υ C= N,1600; υ Si-O-C,1095 cm^{-1}. PMR(ppm):8.70(s,2H,CH=N),7.50-7.69(m,12H,Ar).^{13}CNMR(ppm):166.35,161.00, 154.45, 142.50,133.50,133.00,127.70,119.50,119.17,115.90,116.52; MS (El, 70Ev): m/z 342 (M$^+$,26),316,299,281,209,192,79.

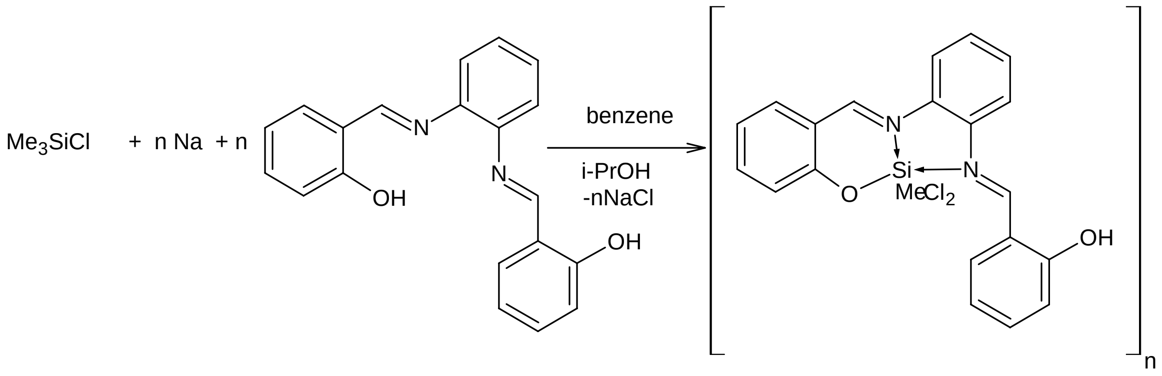
Compound 9 $C_{61}H_{48}N_6O_6Si$ Yield 89%; Mol.Wt.[F(C)]: 869.0(1008.93742);yellow solid; M.P.104-106^{o}c. Analysis[%F(C)]:C,74.06 (74.07);H,4.89(4.89);N.8.50(8.50); O,9.69(9.70) Si,2.84(2.84),IR(cm^{-1}):υC= O,1685; υ C= N,1600; υ Si-O-C,1095 cm^{-1} PMR(ppm):8.70(s,2H,CH=N),7.50-7.69(m,12H,Ar). ^{3}CNMR(ppm):166.35,161.00,154.45,142.50,133.50,133.00,127.70,119.50,119.17,115.90,116.52; MS (El, 70Ev): m/z 342 (M$^+$,26),316,299,281,209,192,79

RESULTS AND DISCUSSION

Triorganosilicon (IV) diorganosilicon(IV) and monoorganosilicon (IV) derivatives of N,N'-o-phenylenebis(salisilideneimine) have been synthesized by the reaction of corresponding triorganosilicon(IV) diorganosilicon(IV) and monoorganosilicon (IV) chlorides with the ligand(prepared in situ by the reaction of sodium isopropoxide with the ligand) in 1:1 ,1:2and 1:3 molar ratios,respectively.



(Where R=Ph.Compd.**1**; R=n-Bu.Compd.**2**) Where R=n-Bu,n=1.Compd.**3**; R=n-Bu, n=2, Compd.**4**; R=Me,n=1,Compd.5; R=Me,n=2, Compd.**6**)



(n=1,Compd.7 n=2,Compd.**8,** ,n=3,Compd.9)

All these newly synthesized compounds are yellow crystalline solids, soluble in common organic and coordinating solvents. Molar conductance values reveal the non-electrolytic nature of the complexes indicating that the ligand is covalently bonded to silicon. Molecular weight determination in $CHCl_3$ solution show their monomeric nature.

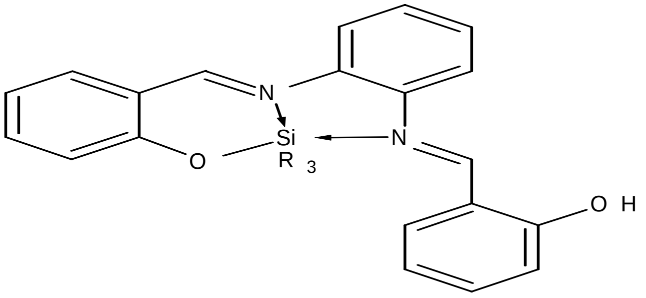
IR Spectral Data

The infrared spectra of these organosilicon (IV)complexes have been recorded in the form of KBr pellets in the range 4000-400 cm^{-1}.Tentative assignments have been made on the basis of earlier publications.[4,5]. The spectrum of the ligand shows bands in the regions 3260-3380, 1620 cm^{-1}, which have been assigned to υ(OH), υ(C=N) respectively.[9] The disappearance of 3260 cm^{-1} indicates the deprotonation of one of the O-H and consequent coordination of phenolic oxygen atom to silicon metal, which is further substantiated by the appearance of bands in the region 570-440 cm^{-1}, that may be due to Si-C and Si-O streaching vibrations.[10-11]The band at 3380 cm^{-1} is uneffected indicates non involvement of the second O-H bond in the coordination. The band present at 1615 cm^{-1} due to υ C=N in the ligand is found to be shifted for about 20-25 cm^{-1} to lower wave number in the complexes suggesting coordination of the two azomethine nitrogens to the central metal atom[13].

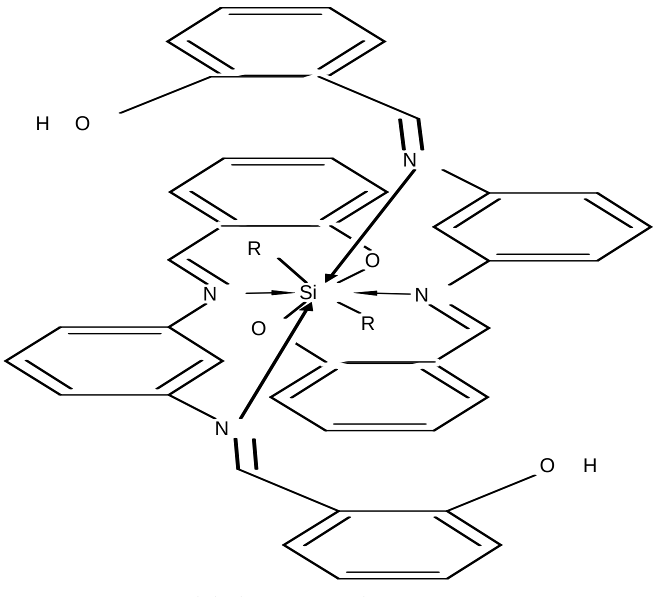
NMR Spectral Data

The PMR spectra of ligand is characterised by appearance of a siginal at 12.40 ppm for two phenolic –OH groups, at 10.60 ppm for azomethine group and a multiplet at 6.84-7.86 ppm attributable to protons of phenyl moiety. The resonance at 12.40 ppm is present in the spectra of the complexes, integration of protons along with appearance of Si -O streaching band in IR and Si NMRsuggesting the selective deprotonation of one of the phenolic –OH and its subsequent involvement in coordination. The coordination through azomethine nitrogen is supported by the high field shift of the free ligand signal at 10.60 ppm to 11.60 ppm in the complexes.[14] The resonance due to the phenyl moiety remains uneffectd. The PMR spectra of complexes exhibit phenylene proton resonances are overlapping with the phenylene proton resonances of the ligand to give a complex pattern at 6.76-8.25 ppm. The resonances due to the butyl protons are observed in the region 0.60-1.86 ppm, with a well defined triplet at 0.85 ppm (J=8Hz) wich is due to methyl protons of butyl group.

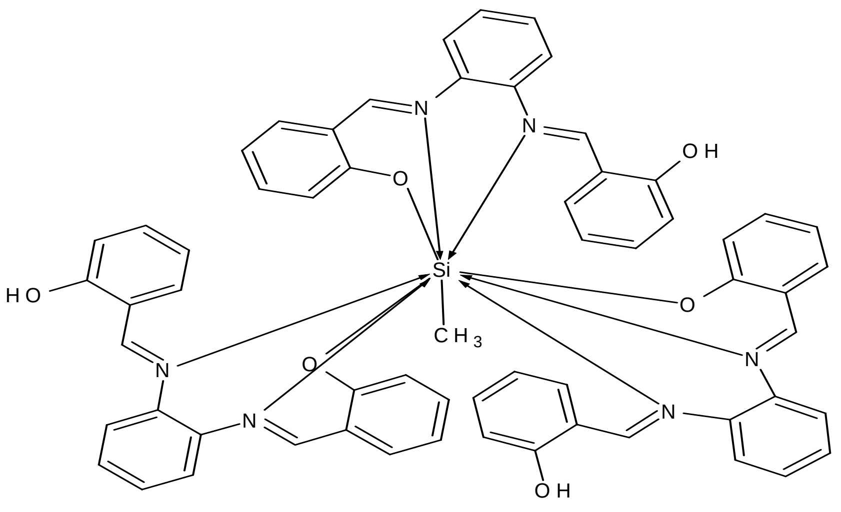
The methyl protons of the dimethylsilicon (IV) derivatives appear as a sharp singlet at 0.44 ppm. A particular advantage of methyl silicon derivatives is the ease with wich proton spin – spin coupling constant can be determined. The coupling constant provides valuable information about hybridisation state of silicon.[15,16] For the four coordinate dimethyl silicon (IV) compounds have been found to be 73 Hz wich is in the range of values observed for six coordinate dimethyl silicon (IV) compounds, indicating that the ligand behaving as bidendate moiety. Thus based on above spectral studies, five-coordinate (a) sixcoordinate (b) and sevencoordinate (c) structures may be tentatively proposed for triorganosilicon(IV) diorganosilicon (IV) and monoorganosilicon(IV derivatives of the ligand, respectively.



(a) (R=Ph ,Bu)



(b) (R=Me,Bu)



(c)

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