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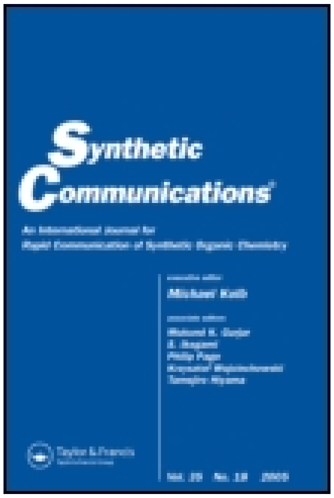

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

HEXACOORDINATE ORGANOSILICON(IV) COMPOUNDS WITH A TETRADENTATE AZOMETHINE LIGAND

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Published online: 23 Aug 2006.

To cite this article: M. S. Singh, T. C. Sharma & P. K. Singh (2002) HEXACOORDINATE ORGANOSILICON(IV) COMPOUNDS WITH A TETRADENTATE AZOMETHINE LIGAND, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 32:24, 3733-3741, DOI: 10.1081/SCC-120015390

To link to this article: http://dx.doi.org/10.1081/SCC-120015390

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SYNTHETIC COMMUNICATIONS
Vol. 32, No. 24, pp. 3733–3741, 2002

HEXACOORDINATE ORGANOSILICON(IV) COMPOUNDS WITH A TETRADENTATE AZOMETHINE LIGAND

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ABSTRACT

Hexacoordinate silicon compounds with the tetradentate azomethine ligand *N*,*N*′-ethylene*bis*(2-hydroxyacetophenoneimine) have been prepared and characterized by elemental analyses, molecular weight determinations and spectral (IR, ^{1}H, ^{13}C and ^{29}Si NMR) studies. The data clearly demonstrate the octahedral geometry around the silicon atom.

Hypervalent silicon compounds attract interest from both the structural and reactivity point of view.[1] The isolation of such compounds allows detailed insight into mechanistic pathways of nucleophilic substitution at silicon.[1e] On the other hand compounds based on such synthons should

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DOI: 10.1081/SCC-120015390
0039-7911 (Print); 1532-2432 (Online)
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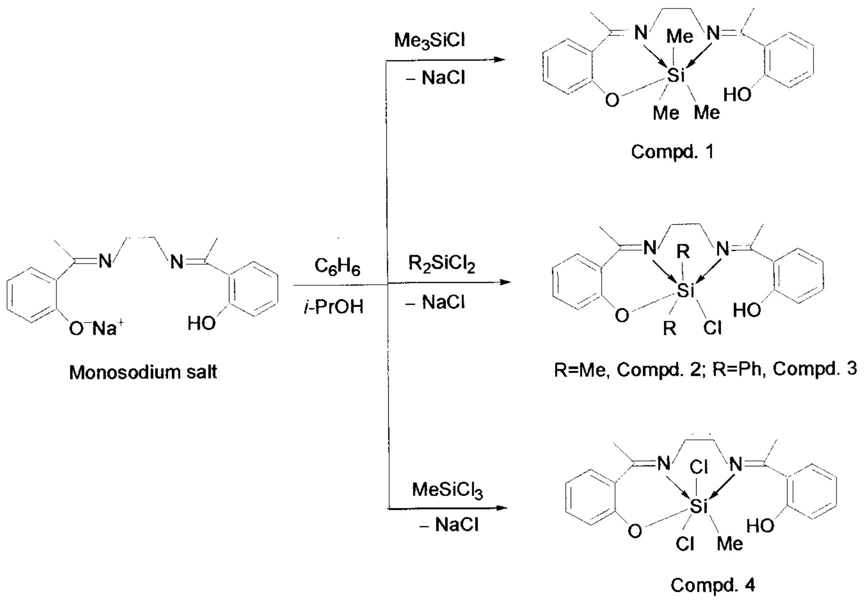
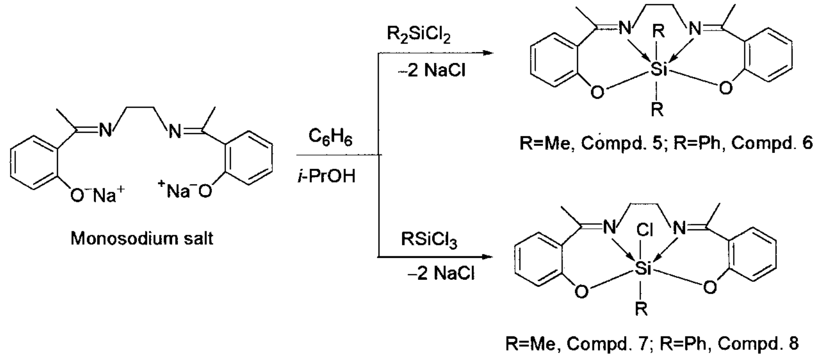
exhibit interesting properties as electronic materials. Different types of hypercoordinated silicon compounds have so far been reported.[1–3] We set out to synthesize hexacoordinate organosilicon complexes containing the salen ligand. This ligand is able to chelate to silicon atom through four O N N O donor atoms. There are some rare example of salen silicon compounds known from the literature.[4,5] Transition metal salen complexes have been investigated extensively.[6–8] In continuation of our studies on organosilicon(IV) compounds,[9–11] we describe here the synthesis and characterization of some new complexes of organosilicon(IV) with the titled ligand.

Different types of salen ligands have been applied recently, mainly in transition metal complex catalysts, for the transformations of organic substrates.[12] We here used a slightly modified salen ligand [*N*,*N*′-ethylene-*bis*(2-hydroxyacetophenoneimine)] with methyl groups at the azomethine carbon instead of hydrogen. This prevents unwanted side reactions caused by the azomethien protons. Tri-, di- and monoorganosilicon(IV) derivatives of the Schiff base ligand have been synthesized by the reaction of the corresponding tri-, di- and monoorganosilicon(IV) chlorides with the sodium salt of the ligand (prepared in situ) in desired molar ratios. These reactions are found to be quite facile and the sodium chloride formed during the course of the reaction is filtered off.



This synthesis involves the initial formation of monoanion and dianion from sequential deprotonations of the Schiff base ligand which attacks organosilicon(IV) chlorides. Intermolecular nucleophilic attack with elimination of chloride ion leads to the formation of products in good yields.



All these synthesized compounds are colored solids, soluble in common organic and coordinating solvents. These were purified by repeated washing with suitable solvent and their purity was checked by T.L.C. on silica gel. Each of the complexes moves as a single spot indicating the presence of only one component. The reported molecular weights refer to the parent ion peak as recorded on a AEI MS 9 mass spectrometer.

IR Spectra

The free Schiff base ligand exhibits a broad band in the region 3565–3315 $\mathrm{cm^{-1}}$ due to ν (O–H), which disappear completely in the complexes **5** to **8** indicating deprotonation of both the –OH groups, whereas only one –OH group deprotonates in complexes **1** to **4**, providing an oxo-coordiantion. This is also evident from the appearance of ν (Si–O) modes[13] at 830–340 $\mathrm{cm^{-1}}$ in the spectra of the complexes (Table 1). The ν (C=N) band observed at 1632 $\mathrm{cm^{-1}}$ in the free liand is shifted to lower frequencies upon complexation in all the complexes indicating coordination by both the C=N groups.[14] This fact is further supported by the appearance of new bands in the region 564–552 $\mathrm{cm^{-1}}$ ascribable to ν (Si $< \cdots$ N) modes[15] (Table 1). In the literature a shift of this frequency to the higher[16] as well as lower[17] wave number side has been reported and in some cases even no

Table 1. Spectral Data of Compounds **1–8**

Compd. No.	IR (cm^{-1})					NMR (δ, ppm)	
	ν (C=N)	ν (O–H)	ν (Si–O)	ν (Si–N)	ν (Si–Cl)	^1H	^{29}Si
1	1605	3380	840	560	—	6.67–7.60 (m, 8H, arom.); 1.45 (s, 6H, CH_3); 3.45 (s, 4H, CH_2); 0.24 (s, 9H, Si–CH_3); 12.45 (s, 1H, OH).	−156.7
2	1612	3394	835	556	515	6.74–7.56 (m, 8H, arom.); 1.58 (s, 6H, CH_3); 3.52 (s, 4H, CH_2); 0.26 (s, 6H, Si–CH_3); 12.30 (s, 1H, OH).	−158.2
3	1600	3386	830	552	488	6.76–7.78 (m, 18H, arom.); 1.60 (s, 6H, CH_3); 3.50 (s, 4H, CH_2); 12.36 (s, 1H, OH).	−157.9
4	1608	3372	836	558	509	6.56–7.48 (m, 8H, arom.); 1.50 (s, 6H, CH_3); 3.58 (s, 4H, CH_2); 0.22 (s, 3H, Si–CH_3); 12.40 (s, 1H, OH).	−159.1
5	1596	—	830	562	—	6.56–7.62 (m, 8H, arom.); 1.56 (s, 6H, CH_3); 3.56 (s, 4H, CH_2); 0.24 (s, 6H, Si–CH_3).	−158.7
6	1610	—	834	554	—	6.72–7.68 (m, 18H, arom.); 1.67 (s, 6H, CH_3); 3.56 (s, 4H, CH_2).	−156.8
7	1610	—	832	557	512	6.62–7.70 (m, 8H, arom.); 1.52 (s, 6H, CH_3); 3.66 (s, 4H, CH_2); 0.22 (s, 3H, Si–CH_3).	−150.9
8	1595	—	838	564	496	6.56–7.73 (m, 13H, arom.); 1.54 (s, 6H, CH_3); 3.78 (s, 4H, CH_2).	−167.1

change has been noted.[18] Strong bands around 760 cm^{-1} may be due to ν (Si–C) vibrations.

NMR Spectra

The protons of the –OH groups of the ligand give signal at 12.35 ppm. This signal disappears completely in the complexes **5–8** resulting from dianion, suggesting deprotonation of both the –OH groups indicating the bonding of silicon with both the oxygen atoms. It appears as a signlet with an integration corresponding to one proton in the region 12.30–12.40 ppm in the spectra of the complexes **1–4**, suggesting deprotonation of only one –OH group and consequently forming one silicon-oxygen bond. The new proton signals in the region 0.22–0.26 ppm are due to the methyl protons attached to the silicon[19] (Table 1).

The ^{13}C NMR spectra of the compounds have been recorded in $CDCl_3$ relative to TMS, which is a good diagnostic tool for determining the mode of bonding. On coordination the resonances of the carbon atoms attached to the C=N and phenolic oxygen shift some 20–32 ppm downfield, suggesting coordination of both the C=N and phenolic oxygen groups to the metal atom.[5] The methyl groups attached to silicon display single resonance at 7.37 ppm for chemically equivalent carbons. Two resonances at 7.32 and 7.36 ppm appear with a 1 : 2 intensity ratio for one equatorial and two axial methyl groups in case of compound **1**.

The ^{29}Si NMR data (Table 1) support that silicon is hexa-coordinated[20] in all the complexes. Since the R group is bound directly to the ^{29}Si nucleus, it is not surprising that the value of δ depends primarily on the nature of this R group. When R = Phenyl the complexes give much more negative values of δ than when R = alkyl. Although the alkyl moiety has a greater electron 'pushing' capacity (σ donation) than the aryl, the delocalized π system in the phenyl compound allows for $d\pi$–$p\pi$ interaction to dominate the overall shielding of the ^{29}Si nucleus.[3b]

From the analytical and spectral data and the monomeric nature of the complexes, as evidenced from the molecular weights, it can be tentatively proposed the hexacoordinated environment around silicon atom in possibly octahedral geometry in the resulting complexes.

EXPERIMENTAL

Chemicals were obtained from Aldrich or Fluka and used as such. Solvents were purified according to the standard procedures.[21] All

Table 2. Synthetic, Physical, and Analytical Data of Compounds **1**–**8**

Compound/Mol. Wt. Found (Calcd.)	Reactants (g)			Molar Ratio	Yield (%)	M.P. (°C)	Analysis: % Found (Calcd.)				
	L	NaH	R_xSiCl_{4-x}				C	H	N	Si	Cl
1 $C_{21}H_{28}N_2O_2Si$ 367 (368)	0.59	0.048	0.217	1 : 1 : 1	72	170	68.05	7.24	7.36	7.40	–
	(2.0)	(2.0)	(2.0)				(68.48)	(7.61)	(7.61)	(7.61)	
2 $C_{20}H_{25}N_2O_2SiCl$ 388 (388.5)	0.59	0.048	0.258	1 : 1 : 1	68	172	61.36	6.20	7.06	7.42	9.37
	(2.0)	(2.0)	(2.0)				(61.78)	(6.44)	(7.21)	(7.21)	(9.14)
3 $C_{30}H_{29}N_2O_2SiCl$ 513 (512.5)	0.59	0.048	0.506	1 : 1 : 1	76	168	70.60	5.46	5.73	5.82	6.67
	(2.0)	(2.0)	(2.0)				(70.24)	(5.66)	(5.46)	(5.46)	(6.93)
4 $C_{19}H_{22}N_2O_2SiCl_2$ 410 (409)	0.59	0.048	0.299	1 : 1 :1	74	171	55.48	5.76	6.68	6.96	17.62
	(2.0)	(2.0)	(2.0)				(55.75)	(5.38)	(6.85)	(6.85)	(17.36)
5 $C_{20}H_{24}N_2O_2Si$ 351 (352)	0.59	0.096	0.258	1 : 2 : 1	66	173	68.44	6.67	8.22	7.76	–
	(2.0)	(4.0)	(2.0)				(68.18)	(6.82)	(7.95)	(7.95)	
6 $C_{30}H_{28}N_2O_2Si$ 475 (476)	0.59	0.096	0.506	1 : 2 : 1	71	174	75.32	5.76	5.63	5.98	–
	(2.0)	(4.0)	(2.0)				(75.63)	(5.88)	(5.88)	(5.88)	
7 $C_{19}H_{21}N_2O_2SiCl$ 373 (372.5)	0.59	0.096	0.299	1 : 2 : 1	69	168	61.12	5.46	7.76	7.84	9.82
	(2.0)	(4.0)	(2.0)				(61.21)	(5.64)	(7.52)	(7.52)	(9.53)
8 $C_{24}H_{23}N_2O_2SiCl$ 434 (434.5)	0.59	0.096	0.423	1 : 2 : 1	72	177	66.06	5.12	6.70	6.86	8.41
	(2.0)	(4.0)	(2.0)				(66.28)	(5.29)	(6.44)	(6.44)	(8.17)

operations were performed under nitrogen atmosphere using standard glassware. IR spectra were recorded as KBr discs on a 983 G Perkin-Elmer spectrophotometer. Melting points were determined using a calibrated thermometer by Remi Digital Melting Point Apparatus and are uncorrected. Elemental analyses were performed with a Carlo-Erba 1100 apparatus from the Central Drug Research Institute, Lucknow. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded at 270.13, 67.5 and 53.67 MHz, respectively on a Bruker AM 270 spectrometer. All chemical shifts are reported in parts per million (ppm) relative to TMS as an internal standard in $CDCl_3$.

The Schiff base *N*,*N*′-ethylene*bis*(2-hydroxyacetophenoneimine) was prepared by the condensation of 2-hydroxyacetophenone and ethylenediamine in 2 : 1 molar ratio in dry ethanol by literature method.[5] Yield, 76%, m.p. 186°C, Found: C, 72.44; H, 6.38; N, 9.12 Calcd. for $C_{18}H_{20}N_2O_2$ (296): C, 72.97; H, 6.76; N, 9.46%.

Reaction Between Trimethylsilicon(IV) Chloride and the Sodium Salt of *N*,*N*′-Ethylene*bis*(2-hydroxyacetophenoneimine) in a 1 : 1 Molar Ratio

Zero point zero four eight gram (2 mmol) of sodium hydride and 20 mL of isopropanol were taken in a two-way round bottom flask, fitted with a cooled water condenser alongwith two way balloon system. It was refluxed for about half an hour till a clear solution of sodium isopropoxide was obtained. After cooling, 0.59 g (2 mmol) of *N*,*N*′-ethylene*bis*(2-hydroxyacetophenoneimine) was added slowly at room temperature. The mixture was stirred under reflux for 6 h. The solution became light brown which was allowed to attain room temperature. Trimethylsilicon(IV) chloride (0.217 g, 2 mmol) was added dropwise with a static-pressure dropping funnel. The solution became yellow, and the reaction mixture was again refluxed for 2 h to ensure the completion of the reaction. The precipitated sodium chloride was removed by filtration. Removal of the solvent under reduced pressure gave the product, which was isolated and purified by column chromatography to give the compound **1**.

All other organosilicon(IV) derivatives of the Schiff base ligand were synthesized analogously as described above in desired molar ratios. The synthetic, physical and analytical data of the compounds are given in Table 2.

ACKNOWLEDGMENT

The authors are highly thankful to Council of Scientific and Industrial Research, New Delhi for providing financial assistance sanctioning scheme No. 01(1561)/98/EMR-II.

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Received in the Netherlands November 26, 2001

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