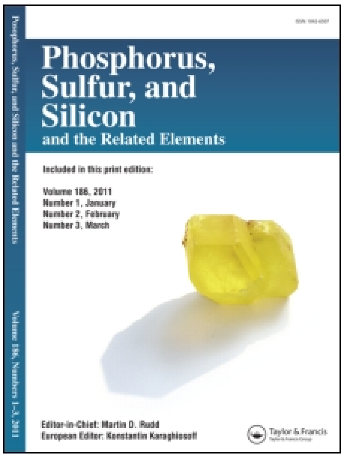

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SYNTHESIS AND SPECTROSCOPIC [IR, NMR (^{1}H, ^{13}C, ^{29}Si)] CHARACTERIZATION OF METHYLSILYL N-ARYLSALICYLALDIMINATES

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Reactions of $MeSiCl_3$ in 1:1, 1:2, and 1:3 molar ratios with $HOC_6H_4CH{=}NAr$ (Ar = $C_6H_3Me_2$-2,6; $C_6H_2Me_3$-2,4,6; and $C_6H_3Et_2$-2,6) in the presence of Et_3N or C_5H_5N as a base afford compounds of the type $MeSiCl_{3-x}(OC_6H_4CH{=}NAr)_x$ (x = 1, 2, and 3). Characterization of all these species have been carried out by elemental analysis, molecular weight determinations, and spectroscopic [IR, NMR (^{1}H, ^{13}C and ^{29}Si)] studies.

Keywords: Methylsilyl compounds; Schiff base complexes; N-arylsalicylaldiminates

INTRODUCTION

Derivatives of silicon containing monofunctional bidentate Schiff base ligands have attracted considerable attention during the last 25 years.(1) Most of these have been conveniently prepared by reacting silicon tetraacetate with monofunctional bidentate Schiff bases.(2,3) Examples in the literature(4) are also available for molecular adducts of the types, $Me_2SiCl_2.2SBH$ and $Ph_2SiCl_2.2SBH$ (where SBH is a β-ketoamine). In all these derivatives the silicon is reported to be in a hypervalent state (*i.e.* coordination number 5/6).

In view of the above, it was considered worthwhile to investigate by spectroscopic methods methylsilicon derivatives containing monofunctional bidentate salicylaldiminate ligands, for the possibility of intramo-

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lecular coordination of azomethine nitrogen to the silicon atom. We, therefore, report herein for the first time, the synthesis and spectroscopic properties of methyl silicon N-arylsalicylaldiminates. These studies assume special significance in view of our earlier observations about the shielding with respect to $SiCl_4$ and $MeSiCl_3$ of the silicon nucleus in derivatives of the types $SiCl_2(OAr)_2$,$SiCl(OAr)_3$, $MeSi(OAr)_3$ ($OAr = OC_6H_3Me_2$-2,6)(5), and $MeSi(OC_6H_3Pr^i_2\text{-}2,6)_3$(6), wherein there is no possibility of enhancing the coordination number of silicon by intra- or intermolecular association. Such results were interpreted on the basis of p_π-d_π bonding involving the lone pair of electrons on aryloxide oxygen and vacant d-orbital of the silicon.

RESULTS AND DISCUSSION

SYNTHESIS

Reactions in 1:1, 1:2, and 1:3 molar ratios of $MeSiCl_3$ with $HOC_6H_4CH{=}NAr$ ($Ar = C_6H_3Me_2$-2,6; $C_6H_2Me_3$-2,4,6; and $C_6H_3Et_2$-2,6) in benzene using Et_3N/C_6H_5N as a base yield derivatives of the type $MeSiCl_{3-x}(OC_6H_4CH{=}NAr)_x$, (eq. (i)):

$$\text{(i)}\quad MeSiCl_3 + x\,HOC_6H_4CH{=}NAr + x\,Et_3N \xrightarrow{C_6H_6} MeSiCl_{3-x}(OC_6H_4CH{=}NAr)_x + x\,Et_3N.HCl\downarrow$$

(1) : $Ar = C_6H_2Me_3$-2,4,6 ($x = 1$); **(2)** : $Ar = C_6H_3Et_2$-2,6($x = 1$);
(3) : $Ar = C_6H_3Me_2$-2,6($x = 2$); **(4)** : $Ar = C_6H_2Me_3$-2,4,6($x = 2$);
(5) : $Ar = C_6H_3Et_2$-2,6($x = 2$); **(6)** : $Ar = C_6H_3Et_2$-2,6 ($x = 3$)

Alternatively, $MeSi(OC_6H_4CH{=}NAr)Cl_2$ can be prepared by the direct equimolar interaction of $MeSiCl_3$ with $HOC_6H_4CH = NAr$ in refluxing benzene (eq. (ii)):

$$\text{(ii)}\quad MeSiCl_3 + HOC_6H_4CH = NC_6H_2Me_3\text{-}2,4,6 \xrightarrow{C_6H_6} MeSi(OC_6H_4CH{=}NC_6H_2Me_3\text{-}2,4,6)Cl_2 + HCl\uparrow$$

GENERAL PROPERTIES

The new derivatives (**1**)-(**6**) (TABLE I) are moisture sensitive, orange coloured solids or liquids, soluble in organic solvents (benzene, toluene, carbon tetrachloride, dichloromethane), and depict monomeric behaviour (ebullioscopically) in benzene. The solid derivatives (**1**) and (**4**) melt at 55°C and 60°C, respectively. The derivatives (**2**), (**3**), (**5**), and (**6**), which are liquids, could not be volatilized upto 300°C/0.5 mm.

TABLE I Preparative and analytical data for methylsilyl N-arylsalicylaldiminates

Reactants (g, mmol)	Product Yield (g, %), Colour and state	Analysis (%) Found (Calcd.)			Molecular weight Found (Calcd.)
		Si	N	Cl	
$MeSiCl_3$(2.22, 14.85) + $HOC_6H_4CH{=}NC_6H_2Me_3$-2,4,6(3.55, 14.83) + Et_3N(1.52, 15.02)	$MeSi(OC_6H_4CH{=}NC_6H_2Me_3$-2,4,6$)Cl_2$(**1**) (5.08, 97) Orange solid	7.94 (7.97)	3.82 (3.97)	20.01 (20.16)	350 (352)
$MeSiCl_3$(3.05, 20.39) + $HOC_6H_4CH{=}NC_6H_3Et_2$-2,6(5.09, 20.12) + Et_3N(2.08, 20.62)	$MeSi(OC_6H_4CH{=}NC_6H_3Et_2$-2,6$)Cl_2$(**2**) (6.95, 94) Orange liquid	7.61 (7.67)	3.71 (3.82)	19.13 (19.35)	370 (366)
$MeSiCl_3$(2.47, 16.52) + $HOC_6H_4CH{=}NC_6H_3Me_2$-2,6(7.44, 33.01) + Et_3N(3.35, 33.11)	$MeSi(OC_6H_4CH{=}NC_6H_3Me_2$-2,6$)_2Cl$(**3**) (8.42, 97) Orange liquid	5.30 (5.32)	5.27 (5.31)	6.70 (6.72)	520 (527)
$MeSiCl_3$(1.46, 9.77) + $HOC_6H_4CH{=}NC_6H_2Me_3$-2,4,6(4.66, 19.47) + C_5H_5N(1.54, 19.55)	$MeSi(OC_6H_4CH{=}NC_6H_2Me_3$-2,4,6$)_2Cl$(**4**) (5.20, 95) Orange solid	5.02 (5.05)	5.12 (5.05)	6.33 (6.39)	560 (555)
$MeSiCl_3$(2.58, 17.28) + $HOC_6H_4CH{=}NC_6H_3Et_2$-2,6(8.74, 34.54) - Et_3N(3.51, 34.69)	$MeSi(OC_6H_4CH{-}NC_6H_3Et_2$-2,6$)_2Cl$(**5**) (9.60, 95) Orange viscious liquid	4.76 (4.81)	4.71 (4.80)	6.01 (6.07)	575 (583)
$MeSiCl_3$(1.01, 6.78) + $HOC_6H_4CH{=}NC_6H_3Et_2$-2,6(5.15, 20.33) + Et_3N(2.05, 20.56)	$MeSi(OC_6H_4CH{=}NC_6H_3Et_2$-2,6$)_3$ (**6**) (5.32, 98) Orange liquid	3.43 (3.50)	5.20 (5.25)	-	817 (800)

SPECTROSCOPIC PROPERTIES

IR Spectra

IR spectra (TABLE II) of (**1**)-(**6**) exhibit: (i) the absence of a broad absorption band characteristic of the OH group in the region of 3250–3550 cm^{-1}, (ii) absorptions due to ν(C=N) at 1624–1632 cm^{-1}, (iii)ν(C-O)(7) at 1285–1308 cm^{-1}, which depict a higher frequency shift of about ~25±10 cm^{-1} with respect to the parent ligands, (iv) appearance of a new intense band at 900–910 cm^{-1}, assignable(8,9) to ν(Si-O), (v) strong absorption at 1244–

1270 and 773–788 cm^{-1} due to Si-CH_3 symmetric deformation and Si-C stretching, respectively(10–12), and (vi) absorption(11,12) due to ν(Si-Cl) at 560 cm^{-1}.

^1H NMR Spectra

As expected, the signal due to the phenolic OH of the N-arylsalicylaldimines at ~δ13.4 is absent in the ^1H NMR spectra of the derivatives (**1**)-(**6**) (TABLE III). A singlet due to the azomethine proton, which appears at δ 8.42–8.78, exhibits a very small downfield shift with respect to the parent ligands. The aromatic protons appear as multiplets in the region δ 6.88–7.89. Ethyl groups of the aniline moiety in (**2**), (**5**) and (**6**) show a triplet and a quartet in the region δ 1.17–1.18 (CH_2CH_3) and 2.63–2.66 (CH_2CH_3), respectively. The methyl protons in (**1**) and (**4**) appear as two singlets at δ 2.19 (Me_2-2,6) and 2.32 (Me-4). The derivative (**3**) exhibits a singlet at δ 2.24 (Me_2-2,6). The hydrogens of the Me-Si group appears as a singlet at δ 0.10–0.13.

^{13}C NMR Spectra

The ^{13}C NMR spectra of (**1**)-(**6**) (TABLE IV) show signals due to C-O and CH=N carbons in the range δ 156.45–157.10 and 152.11–152.44, respectively. These signals exhibit an upfield shift of 8.5 ± 0.5 and 9.5±0.5 ppm for C-O and CH=N group, respectively. The higher field shifting ^{13}C signals of C-O can be explained on the basis of +I effect of the methyl group attached to the Si atom, causing an enhanced electron density around the silicon centre. The shift of ^{13}C NMR signals of the C=N group to higher field may be interpreted in terms of non-involvement of intramolecular coordination through the azomethine nitrogen. The ^{13}C NMR signals for aromatic carbons appear in the range δ 116–97–134.35. The ^{13}C NMR signals due to the ethyl and methyl groups present on the aniline moiety appear in the region δ 14.59–24.59. The carbons of the methyl groups attached to the silicon atom appear at δ(-5.47 to +0.12).

^{29}Si NMR Spectra

The compounds (**1**)-(**6**) show ^{29}Si NMR signals (TABLE III) in the range δ- (47.6 to 70.4), consistent with a tetrahedral(13–16) geometry for these methylsilyl N-arylsalicylaldiminate derivatives.

TABLE II IR data(cm^{-1}) for methylsilyl N-arylsalicylaldiminates

Compounds	*ν(C=N)*	*ν(C-O)*	*ν(Si-O)*	*ν(Si-CH$_3$) deformation*	*ν(Si-C) stretching*	*ν(Si-Cl)*
MeSi(OC$_6$H$_4$CH=NC$_6$H$_2$Me$_3$-2,4,6)Cl$_2$(**1**)	1624s	1285s	905s	1270vs	776m	560w
MeSi(OC$_6$H$_4$CH=NC$_6$H$_3$Et$_2$-2,6)Cl$_2$(**2**)	1628s	1288s	905m	1259vs	788m	559w
MeSi(OC$_6$H$_4$CH=NC$_6$H$_3$Me$_2$-2,6)$_2$Cl(**3**)	1629s	1288s	907m	1251s	773m	559w
MeSi(OC$_6$H$_4$CH=NC$_6$H$_2$Me$_3$-2,4,6)$_2$Cl(**4**)	1625s	1290s	905m	1251vs	773m	560w
MeSi(OC$_6$H$_4$CH=NC$_6$H$_3$Et$_2$-2,6)$_2$Cl(**5**)	1632s	1307s	900m	1244s	788m	560w
MeSi(OC$_6$H$_4$CH=NC$_6$H$_3$Et$_2$-2,6)$_3$(**6**)	1632s	1308s	909s	1244s	778m	-

Abbreviations: m = medium, s = strong, vs = very strong, and w = weak.

TABLE III ^{1}H and ^{29}Si NMR data(δ, ppm) for methylsilyl N- arylsalicylaldiminates

Compound	CH=N	Ar-H	Me/Et	Me Si	^{29}Si
$MeSi(OC_6H_4CH=NC_6H_2Me_3\text{-}2,4,6)Cl_2$(1)	8.42(s,1H)	6.88–7.64(m, 6H)	2.19(s, 6H, CH_3-2,6) 2.32(s, 3H, CH_3-4)	0.13(s,3H)	− 62.5
$MeSi(OC_6H_4CH=NC_6H_3Et_2\text{-}2,6)Cl_2$(2)	8.63(s,1H)	7.00–7.90(m,7H)	1.17(t, 6H, CH_2CH_3) 2.65(q, 4H,CH_2CH_3	0.13(s,3H)	−47.5
$MeSi(OC_6H_4CH=NC_6H_3Me_2\text{-}2,6)_2Cl$(3)	8.78(s,2H)	6.93–7.74(m,14H)	2.24(s, 12H, CH_3-2,6)	0.11(s,3H)	−49.6
$MeSi(OC_6H_4CH=NC_6H_2Me_3\text{-}2,4,6)_2Cl$(4)	8.45(s,2H)	6.93–7.59(m,12H)	2.19(s, 12H, CH_3-2,6) 2.32(s,6H, CH_3-4)	0.11(s,3H)	−70.4
$MeSi(OC_6H_4CH=NC_6H_3Et_2\text{-}2,6)_2Cl$(5)	8.62(s,2H)	7.07–7.89(m,14H)	1.17(t, 12H, CH_2CH_3) 2.63(q,8H,CH_2CH_3)	0.12(s,3H)	−50.3
$MeSi(OC_6H_4CH=NC_6H_3Et_2\text{-}2,6)_3$ (6)	8.64(s,3H)	7.02–7.86(m,21H)	1.18(t, 18H, CH_2CH_3) 2.66(q,12H,CH_2CH_3)	0.10(s,3H)	− 54.5

TABLE IV ^{13}C NMR data (δ, ppm) for methylsilyl N- arylsalicylaldiminates

Compound	*C-O*	*CH=N*	*=N-C(Aniline)*	*Other aromatic carbons*	*Et/Me*	*Me-Si*
$MeSi(OC_6H_4CH{=}NC_6H_2Me_3\text{-}2,4,6)Cl_2$(1)	156.68	152.47	150.95	134.5–117.40	20.81(CH_3-2,6) 18.48(CH_3-4)	0.12
$MeSi(OC_6H_4CH{=}NC_6H_3Et_2\text{-}2,6)Cl_2$(2)	156.45	152.11	150.65	132.88–117.47	24.59(CH_2CH_3) 14.67(CH_2CH_3)	−0.27
$MeSi(OC_6H_4CH{=}NC_6H_3Me_2\text{-}2,6)_2Cl$(3)	157.10	152.44	151.35	132.83–119.28	18.41(CH_3)	−0.38
$MeSi(OC_6H_4CH{=}NC_6H_2Me_3\text{-}2,4,6)_2Cl$(4)	156.71	152.39	151.27	133.93–116.97	20.43($CH_3$2,6) 18.05(CH_3-4)	−0.74
$MeSi(OC_6H_4CH{=}NC_6H_3Et_2\text{-}2,6)_2Cl$(5)	156.57	152.33	150.73	133.01–117.40	24.63(CH_2CH_3) 14.64(CH_2CH_3)	−3.49
$MeSi(OC_6H_4CH{=}NC_6H_3Et_2\text{-}2,6)_3$ (6)	156.61	152.49	150.70	133.75–117.39	24.59(CH_2CH_3) 14.59(CH_2CH_3)	−5.47

EXPERIMENTAL

All reactions and manipulations were performed under anhydrous conditions. The (BDH) solvents were dried by refluxing over appropriate drying agents given in parentheses: benzene, *n*-hexane (Na/benzophenone), $CCl_4(P_2O_5)$ and distilled prior to use. Triethylamine and pyridine were dried by keeping first over KOH pallets for ~48h and then refluxing for a period of ~7h, followed by distillation (b.p. 88.8°C (Et_3N), 115°C(C_5H_5N)). Methylsilyl trichloride (Fluka) was distilled prior to use (b.p. 66°C). The novel N-arylsalicylaldimines were prepared by equimolar condensation of salicylaldehyde and substituted anilines in the presence of isopropyl alcohol in benzene with continuous removal of liberated H_2O as a ternary H_2O-C_6H_6-Pr^iOH azeotrope. After completion of the reaction, the volatile components from the solution were removed under reduced pressure. Analytically pure compounds were obtained by distillation.

Nitrogen and chlorine were estimated by Kjeldahl's or Volhard's methods,(17) respectively. Silicon was determined as SiO_2. ^1H (89.55 MHz) and ^{13}C (22.49 MHz) NMR spectra were recorded in $CDCl_3$ and CCl_4 solutions, repsectively, on a JEOL FX-90Q spectrometer using TMS as an internal reference. ^{29}Si (17.75 MHz) NMR spectra of the compounds were recorded in CCl_4 solutions using TMS as an external reference. IR spectra (4000–200 cm^{-1}) were recorded as Nujol mulls using CsI optics on a Nicolet Magna 550 spectrophotometer. Molecular weights were determined ebullioscopically in benzene using a Gallenkamp ebulliometer.

PREPARATION OF METHYLSILYL N-ARYLSALICYLALDIMINATES

As similar procedure was used to obtain most of the complexes listed in TABLE I, only two typical preparations are being described below. Preparative and analytical data for the new compounds are listed in TABLE I.

Synthesis of $MeSi(OC_6H_4CH{=}NC_6H_3Me_2\text{-}2,6)_2Cl$ (3)

To a benzene (~40 ml) solution of $HOC_6H_4CH{=}NC_6H_3Me_2$-2,6 (7.44 g, 33.01 mmol) and Et_3N(3.35 g, 33.11 mmol) was added $MeSiCl_3$ (2.47 g, 16.52 mmol) dissolved in benzene (~20 ml). The reaction mixture after stirring at room temperature for ~12h, was allowed to reflux for ~2h. The precipitated $Et_3N.HCl$ (4.52 g, 32.85 mmol) was filtered out. Removal of volatile components from the filtrate under reduced pressure afforded an orange coloured liquid. Yield 8.42 g (97%). Further details are summarized in TABLE I.

Synthesis of $MeSiCl_2(OC_6H_4CH=NC_6H_2Me_3$-2,4,6) (1) by the direct reaction of $MeSiCl_3$ with $HOC_6H_4CH=NC_6H_2Me_3$-2,4,6

A benzene (~30 ml) solution containing $MeSiCl_3$ (2.55 g, 17.07 mmol) and $HOC_6H_4CH=NC_6H_2Me_3$-2,4,6 (4.07 g, 17.03 mmol) was refluxed (~5h) till the evolution of HCl gas ceased. The solvent was removed under reduced pressure to afford an orange coloured solid which was recrystallized from a (1:3) mixture of *n*-hexane and toluene at –20°C. Yield 5.23 g (86%). The compound on analysis was found to have: Si, 7.89; N, 3.87; Cl, 20.06%. Calcd. for $C_{17}H_{19}Cl_2NOSi$: Si, 7.97; N, 3.97; Cl, 20.16%.

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