SYNTHESIS, REACTIONS, AND SPECTRAL (IR, ^{1}H, ^{13}C AND ^{29}Si) CHARACTERIZATION OF ORGANOSILICON ARYLOXIDES

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Abstract

Organosilicon aryloxides of the types $Me_nSi(OAr)_{4-n}$(n = 1,2 and 3; OAr = $OC_6H_3Me_2$-2,6; $OC_6H_3Me_2$-3,4;$OC_6H_3Me_2$-3,5; $OC_6H_3Pr^i_2$-2,6; $OC_6H_2Me_3$-2,4,6; $OC_6H_3Bu^t_2$-2,6; $OC_6H_2Bu^t_3$-2,4,6),and two silicon (IV) aryloxide derivatives $ClSi(OC_6H_3Me_2\text{-}2,6)_3$ and $Si(OC_6H_3Me_2\text{-}2,6)_4$ have been prepared by the reactions of Me_nSiCl_{4-n} or $SiCl_4$ and an appropriate substituted phenol in desired molar ratios using pyridine as proton acceptor in benzene. The reactions of $Me_3Si(OAr)$(OAr = $OC_6H_3Me_2$-3,5 or $OC_6H_3Me_2$-3,4) with $TiCl_4$ (or $NbCl_5$) in 1:1 and 1:2 molar ratios have produced corresponding mono-and bis-(aryloxo) derivatives of Ti(IV) and Nb(V) respectively. All these derivatives have been characterized by elemental analysis, molecular weight measurements and spectral (IR and multinuclear NMR) studies.

Introduction

Considerable amount of work have been carried out on silicon alkoxides[1-4] including their use in the preparation of glass ceramic materials by the Sol-Gel[5,6] technique, by contrast only a few simple[7,8] and sterically demanding silicon (IV) and organosilicon (IV) aryloxides have been described so far and for none of these ^{29}Si NMR data are yet available. We therefore, report in this paper the synthesis, chemistry, and spectral characterization of substituted phenoxide derivatives containing organosilicon (IV) and silicon (IV) moieties.

Results and Discussion

Organosilicon- and silicon (IV) aryloxides have been prepared by the reactions of the corresponding chlorosilanes with an appropriate substituted phenol in desired molar ratios in the presence of pyridine in benzene:

$$Me_{4-n}SiCl_n + n\ ArOH + n\ C_5H_5N \xrightarrow{C_6H_6} Me_{4-n}Si(OAr)_n + C_5H_5N.HCl\downarrow$$

1: n = 1,OAr = $OC_6H_3Me_2$-2,6; **2**: n = 1, OAr = $OC_6H_3Me_2$-3,4

3: n = 1, OAr = $OC_6H_3Me_2$-3,5; **4**: n = 1, OAr = $OC_6H_3Pr^i_2$-2,6

5: n = 1, OAr = $OC_6H_2Me_3$-2,4,6; **6**: n = 2, OAr = $OC_6H_3Me_2$-2,6

7: n = 3, OAr = $OC_6H_3Me_2$-2,6; **8**: n = 1,OAr = OC_6H_5

As Me_3SiCl and $HOC_6H_3Bu^t_2$-2,6 do not react in presence of C_5H_5N to any appreciable extent, the synthesis of $Me_3SiOC_6H_3Bu^t_2$-2,6 has been achieved by a modified procedure as shown below :

$$Me_3SiCl + KOAr \xrightarrow{C_6H_6/THF} Me_3SiOAr + KCl\downarrow$$

9: OAr = $OC_6H_3Bu^t_2$-2,6; **10**: OAr = $OC_6H_2Bu^t_3$-2,4,6

Although reactions of $SiCl_4$ with $HOC_6H_3Me_2$-2,6 in 1:1 and 1:2 molar ratios could lead to the formation of the desired mono- and bis- products even in the absence of pyridine in refluxing benzene, that the synthesis of tris- and tetrakis-derivatives required the use of C_5H_5N as a proton acceptor:

$$SiCl_4 + n\ HOC_6H_3Me_2\text{-}2,6 \xrightarrow{C_6H_6} SiCl_{4-n}(OC_6H_3Me_2\text{-}2,6)_n + nHCl\uparrow$$

11: n = 1; **12**: n = 2

$$SiCl_4 + n\ HOC_6H_3Me_2\text{-}2,6 + n\ C_5H_5N \xrightarrow{C_6H_6} SiCl_{4-n}(OC_6H_3Me_2\text{-}2,6)_n + n\ C_5H_5N.HCl\downarrow$$

13: n = 3; **14**: n = 4

In view of the fact that synthesis of $Si(OC_6H_3Me_2\text{-}2,6)_4$ by the reaction of $SiCl_4$ and $HOC_6H_3Me_2$-2,6 in the presence of pyridine in refluxing benzene required 36 h, an alternative and convenient route for the preparation of the above derivative has been designed according to the reaction shown below:

$$SiCl_4 + 4\ NaOC_6H_3Me_2\text{-}2,6 \xrightarrow{C_6H_6} Si(OC_6H_3Me_2\text{-}2,6)_4 + 4\ NaCl\downarrow$$

All these derivatives are highly moisture sensitive, colourless liquids to yellowish white

Table 1 Preparative and analytical data[a] for aryloxo derivatives of silicon (IV)

Reactants (g, mmol)			Product (Colour & state)	Yield g(%)	B.P. °C/mm	Analysis %			Mol. wt.
						Si	C	H	
Me_3SiCl + (2.85,26.22)	$HOC_6H_3Me_2$-2,6 + (3.01,24.66)	CHN (2.07,26.1)	$Me_3SiOC_6H_3Me_2$-2,6 (**1**) Colourless liquid	3.90(82)	90-95.8	14.72 (14.46)	68.04 (68)	9.30 (9.34)	198 (194)
Me_3SiCl + (2.86,26.38)	$HOC_6H_3Me_2$-3,4 + (3.11,25.47)	CHN (2.11,26.62)	$Me_3SiOC_6H_3Me_2$-3,4 (**2**) Colourless liquid	4.57(93)	110.8	14.47 (14.46)	68.02 (68)	9.32 (9.34)	196 (194)
Me_3SiCl + (2.89,26.62)	$HOC_6H_3Me_2$-3,5 + (3.11,25.47)	C_5H_5N (1.45,25.2)	$Me_3SiOC_6H_3Me_2$-3,5 (**3**) Colourless liquid	4.42(90)	95-100.9	14.32 (14.46)	68.02 (68)	9.32 (9.34)	196 (194)
Me_3SiCl + (1.84,16.97)	$HOC_6H_3Pr^i_2$-2,6 + (3.01,16.88)	C_5H_5N (1.37,17.37)	$Me_3SiOC_6H_3Pr^i_2$-2,6 (**4**) Colourless liquid	3.58(85)	85.9	11.20 (11.22)	71.96 (71.92)	10.52 (10.47)	260 (250)
Me_3SiCl + (2.45,22.55)	$HOC_6H_2Me_3$-2,4,6 + (2.81,20.69)	C_5H_5N (1.77,22.36)	$Me_3SiOC_6H_2Me_3$-2,4,6 (**5**) Colourless liquid	3.89(91)	95-110.8	13.61 (13.48)	69.28 (69.15)	9.73 (9.69)	215 (208)
Me_2SiCl_2 + (2.46,19.19)	2$HOC_6H_3Me_2$-2,6 + (4.64,38.00)	2C_5H_5N (3.10,39.2)	$Me_2Si(OC_6H_3Me_2$-2,6$)_2$ (**6**) Colourless liquid	5.12(89)	145.1	9.32 (9.35)	71.92 (71.94)	8.15 (8.05)	305 (300)
$MeSiCl_3$ + (1.23,8.26)	3$HOC_6H_3Me_2$-2,6 + (3.02,24.75)	3C_5H_5N (2.03,25.61)	$MeSi(OC_6H_3Me_2$-2,6$)_3$[e] (**7**) White solid	3.28(98)	(86)e	6.85 (6.91)	73.88 (73.83)	7.43 (7.44)	410 (405)
Me_3SiCl + (2.85,26.26)	HOC_6H_5 + (2.46,26.15)	C_5H_5N (0.36,9.28)	$Me_3SiOC_6H_5$ (**8**) Colourless liquid	3.88(91)	75-80.8	16.96 (16.90)	64.89 (64.98)	8.42 (8.49)	169 (166)
Me_3SiCl + (1.19,10.94)	$HOC_6H_3Bu^t_2$-2,6 + (1.93,9.35)	K (0.36,9.28)	$Me_3SiOC_6H_3Bu^t_2$-2,6 (**9**) Pale yellow solid	2.26(88)	130-140.8 (60)	10.41 (10.09)	73.60 (73.30)	10.92 (10.86)	285 (278)
Me_3SiCl + (0.56,5.15)	$HOC_6H_2Bu^t_3$-2,4,6 + (1.06,4.06)	K (0.16,4.13)	$Me_3SiOC_6H_2Bu^t_3$-2,4,6 (**10**) Pale yellow solid	1.25(93)	140-150.8 (64)	8.61 (8.40)	75.42 (75.36)	11.48 (11.45)	340 (334)
$SiCl_4$ + (2.17,12.78)	$HOC_6H_3Me_2$-2,6 (1.53,12.53)		$SiCl_3OC_6H_3Me_2$-2,6[b] (**11**) colourless liquid	2.46(77)	130.8	11.00 (10.99)	37.60 (37.58)	3.60 (3.55)	270 (255)
$SiCl_4$ + (1.04,6.13)	2$HOC_6H_3Me_2$-2,6 (1.48,12.18)		$SiCl_2(OC_6H_3Me_2$-2,6$)_2$[c] (**12**) colourless liquid	1.98(94)	135.8	8.24 (8.23)	56.30 (56.31)	5.30 (5.32)	350 (341)
$SiCl_4$ + (1.25,7.36)	3$HOC_6H_3Me_2$-2,6 + (2.66,21.78)	3C_5H_5N (1.78,22.51)	$Si(Cl)(OC_6H_3Me_2$-2,6$)_3$[d] (**13**) Light yellow liquid	3.14(98)	150.8	6.52 (6.58)	67.54 (67.49)	6.40 (6.38)	428 (426)
$SiCl_4$ + (2.48,14.59)	4$HOC_6H_3Me_2$-2,6 + (7.07,57.95)	4C_5H_5N (4.65,58.78)	$Si(OC_6H_3Me_2$-2,6$)_4$[e] (**14**) White solid	4.07(94)	(90)e	5.44 (5.48)	74.10 (74.95)	7.18 (7.08)	520 (512)

[a] Calculated values in parentheses. [b] % Cl=41.57(41.63). [c] % Cl=20.62(20.79). [d] % Cl=8.32(8.31). [e] Recrystallized from n-hexane at -20°C.

Table 2 Reaction of $TiCl_4$ or $NbCl_5$ with trimethylsilicon aryloxides

Reactants (g, mmol)			Product (Colour & state)	Yield g(%)	Ti/Nb	Analysis[a] % Cl	C	H	Mol. wt[a].	M.P°C
$Me_3SiOC_6H_3Me_2$-3,5 (0.53,2.73)	+	$TiCl_4$ (0.51,2.68)	$TiCl_3(OC_6H_3Me_2$-3,5) (**15**) Red solid	0.70(93)	17.20 (17.40)	38.60 (38.70)	35.01 (34.90)	3.31 (3.20)	528 (275)	82
$2Me_3SiOC_6H_3Me_2$-3,5 (0.97,4.89)	+	$TiCl_4$ (0.51,2.71)	$TiCl_2(OC_6H_3Me_2$-3,5)$_2$ (**16**) Red solid	0.84(93)	13.20 (13.27)	19.37 (19.65)	53.24 (53.22)	5.04 (5.03)	664 (361)	90
$Me_3SiOC_6H_3Me_2$-3,4 (0.99,5.14)	+	$NbCl_5$ (1.35,5.00)	$NbCl_4(OC_6H_3Me_2$-3,4) (**17**) Red solid	1.56(87)	25.30 (25.52)	38.90 (39.80)	27.08 (26.97)	2.58 (2.54)	665 (356)	85
$2Me_3SiOC_6H_3Me_2$-3,5 (0.82,4.2)	+	$NbCl_5$ (0.58,2.14)	$NbCl_3(OC_6H_3Me_2$-3,5)$_2$ (**18**) Red solid	0.90(95)	21.00 (21.05)	24.00 (24.10)	43.52 (43.51)	4.10 (4.11)	870 (441)	93

[a]Calculated values in parentheses.

crystalline solids (Table-1) soluble in common organic solvents (e.g., benzene, toluene, CCl_4, n-hexane, etc.), and monomeric (ebullioscopically) in benzene. These new silicon aryloxide derivatives have been purified either by distillation under reduced pressure or crystallization from n-hexane at -20°C.

Reactions of organosilicon aryloxides with covalent metal chlorides (e.g.,$TiCl_4$ and $NbCl_5$) in 1:1 and 1:2 molar ratios yield quantitatively mono- and bis- substituted aryloxide derivatives according to the following reactions:

$$TiCl_4 + n\ Me_3SiOAr \longrightarrow TiCl_{4-n}(OAr)_n + n\ Me_3SiCl$$

$$NbCl_5 + n\ Me_3SiOAr \xrightarrow[CH_2Cl_2]{\text{n-hexane}} NbCl_{5-n}(OAr)_n + n\ Me_3SiCl$$

15: OAr = $OC_6H_3Me_2$-3,5; n = 1; **16**: OAr = $OC_6H_3Me_2$-3,5; n = 2

17: OAr = $OC_6H_3Me_2$-3,4; n = 1; **18**: OAr = $OC_6H_3Me_2$-3,5; n = 2

These transition metal chloride-aryloxide derivatives (Table-2) are dark red coloured, moisture sensitive solids soluble in benzene, toluene, dichloromethane, and dimeric ebullioscopically in benzene. All these new derivatives can be recrystallized from hot n-hexane at room temperature. By contrast reactions in 1:1 and 1:2 molar ratios of $TiCl_4$ or $NbCl_5$ with $Me_3SiOC_6H_3Me_2$-2,6 in THF have been reported to yield monomeric solvated products.[10]

These reactions are of considerable utility because they provide a neat and high yield synthesis of mono-aryloxo derivatives of the early transition metals and it avoids the formation of HCl, KCl, or ammonium salt which are often difficult to remove completely, whereas, the liberated Me_3SiCl is easily removed by distillation. Furthermore, preparation of these types of derivatives by other routes like reactions of metal chlorides with: (i) phenols, or (ii) alkali metal aryloxides[11] generally yield mixture of products.

The ^{1}H NMR spectrum of $TiCl_3(OC_6H_3Me_2$-3,5) exhibits signals at δ 2.19 (3,5-Me), 6.48 (aromatic *ortho*-H), 6.57 (aromatic *para*-H), for $TiCl_2(OC_6H_3Me_2$-3,5)$_2$ signals are observed at δ 2.21 (3,5-Me), 6.66 (aromatic *ortho*-H), 6.75(aromatic *para*-H). The niobium derivative $NbCl_4(OC_6H_3Me_2$-3,4) exhibits signals at δ 2.14 and 2.23 (3,4-Me), 6.26-7.19 (br, aromatic-H), while those of $NbCl_3(OC_6H_3Me_2$-3,4)$_2$ shows signals at δ 2.28 (3,5-Me), 6.48 (aromatic *ortho*-H), and at 6.57 (aromatic *para*-H).

The ^{1}H NMR spectra of the organosilicon aryloxides (Table-**3**) show the absence of the signal in the region δ 4.47-5.29 due to the phenolic OH, a feature characterstic of

Table 3 NMR(^{1}H,^{29}Si) data[a] (δ, ppm) for aryloxo derivatives

Compound	Me-Si	C_6H_3/C_6H_2	C_6H_3(or C_6H_2)-Me/Pr^i/Bu^t	^{29}Si NMR data in $CDCl_3$ (δ, ppm)
1	0.25(s,9H)	6.72-7.06(m,3H)	2.22(s,5H,Me)	+19.2
		(6.66-7.07)	(2.25)	
2	0.25(s,9H)	6.43-6.68(m,3H)	2.18(s,3H,Me),2.28(s,3H,Me)	+18.92
		(6.53-7.06)	(2.19)	
3	0.24(s,9H)	6.64(d,2H,*Ortho*-H)		-
		(6.57)	2.19(s,6H,Me)	
		7.02(t,1H,*para*-H)	(2.28)	
		(6.66)		
4	0.27(s,9H)	6.97-7.24(m,3H)	1.20(d,J= 6Hz,12H,Me) 3.19(sep,2H,CH)	+16.73
		(6.88-7.24)		
5	0.25(s,9H)	6.79(s,2H)	2.18(s,6H,Me-2,6),2.22(s,3H,Me-4)	-
		(6.84)	(2.23)	
6	0.36(s,6H)	6.79-7.19(m,6H)	2.32(s,12H,Me)	-7.95
7	0.45(s,3H)	6.75-7.15(m,9H)	2.19(s,18H,Me)	-67.61
9	0.35(s,9H)	6.65-7.35(m,3H)	1.36(s,18H,Bu)	+13.7
		(6.79-7.37)	(1.47)	
8	0.22(s,9H)	6.84-7.46(m,5H)	-	+23.5
10	0.39(s,9H)	7.19(s,2H)	1.29(s,9H,Bu-4),1.43(s,18H,Bu'-2,6)	-
		(7.02)	(1.52) (1.84)	-
11	-	6.75-7.15(m,3H)	2.32(s,6H,Me)	-43
12	-	6.75-7.15(m,6H)	2.30(s,12H,Me)	-65
13	-	6.75-7.15(m,9H)	2.28(s,18h,Me)	-100.23
14	-	6.75-7.15(m,12H)	2.14(s,24h,Me)	-111.37

[a] Corresponding ligand values are in parentheses.

deprotonation of the phenol. The chemical shifts in the region δ 6.43-7.46 due to aromatic ring protons are almost unaltered compared to those of the corresponding parent phenols (δ 6.53-7.51).

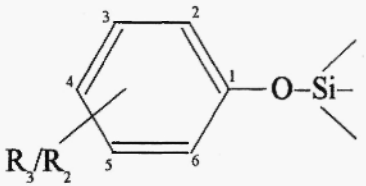
The methyl signals of the organosilicon moieties are observed in the range δ 0.22-0.45 which exhibit deshielding of Si-CH_3 protons with increase in the number of aryloxo moieties attached to the silicon (Table-**3**). Similar observations were also observed for the derivatives of the types $Me_{4-n}SiCl_n$[12] and $Me_{4-n}Si(ON=CEt_2)_n$,[13] such an observation tends to suggest that in organosilicon aryloxides $Me_{4-n}Si(OAr)_n$, the deshielding caused by electronegative aryloxide groups and their bulk counterbalances the shielding effect brought about by the possibility of back bonding from aryloxo oxygen lone pairs into a vacant d orbital of silicon. However, a reverse trend for $SiCH_3$ proton resonances has been observed for $Me_{4-n}Si(OEt)_n$[14] derivatives, indicating the contributions of other factors also like electric field (σ^E), paramagnetic(σ^P) and diamagnetic shielding (σ^d), anisotropy(σ^{anis}) and van der Waals interaction between bulkier aryloxo groups and the Si-methyl protons. Further, hyperconjugation effects may also contribute to the observed behaviour.

Furthermore, in view of reported ^{29}Si chemical shifts, for $Me_{4-n}SiCl_n$[11] derivatives at δ +30.21 (n = 1), + 32.17 (n = 2) and + 12.47 (n = 3), the observed ^{29}Si NMR signal for the derivatives $Me_{4-n}Si(OC_6H_3Me_2\text{-}2,6)_n$ at δ + 19.2, -7.95, -57.61 and -111.37, when n = 1,2,3 and 4 respectively, indicating enhancement of electron density at the silicon centre in the order $Me_3Si(OAr) < Me_2Si(OAr)_2 < MeSi(OAr)_3 < Si(OAr)_4$ which is consistent with the trend observed for the series $Me_{4-n}Si(OEt)_n$(n=1-3).[14]

^{13}C NMR spectra for the derivatives $Me_3Si(OAr)$ (OAr = $OC_6H_3Me_2$-2,6 ; $OC_6H_3Me_2$-3,4 ; $OC_6H_2Me_3$-2,4,6 ; $OC_6H_3Bu^t_2$-2,6) in the range δ 0.88 to 1.07 exhibit resonances due to methylsilicon moieties (Table-**4**). The ^{13}C NMR data for methylsilicon moieties tend to indicate increase in the deshielding effect, with increase in the bulk of the aryloxide groups. However, with the observed data for the series $Me_{3-n}Si(OAr)_n$ (n = 1,2 and 3, OAr = $OC_6H_3Me_2$-2,6) no definite trend could be reflected.

The signals due to aromatic carbon attached to oxygen appear in the range δ 150.29 to 153.9, and depict a down field shift of 0.4-0.76 ppm, while chemical shifts for other carbons remain almost unaltered compared to those of the corresponding parent phenol. The observed ^{13}C chemical shifts of aromatic carbons and for methyls present as substituent are assigned on the basis of the theoretical values calculated[15] using the formula. $\delta c = 128.5 + \Sigma Zi$, where

Table 4 ^{13}C NMR data[a] (δ,ppm) for aryloxo derivatives.



Compound	Me-Si	R=Me/Pr^{i}/Bu^{t}	C_1	C_2	C_3	C_4	C_5	C_6
1	0.88	17.67(**Me**$_2$-2,6)	152.56	121.41	128.40	128.51	128.40	121.41
			(151.8)					
2	0.86	19.39(**Me**)	152.99	112.36	130.24	129.91	137.38	116.58
		19.66(**Me**)	(152.0)					
3	-	-	-	-	-	-	-	-
4	0.82	22.87(**Me**$_2$-CH)	149.80	120.80	133.76	123.42	138.80	122.28
		27.09 (Me$_2$-**CH**)	(149.6)					
5	0.93	17.62(**Me**$_2$-2,6)	150.29	130.30	128.08	129.11	128.08	130.30
		20.48(**Me**-4)	(149.62)					
6	1.61	17.51(**Me**$_2$-2,6)	151.75	121.90	128.29	128.56	128.29	121.90
7	1.16	17.07(**Me**$_2$-2,6)	150.29	122.66	128.51	128.73	128.51	122.66
8	-	-	-	-	-	-	-	-
9	1.07	30.45,31.43(**Bu**$^{t}_2$-2,6)	153.91	120.76	126.07	140.86	124.99	119.79
		34.41,35.22	(153.52)					
10	-	-	-	-	-	-	-	-
11	-	17.50(**Me**$_2$-2,6)	149.80	124.28	128.56	129.05	128.56	124.28
12	-	17.40(**Me**$_2$-2,6)	149.80	123.85	128.45	128.99	128.45	123.85
13	-	17.13(**Me**$_2$-2,6)	150.34	122.71	128.51	128.73	128.51	122.71
14	-	17.40(**Me**$_2$-2,6)	150.94	123.09	128.51	128.73	128.51	123.09

[a] Corresponding ligand values in parantheses.

Zi is the substituent constant for α–,β–,γ–positions.

All the organosilicon aryloxides show infrared absorptions characterstic of methylsilicon moieties in the region 1254-1209 (ν Si-CH_3 deformation), 932-797 (ν Si-Me asym. rocking), 706-778 (ν Si-CH_3 sym. rocking) and 650-733 (ν Si-C asym. stretching). The new derivatives exhibit disappearance of the absorption due to the phenolic OH in the range 3680-3560 cm^{-1}. The new band appearing between 945 and 800 cm^{-1} may be assigned to Si-O stretch.[15] The ν (C-O) is observed at 1267-1337 cm^{-1}, indicating a lowering of ~19 cm^{-1} compared with that of the parent aryloxo ligand.

Experimental

The reactions were carried out under strictly anhydrous conditions. All solvents were dried by standard methods[16] and distilled prior to use. Organosilicon chlorides were distilled before use: Me_3SiCl(b.p.= 60°C), Me_2SiCl_2(b.p.= 70°C), $MeSiCl_3$(b.p.= 67°C). Phenols were either distilled (under reduced pressure) or recrystallised (from n-hexane). silicon was estimated as silicon oxide.[17] IR spectra in the range 4000-200 cm^{-1} were recorded on a Perkin Elmer-557 spectrophotometer using nujol mull. NMR spectra (^1H at 89.55 MHz, ^{13}C at 22.49 MHz and ^{29}Si at 17.75 MHz) were recorded in $CDCl_3$ solution on a JEOL FX-90Q spectrometer using TMS as an internal reference.

Synthesis of Organosilicon Aryloxides

Since a number of derivatives have been prepared by similar procedures, only typical preparations are being illustrated below. Further details have been compiled in Table-1.

(a) $Me_3SiOC_6H_3Me_2$-2,6

To a benzene (~30 ml) solution of Me_3SiCl(2.85g, 26.22 mmol) was added a solution containing pyridine (2.07g, 26.1 mmol) and 2,6-dimethylphenol (3.01g, 24.66 mmol) in benzene (~20 ml) , and allowed to stir at room temperature for 12h. The precipitated C_5H_5NHCl(2.84g, 24.56 mmol) was removed by filtration. Removal of the volatiles from the filtrate under reduced pressure, afforded $Me_3Si(OC_6H_3Me_2$-2,6) as a colourless liquid (4.2g, 88.0%), which distilled at 90-95°C/.8 mm in 82% yield.

Similar procedures were adopted for the syntheses of $Me_3SiOC_6H_3Me_2$-3,4 (b.p.110°C/.

8 mm), $Me_3SiOC_6H_3Me_2$-3,5(b.p.95°C/.9 mm),$Me_3SiOC_6H_2Me_3$-2,4,6 (b.p.95-110°C/.8 mm). Further details are listed in Table-1.

(b) $Me_3SiOC_6H_2Bu^t_3$-2,4,6

As the above procedure failed to yield the desired product in this case, it was modified as discribed below:

$KOC_6H_2Bu^t_3$-2,4,6 (prepared by refluxing K (0.16g, 4.13 mmol) and phenol (1.06g, 4.06mmol) in THF) was added to Me_3SiCl (0.56g, 5.15 mmol) in benzene (20ml). The resulting reaction mixture was refluxed for 8h, followed by cooling to room temprerature and filtration to remove the precipitated KCl (0.25g; 3.37 mmol). Removal of volatiles (under reduced pressure) from the filtrate, afforded light yellow solid product $Me_3SiOC_6H_2Bu^t_3$-2,4,6 (1.32g, 98.05%), which was distilled at 140°C/.8 mm in 93% yield.

Reactions of Trimethylsilicon Aryloxides With Early Transition Metal Chlorides

(a) With $TiCl_4$

To a n-hexane (~25ml) solution of $TiCl_4$(0.51g, 2.68 mmol) was added $Me_3SiOC_6H_3Me_2$-3,5 (0.53g, 2.73 mmol) and allowed to stir at room temperature for ~12h, during which the colour of the reaction mixture changed from light yellow to red; a red solid was precipitated out, which was removed by filtration and washed several times with n-hexane to obtain $TiCl_3(OC_6H_3Me_2$-3,5) in 93% yield. Similar procedure was adopted for the synthesis of $TiCl_2(OC_6H_3Me_2$-3,5)$_2$, $NbCl_4(OC_6H_3Me_2$-3,4), and $NbCl_3(OC_6H_3Me_2$-3,5)$_2$.

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