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Preparation and spectroscopic characterisation of a series of heterobimetallic *N*-phenyldiethanolaminate-alkoxide derivatives of oxovanadium(V)

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Reaction of VO(OPr^i)$_3$ with two equivalents of *N*-phenyldiethanolamine (PhDEAH$_2$) yields a homometallic complex [VO(PhDEA)(PhDEAH)] **1**, which reacts with a number of metal alkoxides to afford heterobimetallic oxovanadium(V) complexes of the types [VO(PhDEA)$_2${M(OR)$_{n-1}$}] [where PhDEA = $C_6H_5N(CH_2CH_2O^-)_2$], [M = : Al (*n* = 3, R = Pr^i) **2**; Al (*n* = 3, R = Bu^t) **3**; Ti (*n* = 4, R = Pr^i) **4**; Zr (*n* = 4, R = Pr^i) **5**; Nb (*n* = 5, R = Pr^i) **6**; Ta (*n* = 5, R = Pr^i) **7**. The derivative [VO(PhDEA)(OSiPh$_3$)] **8** has been prepared by the equimolar interaction of [VO(PhDEA)(OPr^i)] with Ph$_3$SiOH. All of these complexes have been characterised by spectroscopic (IR; ^{1}H, ^{13}C, ^{27}Al and ^{51}V NMR) studies, elemental analyses, and molecular weight measurements. The derivative **2** has also been characterised by FAB mass spectral studies, which supports for its monomeric nature.

Keywords: heterobimetallic oxovanadium(V) complexes, *N*-phenyl- diethanolaminates, oxovanadium(V) complexes

The reactivity and solubility (in organic solvents) of metal-alkoxides were generally modified by the use of chelating ligands such as acetylacetone[1], carboxylic acids,[2] glycols[3] and alkanolamines,[4] *etc.*, and such mixed ligand derivatives have shown their potential as precursors for the preparation of metal-oxide based ceramic materials by the sol-gel[5,6] process. In spite of some interesting studies on complexation of diethanolamine and related ligands[7,8] with vanadium(V) in aqueous medium and reported examples of many homo-metallic derivatives of transition metals,[9-16] heterometallic systems containing both diethanolaminate and alkoxide groups are very limited in number.[17-19] By contrast, homo- and heterometallic derivatives of oxovanadium(V) derived from *N*-phenyldiethanolamine appear to have not been investigated so far.

In view of the biological importance of vanadium complexes[20-24] and non-availability of heterobinuclear derivatives of oxovanadium(V) containing both alkoxide and diethanolaminate ligands, it was considered worthwhile to investigate heterobimetallic oxovanadium(V) *N*-phenyldiethanolaminate-alkoxides of desired structural formulation and stability.

Results and discussion

Reaction of VO(OPr^i)$_3$ with two equivalents of *N*-phenyldiethanolamine (abbreviated as PhDEAH$_2$) in benzene affords homometallic complex **1** (Eqn (1)), which on equimolar reactions with a variety of metal alkoxides (Eqn (2)) yield heterobimetallic complexes **2**–**7**:

$$\mathrm{VO(OPr^i)_3 + 2\,PhDEAH_2 \xrightarrow[\text{reflux, ~ 5 h}]{C_6H_6} \underset{\mathbf{1}}{VO(PhDEA)(PhDEAH)} + 3\,Pr^iOH\uparrow} \quad (1)$$

(where PhDEAH = $PhN(CH_2CH_2O)(CH_2CH_2OH)$)

$$1 + M(OR)_n.x\,ROH \xrightarrow[\text{reflux, ~ 1 h}]{C_6H_6} VO(PhDEA)_2\{M(OR)n\text{-}1\} + (x + 1)\,ROH\uparrow \quad (2)$$

2 (M = Al, R = Pr^i, *n* = 3, *x* = 0); **3** (M = Al, R = Bu^t, *n* = 3, *x* = 0); **4** (M = Ti, R = Pr^i, *n* = 4, *x* = 0); **5** (M = Zr, R = Pr^i, *n* = 4, *x* = 1); **6** (M = Nb, R = Pr^i, *n* = 5, *x* = 0); **7** (M = Ta, R = Pr^i, *n* = 5, *x* = 0)

A heterobinuclear complex **8** containing oxovanadium(V) and silicon(IV) has been prepared by the equimolar reaction of VO(PhDEA)(OPr^i) with Ph$_3$SiOH (Eqn (3)):

$$\mathrm{VO(PhDEA)(OPr^i) + Ph_3SiOH \xrightarrow[\text{reflux, ~ 4 h}]{C_6H_6} \underset{\mathbf{8}}{VO(PhDEA)(OSiPh_3)} + Pr^iOH\uparrow} \quad (3)$$

All these complexes **1**–**8** are coloured (orange or black) solids, soluble in organic solvents (such as benzene, toluene, tetrahydrofuran, dichloromethane, and chloroform). The cryoscopic molecular weight measurements depict monomeric behaviour for **1**–**7**, whereas **8** appears to be dimeric.

Spectroscopic studies

The IR spectrum of **1** (Table 1) consists of (i) a broad band at 3359 cm^{-1} due to hydrogen bonded O–H group, (ii) medium intensity bands at 1365 and 1210 cm^{-1} for νC–N of aromatic[25] and aliphatic[26] amino groups, respectively. A comparison of the observed νC–N value of the aromatic component with that found in the free *N*-phenyldiethanolamine shows a lowering of 30 cm^{-1} on formation of the transannular N→V dative bond (structure **I**), (iii) a strong band due to νC–O at 1047 cm^{-1}, (iv) a strong band at 976 cm^{-1} due to the V=O stretching vibration in six-coordinate oxovanadium(V) complexes,[27-30] (v) a medium intensity band at 569 cm^{-1} assignable to νV–O,[31] and (vi) a weak intensity band due to νN→V at 484 cm^{-1}.

The ^{13}C{^{1}H} NMR spectrum of *N*-phenyldiethanolamine shows signals at δ 55.11 (N**C**H$_2$), 60.42 (**C**H$_2$O), 112.22 (*o*-aromatic-**C**), 116.56 (*p*-aromatic-**C**), 129.21 (*m*-aromatic-**C**), and 147.61 (due to aromatic carbon bonded to nitrogen). The complex **1** exhibits signals at 55.89 (N**C**H$_2$), 61.28 (**C**H$_2$O), 113.34 (*o*-aromatic-**C**), 117.61 (*p*-aromatic-**C**), 129.67 (*m*-aromatic-**C**), and 148.55 (**C**–N, aromatic). The downfield (0.94 ppm) shift of the aromatic **C**–N signal with respect to the corresponding signal in the *N*-phenyldiethanolamine may be interpreted in terms of decreased electron density at this position on formation of N→V dative bond (structure **I**).

The appearance of a sharp ^{51}V NMR signal at δ –514 ppm supports for an octahedral environment[13,32,33] (structure **I**) around vanadium in the complex **1**.

Heterobimetallic complexes **2**–**7** show structurally important IR absorption bands (Table 1) in the regions expected for

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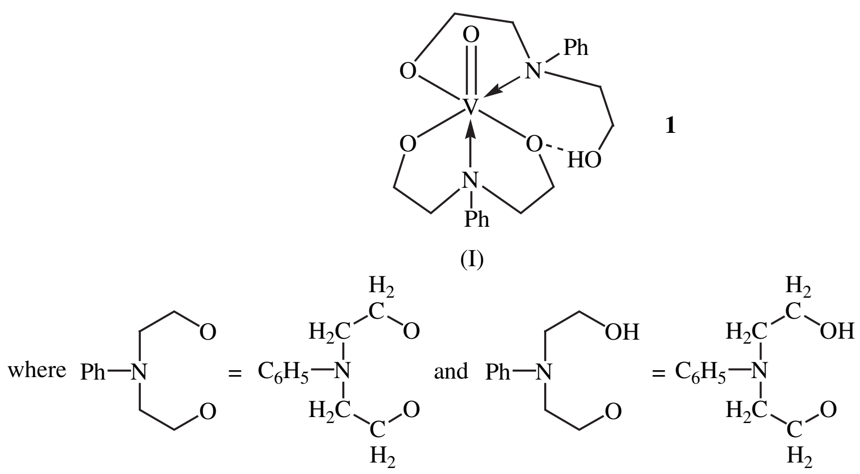
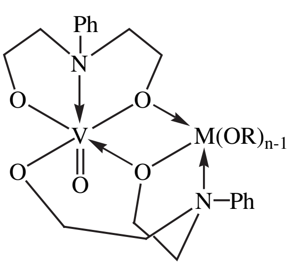
Table 1 IR spectral data (cm^{-1}) for complexes **1–8**

Compound	*N*-Phenyldiethanolaminate group			OPr^i (terminal)		ν(V=O)	ν(V-O)	ν(M-O)	ν(V←N)	ν(M←N)
	ν(C-N) (aromatic)	ν(C-N) (aliphatic)	ν(C-O) terminal/ bridging	ν(Pr^i)	ν(C-O)					
1	1365 m	1210 m	1047 s	–	–	976 s	569 m	–	484 w	–
2	1362 s	1203 m	1060 s	1172 s	1078 s	970 s	559 m	630 m	480 w	507 w
	1359 m	1190 m	942 s	1135 s						
3	1365 s	1209 m	1048 s	–	–	969 s	567 m	625 m	480 w	510 w
	1359 m	1190 m	954 m							
4	1367 s	1209 m	1047 s	1180 s	1077 s	979 s	569 m	615 m	485 w	491 w
	1360 m	1199 m	950 m	1133 s						
5	1368 s	1216 m	1048 s	1170 s	1083 s	975 s	562 m	500 m	488 w	454 w
	1359 s	1200 m	955 m	1133 s						
6	1366 s	1220 m	1049 s	1169 s	1091 s	979 s	560 m	500 m	481 w	452 w
	1348 s	1192 m	947 m	1131 s						
7	1366 s	1220 m	1048 s	1172 s	1078 s	977 s	569 m	508 m	482 w	450 w
	1348 s	1192 m	947 m	1138 s						
8	1368 s	1212 m	1049 s	–	–	968 s	564 m	1000 m	483 w	–

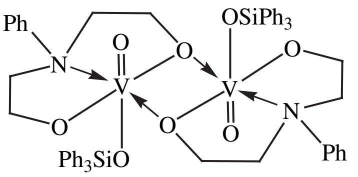


Structure I



		M	R	n
2	:	Al	Pr^i	3
3	:	Al	Bu^t	3
4	:	Ti	Pr^i	4
5	:	Zr	Pr^i	4
6	:	Nb	Pr^i	5
7	:	Ta	Pr^i	5

Structure II



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Structure III

metal–ligand vibrations,[13,17-19,27-30] which are consistent with the structure (**II**).

^{1}H NMR spectral data for the complexes **1**–**8**, which are listed in Table 2, have the expected pattern characteristic for the organic ligands bonded to vanadium / heterometal atom. The NC**H**$_2$ and OC**H**$_2$ protons appear as broad signals at δ 3.61 ± 0.03 and 3.90 ± 0.09, respectively. The appearance of the PhDEA signals in the ^{1}H NMR in almost the same position or with only very slight shift from the free ligand is intriguing, because tridentate ligation of aminodiethoxide ligand would be expected to bring about noticeable shifting to lower field, particularly in the signal position of NC**H**$_2$ group protons. Furthermore, depending upon the nature of the metal to which the amino nitrogen is ligated, one would also expect variation in the chemical shift value for NC**H**$_2$ protons.

In view of the above, we believe that the lone pair of the nitrogen atom in the deprotonated *N*-phenyldiethanolamine moiety is involved in resonance delocalisation brought about by the phenyl ring, which would result in the formation of a very weak nitrogen to vanadium / heteroatom dative bond with no or slight change in the signal positions of NC**H**$_2$ group protons compared with the unbound parent ligand.

The ^{51}V NMR signals (Table 2) for the derivatives **2**–**7** appear at δ –550 ppm, consistent with an octahedral environment[13,32,33] around vanadium in these complexes (structure II).

The complexes **2** and **3** show broad ^{27}Al NMR signals at δ 26.13 and 36.73 ppm, respectively, in accordance with the five-coordinate environment[34,35] around aluminium (structure **II**).

A more supportive evidence for the proposed structure (**II**) for **2** has been obtained from the ^{13}C{^{1}H}NMR spectrum of **2**, which shows two signals for carbons of NCH$_2$ and OCH$_2$ groups as well as for *o*-, *m*-, *p*-, and **C**-1 carbons

Table 2 ^1H and ^{51}V NMR spectral data[a] (δ, ppm) for $PhDEAH_2$ and its complexes **1**-**8**

Compound	^1H	^{51}V
$PhDEAH_2$	3.60 (t, J = 4.96 Hz, 4H, NCH_2) ; 3.83 (m, 6H, CH_2O+OH) ; 6.81 (t, 3H, *o,p*-aromatic-**H**) ; 7.20 (m, 2H, *m*-aromatic -**H**)	
1	3.62 (t, J = 4.90 Hz, 8H, NCH_2) ; 3.90 (t, J = 4.90 Hz, 8H, CH_2O) ; 5.07 (br, 1H, CH_2OH) ; 6.80–7.40 (m, 10H, aromatic -**H**)	-514
2	1.21 (d, J = 6.17 Hz, 12H, OCH**Me**$_2$) ; 3.62 (m, 8H, NCH_2) ; 3.90 (m, 8H, CH_2O) ; 4.04 (m, 2H, OC**H**Me$_2$) ; 6.78-7.42 (m, 10H, aromatic –**H**)	-540
3	1.26 (s, 18H, OCH**Me**$_3$); 3.59 (m, 8H, NCH_2); 3.87 (m, 8H, CH_2O); 6.76-7.35 (m, 10H, aromatic-**H**)	-551
4	1.24 (d, J = 5.80 Hz, 18H, OCH**Me**$_2$) ; 3.65 (m, 8H, NCH_2) ; 3.99 (m, 8H, CH_2O) ; 4.64 (m, 3H, OC**H**Me$_2$) ; 6.78-7.42 (m, 10H, aromatic-**H**)	-560
5	1.20 (d, J = 6.31 Hz, 18H, OCH**Me**$_2$) ; 3.60 (m, 8H, NCH_2) ; 3.86 (m, 8H, CH_2O) ; 4.05 (m, 3H, OC**H**Me$_2$); 6.70-7.25 (m, 10H, aromatic-**H**)	-551
6	1.26 (d, J = 5.91 Hz, 24H, OCH**Me**$_2$) ; 3.64 (m, 8H, NCH_2) ; 3.97 (m, 8H, CH_2O) ; 4.60 (m, 4H, OC**H**Me$_2$) ; 6.69-7.25 (m, 10H, aromatic –**H**)	-548
7	1.22 (d, J = 6.09 Hz, 24H, OCH**Me**$_2$); 3.61 (m, 8H, NCH_2); 3.90 (m, 8H, CH_2O); 4.09 (m, 4H, OC**H**Me$_2$); 6.69-7.24 (m, 10H, aromatic **H**)	-553
8	3.58 (m, 4H, NCH_2); 3.89 (m, 4H, CH_2O); 6.72-7.56 (m, 20H, aromatic-H)	-558

[a]Abbreviations : d = doublet, t = triplet, m = multiplet, br = broad

Table 3 Analytical and molecular weight data for complexes **1**-**8**

Compound Molecular Formula	Colour m.p. °C	Yield[a] g (%)	Liberated Pr^iOH (g) Found (Calc.)	Analysis (%) Found (Calc.)					Mol. Wt.[c] Found (Calc.)
				V	M[b]	C	H	N	
1 $C_{20}H_{27}N_2O_5V$	Orange 120	5.12, 71 3.04	(3.04)	11.90 (11.94)	–	56.37 (56.32)	6.44 (6.38)	6.51 (6.56)	432 (426)
2 $C_{26}H_{40}AlN_2O_7V$	Black 125	1.77, 74	0.25 (0.25)	8.84 (8.92)	4.70 (4.73)	54.57 (54.72)	6.94 (7.06)	4.83 (4.90)	577 (570)
3 $C_{28}H_{44}AlN_2O_7V$	Black 110	1.65, 75	-	8.48 (8.51)	4.42 (4.51)	56.37 (56.17)	7.28 (7.40)	4.42 (4.67)	610 (598)
4 $C_{29}H_{47}N_2O_8TiV$	Black 118	1.26, 54	0.21 (0.21)	7.56 (7.83)	7.30 (7.36)	53.21 (53.54)	6.97 (7.28)	4.16 (4.30)	662 (650)
5 $C_{29}H_{47}N_2O_8VZr$	Black 165	1.45, 65	0.39 (0.39)	7.29 (7.34)	13.03 (13.14)	50.58 (50.19)	6.60 (6.82)	4.00 (4.03)	697 (693)
6 $C_{32}H_{54}N_2NbO_9V$	Black 108	1.49, 72	0.16 (0.16)	6.63 (6.75)	12.23 (12.31)	50.98 (50.92)	7.00 (7.21)	3.66 (3.71)	761 (754)
7 $C_{32}H_{54}N_2O_9TaV$	Black 112	2.61, 75	0.24 (0.24)	5.91 (6.04)	21.27 (21.47)	45.36 (45.60)	6.18 (6.45)	3.20 (3.32)	855 (842)
8 $C_{28}H_{28}NO_4SiV$	Orange 139	3.17, 70	0.51 (0.52)	9.70 (9.76)	5.15 (5.38)	64.03 (64.47)	5.46 (5.41)	2.51 (2.68)	966 (521)

[a]Refers to crystallised product.
[b]M stands for a metal other than vanadium.
[c]Determined cryoscopically.

of phenyl group at δ 55.53, 57.65 (N**C**H$_2$); 60.72, 61.73 (**C**H$_2$O); 112.00, 114.84 (*o*-aromatic-**C**); 118.69, 120.13 (*p*-aromatic-**C**); 129.13, 129.56 (*m*-aromatic-**C**); 149.08, 149.72 (aromatic-**C**–N). The isopropoxy groups show signals at δ 21.94 (O**C**HMe$_2$) and 63.03 (O**C**HMe$_2$). This type of spectral pattern is consistent with the structure (**II**).

Complex **8** shows IR absorption bands (Table 1) and ^1H NMR signals (Table 2) for ligated PhDEA and Ph_3SiO moieties. The $^{13}C\{^1H\}$NMR spectrum of **8** shows signals at δ 55.34 (N**C**H$_2$); 60.91 (**C**H$_2$O); 112.72, 113.28 (*o*-aromatic-**C**); 117.07, 119.11 (*p*-aromatic-**C**) 128.32, 129.92 (*m*-aromatic-**C**); 135.22 (aromatic-**C**–Si); 147.81 (aromatic-**C**–N). As expected, signals due to phenyl groups bonded to nitrogen (δ 113.28, 119.11, 129.92, 147.81) and silicon (δ 112.72, 117.07, 128.32, 135.22) are observed at different positions. The complex **8** shows a sharp ^{51}V NMR signal at δ –558 ppm, which is consistent with an octahedral geometry[13,32,33] for vanadium.

The above spectroscopic findings for complexes **1**–**8** along with their observed moleculer weight data favour the structures (**I**), (**II**) and (**III**). However, it may be pointed out that structural changes in solution involving variations in the connectivity of ligand moieties may not be completely ruled out.

Experimental

All the preparative work and other manipulations were conducted under strictly anhydrous conditions. Solvents (Merck analytical grade) benzene (Na/benzophenone), *n*-hexane (Na/benzophenone), isopropyl alcohol ($NaOPr^i$ / $Al(OPr^i)_3$), tertiary butyl alcohol ($NaOBu^t$), and dichloromethane (P_2O_5) were dried and purified by refluxing over appropriate drying agents (given in parentheses) followed by distillation prior to use. *N*-phenyldiethnaolamine (Aldrich) was purified by distillation under reduced pressure (158 °C / 0.2 mmHg). Triphenylsilanol (Fluka) was used as received.

$VO(OPr^i)_3$,[36] $Al(OPr^i)_3$,[37] $Al(OBu^t)_3$,[38] $Ti(OPr^i)_4$,[39] $Zr(OPr^i)_4.Pr^iOH$,[40] $Nb(OPr^i)_5$,[41] and $Ta(OPr^i)_5$[41] were prepared by the published methods. [VO(PhDEA)(OPr^i)] was prepared by the literature method.[13]

Vanadium was determined by a redox titration method.[42] Ti, Zr, Nb, Ta and Si were estimated gravimetrically[43] as their oxides, whereas aluminium was determined as its oxinate. Nitrogen was determined by Kjeldahl's method.[43] Isopropyl alcohol in the azeotrope was estimated by an oxidimetric method.[44]

Infrared spectra (4000–200 cm^{-1}) were recorded on a Nicolet Magna-550 spectrophotometer in Nujol mulls. NMR spectra for ^1H (89.55

MHz, $CDCl_3$, TMS as internal reference), ^{13}C (22.49 MHz, $CDCl_3$, TMS as internal reference), ^{27}Al (23.79 MHz, $CDCl_3$, $Al(NO_3)_3.xH_2O$ as external reference), and ^{51}V (23.51 MHz, $CDCl_3$ or C_6H_6, $VOCl_3$ as external reference) were recorded on JEOL FX 90Q and JEOL AL 300 FT NMR spectrometers. Microelemental analyses (C, H, and N) were performed on a Perkin Elemer 2400 CHNS/O analyser. Molecular weights were measured cryoscopically in benzene.

Synthesis of new derivatives

[VO(PhDEA)(PhDEAH)] (where $PhN(CH_2CH_2O)(CH_2CH_2OH)$ is abbreviated as PhDEAH) **1**: When *N*-phenyldiethanolamine (6.12 g, 33.76 mmol) was added to a colourless benzene (~ 30 ml) solution of $VO(OPr^i)_3$ (4.12 g, 16.86 mmol), the solution attained red-brown colour. The resulting reaction mixture was refluxed under a fractionating column with continuous removal of the liberated isopropyl alcohol as its azeotrope with benzene. When, after ~ 5 h, the distillate showed negligible presence of isopropyl alcohol, refluxing was stopped and reaction mixture was allowed to cool to room temperature. Volatile components from the solution were removed under reduced pressure (~10 mmHg) to obtain orange solid **1** (7.17 g, 99%) quantitatively. Recrystallisation from a 1:1 mixture of dichloromethane and *n*-hexane at –20 °C gave an analytically pure orange solid (5.12 g, 71 %), m.p., 120 °C. FAB mass, *m/z* (relative intensity) : 426 $[(M)^+$, 5], 399 $[(M–C_2H_3)^+$, 10], 383 $[(M–C_2H_3O)^+$, 5], 381 $[(M–C_2H_5O)^+$, 10], 355 $[(M–C_4H_7O)^+$, 15], 341 $[(M–C_5H_9O)^+$, 10], 281 $[(M–C_{10}H_{11}N)^+$, 50], 267 $[(M–C_{11}H_{13}N)^+$, 10]. Analytical details are given in Table 3.

$\mathit{[VO(PhDEA)_2\{Al(OPr^i)_2\}]}$ **2**: On addition of $Al(OPr^i)_3$ (0.85 g, 4.16 mmol) to a red-brown solution of **1** (1.78 g, 4.17 mmol) in benzene (~30 ml), black-brown coloured solution was obtained. The reaction mixture was then refluxed with continuous removal of isopropyl alcohol azeotropically. When liberation of isopropyl alcohol ceased, as was evident by the lack of consumption of 1 N $K_2Cr_2O_7$ during redox titration of the finally collected distillate, the solvent was removed under reduced pressure to obtain the compound **2** as a black solid in 2.33 g (98%) yield. Recrystallisation from a 1 : 2 mixture of dichloromethane and *n*-hexane afforded analytically pure product as a black solid (1.77 g, 74 %), m.p., 125 °C. FAB mass *m/z* (relative intensity) : 570 $[(M)^+$, 5], 511 $[(M–C_3H_7O)^+$, 8], 381 $[(M–C_8H_{18}AlO_3)^+$, 10], 246 $[(M–C_{13}H_{20}AlNO_3)^+$, 10], 182 $[(C_{10}H_{16}NO_2)^+$, 50], 181 $[(C_{10}H_{15}NO_2)^+$, 25], 150 $[(C_9H_{12}NO)^+$, 100].

Adopting a method similar to **2,** complexes **3–7** were also prepared by using appropriate reactants in desired stoichiometry. Analytical details are summarised in Table 3.

$\mathit{[VO(PhDEA)(OSiPh_3)]}$ **8**: To a red-brown solution of $VO(PhDEA)(OPr^i)$ (2.64 g, 8.64 mmol) in benzene (~ 30 ml) was added Ph_3SiOH (2.39 g, 8.64 mmol) and the resulting solution was refluxed over a period of ~ 4 h, with continuous fractionation of isopropyl alcohol as an azeotrope with benzene, which was estimated periodically. When the required amount of isopropyl alcohol was distilled out and the distillate showed negligible presence of an oxidisable material, refluxing was stopped and reaction mixture was allowed to cool to room temperature. Solvent was removed under reduced pressure to obtain **8** as an orange solid (4.50 g, 99%). Recrystallisation from a 1:2 mixture of dichloromethane and *n*-hexane afforded **8** as an orange solid (3.17 g, 70 %), m.p., 139 °C. Analytical details are listed in Table 3.

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