Syntheses of Organofunctional Siloxanes containing Metal-ligating Side-chains†

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A range of tri-, tetra-, and penta-siloxanes of general formula $Me_3SiO[SiMe(R)O]_nSiMe_3$ (R = vinyl, n = 1—3; R = an alkyl chain terminated by the potential metal-ligating entities $CH=CH_2$, Ph, CN, cyclohexenyl, pyridine, and PPh_2, n = 1 or 2) have been synthesised from commercially available dichlorosilanes by one of three procedures. The products are air-stable oils with the exception of the pyridine- and phosphine-functionalised compounds which react vigorously with oxygen, and the spectroscopic properties of corresponding organofunctional siloxanes are very similar showing little dependence on n.

The concept of attaching transition-metal species to solid supports to produce catalysts which combine the versatility, selectivity, and reproducibility of homogeneous catalysts with the separation advantages of heterogeneous systems has attracted widespread interest.[1-3] Many solid polymeric organic materials, modified to bear pendant metal-binding entities, have been used to anchor catalytically active metal species,[1-5] but all such systems exhibit limited thermo-oxidative stability, and most suffer from lack of chemical reproducibility. Of the solid, inorganic supports available, silica and its minerals have received most attention. Metal species are usually attached *via* ligating groups which are chemically bonded to the solid *via* surface silanol reactions, but again reproducibility and precise determination of the degree of surface modification and metallation are difficult to establish.[6-8]
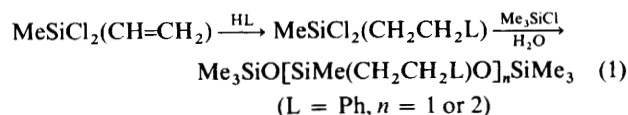
The ideal supported catalyst should combine the thermal stability of inorganic supported systems with the beneficial attributes of homogeneous catalysts. We believe that thermally stable, macromolecular liquid supports offer many advantages over conventional solid support systems, and therefore warrant further attention. For example, reactions on substrates miscible with such a polymer could be carried out in a liquid phase devoid of conventional solvents, and thus suitable for use over a wide range of temperature and pressure. In addition many of the separation problems encountered in homogeneous catalysis could also be circumvented by bonding the catalytically active metal centres to such a support. Of the various liquid polymers available, those based on linear or cyclic polysiloxanes are prime candidates for such an examination. These materials are chemically robust, thermally stable, readily available, and capable of systematic structural modification.[9] In order to bind metal entities to the polymer in a regular and well defined way, it is necessary to have available a range of synthetic procedures for introducing various functional groups into the polymer. In this paper we describe the synthesis of a range of functionalised tri-, tetra-, and penta-siloxanes, containing respectively one, two, or three identical substituents capable of binding metal entities, which will serve as models for future syntheses and investigations of long-chain organofunctional polysiloxanes.

Results and Discussion

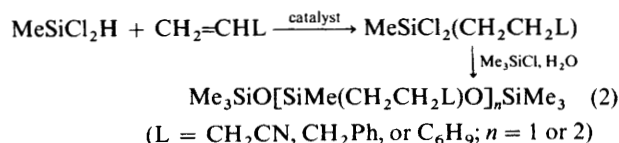The compounds $SiMeCl_2H$ and $SiMeCl_2(CH=CH_2)$ have been used to prepare the dichlorosilanes (1)—(4) for conversion

	L		n	R		n	R
(1)	Ph	(5)	1	$(CH_2)_2Ph$	(16)	1	$CH_2CH=CH_2$
(2)	CH_2Ph	(6)	2	$(CH_2)_2Ph$	(17)	2	$CH_2CH=CH_2$
(3)	CH_2CN	(7)	1	$(CH_2)_3Ph$	(18)	1	$(CH_2)_2Br$
(4)	C_6H_9	(8)	2	$(CH_2)_3Ph$	(19)	1	$(CH_2)_3C_5H_4N$
	(cyclo-	(9)	1	$(CH_2)_3CN$	(20)	1	$(CH_2)_2PPh_2$
	hexenyl)	(10)	2	$(CH_2)_3CN$	(21)	2	$(CH_2)_2PPh_2$
		(11)	1	$(CH_2)_2C_6H_9$	(22)	1	$(CH_2)_3PPh_2$
		(12)	2	$(CH_2)_2C_6H_9$			
		(13)	1	$CH=CH_2$			
		(14)	2	$CH=CH_2$			
		(15)	3	$CH=CH_2$			

into the majority of the organofunctional siloxanes $Me_3SiO[SiMe(R)O]_nSiMe_3$ listed above [compounds (5)—(22)]. The syntheses have followed one of three routes. In the first of these, chemical modification of dichloromethylvinylsilane is followed by hydrolysis in the presence of chlorotrimethylsilane [equation (1)]. Under Friedel Crafts conditions, anti-Markownikoff

$$MeSiCl_2(CH=CH_2) \xrightarrow{HL} MeSiCl_2(CH_2CH_2L) \xrightarrow[H_2O]{Me_3SiCl}$$
$$Me_3SiO[SiMe(CH_2CH_2L)O]_nSiMe_3 \quad (1)$$
$$(L = Ph, n = 1 \text{ or } 2)$$

addition of benzene across the vinyl group of $SiMeCl_2(CH=CH_2)$ readily occurs to yield $SiMeCl_2(CH_2CH_2Ph)$ as a moisture-sensitive colourless oil. Only the terminal adduct is formed in this reaction, but under similar conditions alkyl-substituted arenes such as toluene or mesitylene react to form a mixture of several chlorosilanes from which the required terminal product could not be isolated in a pure state.

An alternative procedure involving the platinum-catalysed hydrosilylation of 1-alkenes proved more versatile for the synthesis of a larger range of pure analogues [equation (2)].

$$MeSiCl_2H + CH_2=CHL \xrightarrow{catalyst} MeSiCl_2(CH_2CH_2L)$$
$$\downarrow{Me_3SiCl, H_2O}$$
$$Me_3SiO[SiMe(CH_2CH_2L)O]_nSiMe_3 \quad (2)$$
$$(L = CH_2CN, CH_2Ph, \text{ or } C_6H_9; n = 1 \text{ or } 2)$$

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† *Non-S.I. units employed:* eV $\approx 1.60 \times 10^{-19}$ J, mmHg ≈ 133 Pa.

Table 1. Analytical data[a] for siloxane derivatives

| | Yield | | | Analysis (%) | |
Compound	n	%	B.p.[b] (°C)	C	H
(5) $Me_3SiO[SiMe(CH_2CH_2Ph)O]_nSiMe_3$	1	33	116 (0.1)	54.9 (55.1)	9.15 (9.20)
(6)	2	24	198 (0.8)	57.8 (58.8)	8.65 (8.55)
(7) $Me_3SiO[SiMe(CH_2CH_2CH_2Ph)O]_nSiMe_3$	1	57	106 (0.1)	56.7 (56.5)	8.90 (9.40)
(8)	2	19	192 (0.2)	59.6 (60.2)	8.80 (8.90)
(9) $Me_3SiO[SiMe(CH_2CH_2CH_2CN)O]_nSiMe_3$	1	22	106 (1.2)	44.5 (45.5)	9.05 (9.35)
(10)	2	11	194 (3.1)	45.4 (46.2)	8.90 (8.65)
(11) $Me_3SiO[SiMe(CH_2CH_2C_6H_9)O]_nSiMe_3$	1	50	92 (0.2)	53.0 (54.5)	10.5 (10.3)
(12)	2	23	172 (0.2)	56.8 (57.8)	10.4 (10.0)
(13) $Me_3SiO[SiMe(CH=CH_2)O]_nSiMe_3$	1	12	46 (1.2)	43.4 (43.5)	9.30 (9.65)
(14)	2	40	82 (1.3)	43.1 (43.1)	8.85 (9.00)
(15)	3	32	97 (1.3)	43.2 (42.9)	8.75 (8.55)
(16) $Me_3SiO[SiMe(CH_2CH=CH_2)O]_nSiMe_3$	1	36	29 (0.1)	44.1 (45.8)	9.95 (9.90)
(17)	2	8	54 (0.01)	43.6 (46.4)	9.70 (9.40)

[a] Calculated data in parentheses. [b] P/mmHg in parentheses.

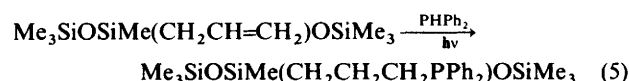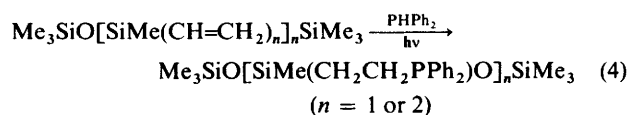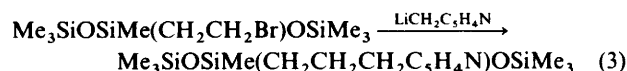**Table 2.** Proton and ^{13}C n.m.r. data for selected siloxanes*

	Me_3SiO	SiMe	C^1/H^1	C^2/H^2	C^3/H^3	Others	Aromatics
(5)	0.10 (18 H, s)	0.10 (3 H, s)	0.80 (2 H, m)	2.64 (2 H, m)			7.18 (5 H, m)
	1.90	−0.27	19.8	29.4			145.1, 128.3, 127.9, 125.5
(7)	0.07 (18 H, s)	0.07 (3 H, s)	0.45 (2 H, m)	1.60 (2 H, m)	2.58 (2 H, m)		7.12 (5 H, m)
	−0.19	−0.10	17.5	25.2	39.5		142.7, 128.5, 128.3, 125.7
(9)	0.54 (18 H, s)	0.48 (3 H, s)	1.04 (2 H, m)	2.13 (2 H, m)	2.80 (2 H, m)	119.3 (CN)	
	1.54	−0.57	16.8	19.8	20.2		
(11)	0.08 (18 H, s)	0.08 (3 H, s)	0.48 (2 H, m)	1.30 (2 H, m)		1.80 (7 H, m),	
	1.57	−0.32	14.7	30.3		5.64 (2 H, m)	127.0, 126.7, 36.4, 31.8, 28.7, 25.5
(13)	0.46 (18 H, s)	0.46 (3 H, s)	6.25 (3 H, m)	132.0			
	2.31	0.00	137.5				
(16)	0.12 (18 H, s)	0.12 (3 H, s)	1.51 (2 H, d)	5.80 (1 H, m)	4.88 (2 H, m)		
	2.71	0.01	26.7	135.0	114.5		
(18)	0.54 (18 H, s)	0.54 (3 H, s)	1.74 (2 H, m)	3.94 (2 H, m)			
	1.84	0.49	25.1	30.1			
(19)	0.50 (18 H, s)	0.05 (3 H, s)	0.46 (2 H, m)	1.65 (2 H, m)	2.58 (2 H, t)		7.02 (2 H, d), 8.41 (2 H, d)
	0.16	0.00	17.4	24.3	38.7		151.4, 149.9, 124.1
(20)	0.80 (18 H, s)	0.80 (3 H, s)	0.56 (2 H, m)	2.02 (2 H, m)			7.28 (5 H, m)
	1.90	−0.49	13.2 (d, 9.8)	21.0 (d, 14.7)			139.2 (d, 13.7), 134.0 (d, 17.1), 132.8 (d, 18.3), 128.3 (d, 3.7)
(22)	0.06 (18 H, s)	0.06 (3 H, s)	0.67 (2 H, m)	1.54 (2 H, m)	2.12 (2 H, m)		7.38 (5 H, m)
	2.06	0.22	19.7 (d, 10.3)	19.9 (d, 12.7)	32.7 (d, 13.1)		139.4 (d, 13.1), 134.1 (d, 17.1), 132.9 (d, 17.1), 128.5 (d, 3.7)

* Carbon chain numbered from the Si atom.

Only the required terminal dichlorosilanes were formed in this reaction, with no n.m.r. evidence of CH or CH_3 moieties produced by internal addition. Siloxanes were prepared by co-hydrolysis of the appropriate organofunctional dichlorosilane and chlorotrimethylsilane in diethyl ether–water mixtures, and provided this reaction was carried out at low temperature, the HCl liberated on hydrolysis did not cause significant cleavage of Si–O bonds. Hexamethyldisiloxane was formed as a by-product in each reaction, but the separation of the two series of siloxanes ($n = 1$ and $n = 2$) from the reaction mixture was readily achieved by fractional distillation under reduced pressure (Table 1). A third member of the series ($n = 3$) was isolated in a pure state only for the vinyl-functionalised siloxanes. A similar hydrolytic procedure has been used previously by Brzezinska and Cullen [10] in the preparation of $Me_3SiO[SiMe-(CH=CH_2)O]_nSiMe_3$ ($n = 1$ or 3) from $SiMeCl_2(CH=CH_2)$, but they were unable to isolate the analogue with $n = 2$, which was the major product under our reaction conditions.

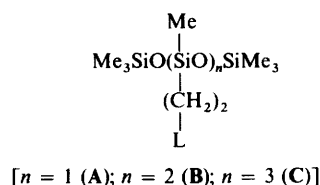The remaining siloxanes were prepared from other organo-functional siloxanes either by substitution of the halogen in compound (18) or by addition across the carbon–carbon double bond in (13), (14), or (16) as shown in equations (3)—(5). Although the pyridine derivative (19) was readily

$$Me_3SiOSiMe(CH_2CH_2Br)OSiMe_3 \xrightarrow{LiCH_2C_5H_4N} $$
$$Me_3SiOSiMe(CH_2CH_2CH_2C_5H_4N)OSiMe_3 \quad (3)$$

$$Me_3SiO[SiMe(CH=CH_2)_n]_nSiMe_3 \xrightarrow[hv]{PHPh_2} $$
$$Me_3SiO[SiMe(CH_2CH_2PPh_2)O]_nSiMe_3 \quad (4)$$
$$(n = 1 \text{ or } 2)$$

$$Me_3SiOSiMe(CH_2CH=CH_2)OSiMe_3 \xrightarrow[hv]{PHPh_2} $$
$$Me_3SiOSiMe(CH_2CH_2CH_2PPh_2)OSiMe_3 \quad (5)$$

formed by treating $Me_3SiOSiMe(CH_2CH_2Br)OSiMe_3$ with $LiCH_2C_5H_4N$ in tetrahydrofuran (thf), attempts to prepare phosphinated siloxanes by reaction of compound (18) with

Li[PPh$_2$] or Na[PPh$_2$] were unsuccessful under any of the reaction conditions tried, and resulted instead in cleavage of Si–O bonds and degradation of the trisiloxane backbone. Interestingly, this reaction has been carried out successfully on both chloromethylated polyphenylsiloxanes[11] and halogen-containing polymethylsiloxanes,[12] without, apparently, any such degradation problems. Since the photochemical addition of Ph$_2$PH to vinyl-functionalised tri- or tetra-siloxanes or to the allyl-functionalised trisiloxane (16) gave the required phosphinated derivatives (20)—(22) in high yields, attempts to prepare these compounds by halogen substitution were abandoned.

All the siloxane derivatives are air-stable oils with the exception of the pyridine- and phosphine-functionalised compounds (19) and (20)—(22) which are readily oxidised, the latter three being pyrophoric. Spectroscopic data on the three series of complexes (A)—(C) are very similar, and we were able to detect

$$
\begin{array}{c}
\text{Me} \\
| \\
\text{Me}_3\text{SiO(SiO)}_n\text{SiMe}_3 \\
| \\
(\dot{\text{C}}\text{H}_2)_2 \\
| \\
\text{L}
\end{array}
$$

[n = 1 (A); n = 2 (B); n = 3 (C)]

signs of separate n.m.r. signals for the two or four diastereo-isomers expected for compounds of types (B) or (C), repectively only for compounds (6) and (10), and then only in the MeSi region of their ^{13}C n.m.r. spectra additional shoulders were observed compared with the spectra of compounds of type (A), data for which are given in Table 2. Compounds (5)—(22) all show strong i.r. absorptions characteristic[13,14] of methyl-siloxanes at *ca.* 2 940 (C–H str.) 1 430 (C–H bend), 1 410 and 1 270 (CH$_3$ asym. and sym. deformations), and 1 100—1 000 cm^{-1} (Si–O–Si asym. str.) in addition to bands typical of the functional group (R) in each individual compound.

Mass Spectral Data.—With a few exceptions the literature on the mass spectra of siloxanes is limited to studies on small cyclic and long-chain linear siloxanes,[15–17] consequently the mass spectra of the more volatile siloxanes prepared in this study [type (A), compounds (5), (7), (9), (11), (13), (16), (18), and (20)] have been obtained. In each spectrum the molecular ion $M^{\cdot +}$ is very weak or entirely absent [although $(M + H)^+$ is clearly seen in chemical ionisation (c.i.) spectra], and facile loss of Me$^{\cdot}$ or R$^{\cdot}$ is reflected in the high intensities of the $(M - \text{Me})^{\cdot +}$ and $(M - \text{R})^{\cdot +}$ peaks. Other common fragments observed include those due to $(M - \text{R} - \text{CH}_2)^+$, (Me$_3$SiOSiMe$_2$)$^+$, Me$_2SiR^+$, and Me$_3Si^+$, and indicate a similar fragmentation mechanism for all compounds irrespective of the nature of R, with the single exception of compound (18) where simple Me$^{\cdot}$ loss from the parent molecular ion is not observed. Doubly charged ions have been observed previously in other studies on methylsiloxanes,[16] and weak $(M - 2\text{Me})^{2+}$ ions occur in the spectra of compounds (9), (13), (16), and (20). The remaining intense ions in the mass spectra of (9), (13), and (18) with m/z = 246, 205, and 287, respectively, result from the loss of ethene and Me$^{\cdot}$ (43 mass units) from their molecular ions, and for (16) the ion with m/z = 205 corresponds to loss of propene and Me$^{\cdot}$ (57 mass units) from the molecular ion.

Experimental

All work with air-sensitive materials was carried out in a dry, oxygen-free atmosphere using freshly distilled, deoxygenated solvents. I.r. spectra were measured on a Perkin-Elmer 599b

spectrometer. Proton and ^{13}C-{^{1}H} n.m.r. spectra were recorded with JEOL PS 100 and FX 90Q spectrometers respectively, using CDCl$_3$ as solvent unless otherwise stated. Data given are for room-temperature measurements, and chemical shifts are given in p.p.m. downfield from internal SiMe$_4$. Mass spectra were recorded on a VG 70 70E instrument using direct-insertion probes and ionising energies of 12 and 70 eV, and for compounds which did not show molecular ions under these conditions c.i. spectra were also obtained. Analyses were by Butterworth Laboratories Ltd.

The silanes SiMe$_3$Cl, SiMeCl$_2$H, SiMeCl$_2$(CH=CH$_2$), and SiMeCl$_2$(CH$_2$CH=CH$_2$) were commercial samples used as received; LiCH$_2$C$_5$H$_4$N was prepared from 4-methylpyridine by literature methods.[18]

Syntheses.—SiMeCl$_2$(CH$_2$CH$_2$Ph) (1). Anhydrous AlCl$_3$ (0.36 g, 2.7 mmol) was added to a solution of dichloromethyl-vinylsilane (10.0 g, 70.9 mmol) in benzene (11.0 g, 0.14 mmol) and the mixture heated under reflux for 1 h. After cooling to 0 °C, the mixture was filtered and the filtrate treated with NEt$_3$ (0.3 cm^3) in order to complex undissolved AlCl$_3$. A further small quantity of solid was removed by filtration and the filtrate distilled under reduced pressure, yielding compound (1) as a colourless oil (9.8 g, 63%), b.p. 89 °C (0.5 mmHg) (Found: C, 48.2; H, 5.60; Cl, 30.6. C$_9$H$_{12}$Cl$_2$Si requires C, 49.3; H, 5.50; Cl, 32.4%). N.m.r. (CDCl$_3$): ^{1}H, 7.2 (m, 5 H, aromatic H), 2.81 (m, 2 H, CH$_2$Ph), 1.42 (m, 2 H, SiCH$_2$), and 0.64 (s, 3 H, Me); ^{13}C, 142.3, 128.5, 127.8, 126.1 (aromatics), 28.5 (CH$_2$Ph), 23.4 (SiCH$_2$), and 5.2 (Me).

The compound SiMeCl$_2$(CH$_2$CH$_2$CH$_2$Ph) (2) was prepared in 70% yield by the procedure described by Musolf and Speier,[19] while SiMeCl$_2$(CH$_2$CH$_2$CH$_2$CN) (3) and SiMeCl$_2$-(CH$_2$CH$_2$C$_6$H$_9$) (4) were synthesised from SiMeCl$_2$H in yields of over 80% by literature methods.[20]

Me$_3$SiO[SiMe(CH$_2$CH$_2$Ph)O]$_n$SiMe$_3$ (n = 1 *or* 2). A solution of SiMeCl$_2$(CH$_2$CH$_2$Ph) (10.2 g, 46.6 mmol) and SiMe$_3$Cl (10.1 g, 93.2 mmol) in Et$_2$O (25 cm^3) was added dropwise with stirring to water (20 cm^3) cooled in ice. The stirred mixture was allowed to warm to ambient temperature over 1 h. The ether layer was separated, dried, and the solvent removed *in vacuo*. Distillation of the residual oil under reduced pressure yielded compounds (5) and (6) as colourless oils (Table 1). Higher siloxanes remained undistilled.

By an analogous procedure using a 2:1 mole ratio of SiMe$_3$Cl to dichlorosilane derivative, a range of siloxanes was produced [(7)—(17), Table 1].

Me$_3$SiOSiMe(CH$_2$CH$_2$Br)OSiMe$_3$ (18). A slow stream of anhydrous HBr was passed through compound (16) (14.8 g, 59.6 mmol) containing a catalytic quantity of benzoyl peroxide (0.1 g). An exothermic reaction occurred and the temperature of the solution increased to 35—40 °C. Reaction was assumed to be complete when the solution temperature returned to ambient. Fractionation under reduced pressure yielded compound (18) as a colourless oil (17.2 g, 88%), b.p. 74 °C (1.3 mmHg) (Found: C, 33.1; H, 7.35; Br, 27.5. C$_9$H$_{25}$BrO$_2$Si$_3$ requires C, 32.8; H, 7.60; Br, 24.3%).

Me$_3$SiOSiMe(CH$_2$CH$_2$CH$_2$C$_5$H$_4$N)OSiMe$_3$ (19). A solution of LiCH$_2$C$_5$H$_4$N (7.78 g, 1.81 mmol) in thf (15 cm^3) was added dropwise with rapid stirring to a solution of compound (18) in thf (15 cm^3). The mixture was stirred for 3 d prior to distillation in the complete absence of oxygen. The product was isolated as a yellow, air-sensitive oil (4.7 g, 76%), b.p. 122 °C (0.25 mmHg) (Found: C, 51.9; H, 9.2; N, 3.60. C$_{15}$H$_{31}$NO$_2$Si$_3$ requires C, 52.8; H, 9.1; N, 4.00%).

Me$_3$SiOSiMe(CH$_2$CH$_2$PPh$_2$)OSiMe$_3$ (20). A mixture of compound (13) (4.00 g, 1.61 mmol) and PHPh$_2$ (2.50 g, 1.34 mmol) was sealed under a N$_2$ atmosphere in a thick-walled Pyrex tube (50 cm^3). The tube was irradiated with light from a

400-W mercury lamp for 48 h while the contents were continuously stirred. On completion of the reaction the product was isolated as a colourless, air-sensitive oil (5.5 g, 79%) by distillation under reduced pressure (b.p. 178 °C at 0.9 mmHg) (Found: C, 58.7; H, 8.00; P, 6.95. $C_{21}H_{35}O_2PSi_3$ requires C, 58.1; H, 8.05; P, 7.15%).

$Me_3SiO[SiMe(CH_2CH_2PPh_2)O]_2SiMe_3$ **(21)**. This compound was isolated as an air-sensitive oil in almost quantitative yield on irradiation of **(14)** (1.72 g, 5.14 mmol) and $PHPh_2$ (1.91 g, 10.3 mmol) as above. Distillation without decomposition did not prove possible, but the oil appeared analytically pure after pumping *in vacuo* (0.01 mmHg) and there was no spectroscopic evidence for unreacted starting materials (Found: C, 60.4; H, 7.40; P, 8.60. $C_{36}H_{52}O_3P_2Si_4$ requires C, 61.2; H, 7.35; P, 8.80%).

$Me_3SiOSiMe(CH_2CH_2CH_2PPh_2)OSiMe_3$ **(22)**. This compound was prepared by a similar procedure to that used for **(20)**, from **(16)** (2.00 g, 7.63 mmol) and $PHPh_2$ (1.18 g, 6.34 mmol), and was isolated as an air-sensitive, colourless oil (2.1 g, 58%), b.p. 190 °C (0.1 mmHg) (Found: C, 59.6; H, 7.90; P, 7.60. $C_{22}H_{37}O_2PSi_3$ requires C, 58.9; H, 8.25; P, 6.90%).

Acknowledgements

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