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Journal of Organometallic Chemistry 521 (1996) 75-91

Journal of Organometallic Chemistry

Reactions of symmetrical and unsymmetrical disilanes in the presence of $Cp_2MCl_2/^nBuLi$ (M = Ti, Zr, Hf) [1]

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Received 10 January 1996

Abstract

The reactions of disilanes with catalytic quantities of $Cp_2MCl_2/^nBuLi$ (M = Ti, Zr) and *cis*-cyclooctene in a disilane/cyclooctene/metal ratio of approximately 30: ≥ 30: 1 exhibited rapid formation of monosilanes and trisilanes. The product distributions produced from $H(PhMeSi)_2H$, $H(BuMeSi)_2H$ (symmetrical disilanes) and from $HPh_2SiSiPhMeH$, $HPhMeSiSiMe_2H$, HPhMeSiSiPrMeH and $HPh_2SiSiPhH_2$ (unsymmetrical disilanes) were determined by GCMS in all cases and the trisilanes from $HPh_2SiSiPhMeH$ and $HPhMeSiSiMe_2H$ were isolated and characterized spectroscopically. Major and minor isomers of $Ph_4Me_2Si_3H_2$ and $Ph_5MeSi_3H_2$ (formed from $HPh_2SiSiPhMeH$) and of $PhMe_5Si_3H_2$ and $Ph_2Me_4Si_3H_2$ (formed from $HPhMeSiSiMe_2H$) were identified. Analysis of the product distribution in these reactions indicated that both Si–Si bond cleavage and Si–H dehydrocoupling of the starting disilane occurs. Rationalization of the product distributions and apparent isomer preferences through both σ-bond metathesis steps and metal silylene intermediates is presented. The rapid reaction of the Si–Si bond in $H(SiPhMe)_xH$ was found to be characteristic of the disilane and occurred only to a minor extent in the trisilane and was absent in the tetrasilane.

Keywords: Silicon; Disilanes; Titanium; Zirconium; Hafnium; Cyclopentadienyl catalysis

1. Introduction

Dehydrocoupling involves the elimination of dihydrogen between two (or more) EH or between EH and E′H units to produce E–E or E–E′. This general reaction has been particularly successful in the formation of silicon oligomers and polymers [1]. Several transition metal complexes promote the formation of Si–Si bonds, the most successful of which have involved metallocene-type precursors of the titanium triad. The coupling with these Group 4 triad catalysts appears to occur through σ-bond metathesis steps. Reactivity of hydrosilanes towards dehydrocoupling follows the order primary > secondary ≫ tertiary, which most probably reflects steric constraints in the condensation reaction. A peculiar feature of Group 4 metallocene catalysts is that coupling of $H_2RSiSiRH_2$ occurs more rapidly than does that of $RSiH_3$. Harrod and coworkers reported that $H_2PhSiSiPhH_2$ formed tetramer and even-numbered oligomers in the presence of Cp_2TiMe_2 (or Cp_2ZrMe_2) faster than $PhSiH_3$ was polymerized and that 1,2,3-triphenyltrisilane polymerized stepwise to Si_6, Si_9, Si_{12}, etc. In the polymerization of 1,2-diphenyldisilane, no trimer was observed [1b,2]. The $Cp_2^*HfH_2$ catalyzed reaction of $H_2PhSiSiPhH_2$ occurred more rapidly than that of $PhSiH_3$, however, in this case trisilane was observed [3]. This result supported the reversibility of the σ-bond metathesis steps that lead to Si–Si bond formation. Hengge and coworkers observed that methyl-substituted disilanes with at least one Si–H bond reacted in the presence of Cp_2MMe_2 (M = Ti, Zr) to give both odd- and even-numbered oligomers and, in some cases, polymers [4]. An interesting feature of the reactions reported by Hengge and coworkers is an overall disproportionation. For instance, $HMe_2SiSiMe_2H$ gave $HMe_2Si(SiMe_2)_{n-1}SiMe_2H$ and $(n-1)Me_2SiH_2$ and the oligomers observed contained both odd- and even-numbered silicon chains. Even the "tertiary"

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[1] Dedicated to Professor Robert Corriu in recognition of his outstanding contributions to organosilicon chemistry.

PII S0022-328X(96)06298-5

silane $Me_3SiSiMe_2H$ reacted to give $Me_3Si(SiMe_2)_{n-1}SiMe_2H$ instead of $Me_3Si(SiMe_2)_2SiMe_3$ (the product expected from direct Si–H dehydrocoupling) [4e]. A unique feature in the reaction of $H_2MeSiSiMeH_2$ was the formation of branched as well as linear structures. The presence of $[Si(Si_3)]$ units in the products was verified by ^{29}Si NMR data [4d]. Hengge and coworkers concluded that hydrogen-rich disilanes reacted through the Si–H bond, producing dihydrogen by a mechanism similar to that formulated by Tilley. However, the products that form from disilanes with only one or two Si–H groups appear to involve Si–Si bond cleavage and subsequent reactions lead to polymer products. An additional mechanism was suggested for these latter disilanes, involving the formation of metal silylene intermediates M=Si from which the silylene was released [4b]. Insertion of the silylene into Si–H or Si–Si bonds was then responsible for chain growth. Transition metal carbene complexes are common and their chemistry has been well studied [5a], but metal–silylenes of the early transition metals are rare. The silylene complex $TiSiH_2$ has been studied experimentally in the gas phase using ion-beam techniques [5b] and the nature of the Ti=Si double bond has been investigated using ab initio calculations [5c]. A theoretical study of Cp_2TiSiH_2 and its role in dehydrocoupling of primary organosilanes has appeared [5d], but no M=Si (M = Group 4) derivative has been isolated or characterized in solution.

In the current study the reactions of 1,2-dihydrodisilanes (in the presence or absence of stoichiometric quantities of cyclic olefin) with the catalyst generated from the combination $Cp_2MCl_2/^nBuLi$ are reported. The disilanes contain either the same substituent pattern at each silicon, i.e. $H(PhMeSi)_2H$ and $H(BuMeSi)_2H$ (symmetrical disilanes), or differently substituted silicon centers such as $HPh_2SiSiPhMeH$, $HPhMeSiSiMe_2H$, HPhMeSiSiPrMeH and $HPh_2SiSiPhH_2$ (unsymmetrical disilanes). In addition, the reactions of $H(PhMeSi)_3H$ and $H(PhMeSi)_4H$ were briefly examined. A rationalization of the product distribution from these disilanes based on both σ-bond metathesis and silylene mechanisms is presented.

2. Results

2.1. Preparation of disilanes

The condensation of $PhMeSiH_2$ or Ph_2SiH_2 in the presence of stoichiometric amounts of *cis*-cyclooctene and catalytic quantities of $Cp_2TiCl_2/^nBuLi$ under a variety of conditions provided $H(PhMeSi)_xH$ [$x = 2$ (disilane), 3 (trisilane), 4 (tetrasilane)] and $HPh_2SiSiPh_2H$ [6]. The tetraalkylated disilane HBuMeSiSiMeBuH was prepared by removal of the phenyl groups from HPhMeSiSiMePhH with triflic acid followed by reaction with BuMgCl [6]. Disilanes with different substituents at each of the silicon centers were prepared by removal of a phenyl group from $H(PhMeSi)_2H$ or $H(Ph_2Si)_2H$ with one equivalent of triflic acid followed by addition of RMgX or $LiAlH_4$ to give $HPhMeSiSiMe_2H$ [6], HPhMeSiSiPrMeH, $HPh_2SiSiPhMeH$ [6] and $HPh_2SiSiPhH_2$ [7].

2.2. Condensation of $H(PhMeSi)_xH$ ($x = 2, 3, 4$) and $H(BuMeSi)_2H$

The reaction of $H(PhMeSi)_2H$ with $Cp_2TiCl_2/^nBuLi$ in the presence of *cis*-cyclooctene (stoichiometric relative to the disilane) showed formation of $PhMeSiH_2$ (29% by GC) and $H(PhMeSi)_3H$ (35%) and residual disilane (25%) within 1 h. In addition, $H(PhMeSi)_4H$ was produced and the ratio of trisilane/tetrasilane was 5 (1 h of reaction). Slow growth of trisilane and tetrasilane and minor quantities of pentasilane followed, as shown in Table 1. After 96 h the initially produced monosilane was consumed and the concentration of both trisilane and tetrasilane increased, but the trisilane/tetrasilane ratio decreased to about 2. With $Cp_2ZrCl_2/^nBuLi$, under similar conditions with added

Table 1
Reaction of $H(PhMeSi)_xH$ ($x = 2, 3, 4$) and *cis*-cyclooctene in the presence of $Cp_2TiCl_2/^nBuLi$ [a]

Product [b]	$H(PhMeSi)_2H$			$H(PhMeSi)_3H$ [c]		$H(PhMeSi)_4H$ [d]		
	1 h	3.5 h	96 h	2 h	24 h [e]	1 h	4 h	12 h [f]
$PhMeSiH_2$	29	24	—	4.0		—	—	—
PhMeBuSiH	3.9	4.8	12					
$Ph_2Me_2Si_2H_2$	25	23	18	4.7	4.8	—	—	—
$Ph_3Me_3Si_3H_2$	35	35	47	87	87	9.1	12	11
$Ph_4Me_4Si_4H_2$	7.1	13	23	4.6	8.1	82	76	75
$Ph_5Me_5Si_5H_2$	—	—	< 1			9.4	13	14

[a] Reactions conducted in toluene at an oligomer to titanium ratio of between 30 and 40 to 1 and 80°C for the disilane and trisilane and 90°C for the tetrasilane. [b] Products determined by GCMS; data recorded are GC percentages and are uncorrected. [c] 94.7% trisilane and 5.3% disilane. [d] 92.8% tetrasilane and 7.2% trisilane. [e] Reaction decolorizes between 2 and 24 h. [f] Reaction run at 90°C for 4 h then at room temperature for 12 h.

olefin, the extent of conversion to monosilane was less after 1 h than that observed in the titanium system with a monosilane/disilane/trisilane/tetrasilane ratio of about 1.6 : 11 : 1 : 1.9 (GC). The higher proportion of tetrasilane suggests that some direct dehydrocoupling of the disilane takes place. The amount of disilane slowly decreased and after 16 h the monosilane/disilane/trisilane/tetrasilane ratio had become 1 : 5.6 : 1.5 : 1.5.

In the case of $H(BuMeSi)_2H$, any $BuMeSiH_2$ formed would be masked in GC traces by the solvent. Within 1 h, both $H(BuMeSi)_3H$ and $H(BuMeSi)_4H$ had formed and the ratio of disilane/trisilane/tetrasilane was 1.1 : 2.4 : 1.0. The change was only marginal over the next 70 h. In contrast to $H(PhMeSi)_2H$, the tetrasilane $H(BuMeSi)_4H$ formed rapidly at the same time as the trisilane.

The reaction of $H(PhMeSi)_3H$ showed only minor conversion to monosilane and tetrasilane at 80°C in the presence of $Cp_2TiCl_2/^nBuLi$ (Table 1). The tetrasilane exhibited only slight reaction at 80°C and at 90°C less than 20% of the original tetrasilane reacted within 12 h and no monosilane was observed (Table 1). Monosilane was not observed at any temperature at which the reaction of the trisilane and tetrasilane was conducted with $Cp_2ZrCl_2/^nBuLi$.

2.3. Condensation of unsymmetrical disilanes

The oligomers formed from the condensation reactions of unsymmetrical disilanes were identified by GC and GCMS. Whenever possible products from the condensation reactions were isolated by distillation or preparative gas chromatography (PGC). The degree to which oligomers could be isolated by PGC depended greatly on the number of phenyl groups in the oligomer. Generally, it was not possible to purify trisilanes with more than two phenyl groups or tetrasilanes with more than one phenyl group. The oligomers that were isolated by PGC were additionally characterized by ^1H and ^{29}Si NMR spectroscopy. Integration of the Si–H region led to the determination of the ratio between structural isomers with the same general formula or between

Table 2
Products from the condensation of $HPh_2SiSiPhMeH$ and C_8H_{14} in the presence of $Cp_2MCl_2/^nBuLi$ (M = Ti, Zr) identified by mass spectroscopy [a,b]

Molecular ion (% base peak)	Fragment ions (assignment; % base peak)
Monosilanes	
* $PhMeSiH_2$, 122 (87)	121 ($PhMeSiH^+$, 100), 107 ($PhSiH_2^{\dot{+}}$, 72), 105 ($PhSi^+$, 51)
PhMeBuH, 178 (4.6)	121 (100), 107 (19), 105 (14)
* Ph_2SiH_2, 184 (41)	106 ($PhSiH^+$, 100), 105 (63)
$PhMe(C_8H_{13})SiH$, 230 (2.4)	121 (100), 105 (20)
$PhMe(C_8H_{15})SiH$, 232 (0.25)	121 (100), 105 (13)
* Ph_2BuSiH, 240 (2.2)	183 (Ph_2SiH^+, 100), 181 (22), 162 ($PhBuSi^+$, 37), 134 ($PhEtSi^+$, 22), 105 (37)
$Ph_2(C_8H_{13})SiH$, 292 (1.2)	183 (100), 105 (17)
Disilanes	
$HPh_2SiSiPhMeH$, 304 (6.0)	259 (Ph_3Si^+, 60), 197 ($PhMe_2Si^+$, 97), 183 (63), 181 (46), 121 (26), 105 (100)
* $Ph_2Me_2Si_2H_2$, 242 (5.3)	197 (100), 121 (45), 105 (37)
* $Ph_3MeBuSi_2H$, 360 (13)	259 (13), 177 ($PhMeBuSi^+$, 29), 121 (100), 105 (18)
$Ph_3MeBuSi_2H$, 360 (6.0)	239 (Ph_2BuSi^+, $\{P-PhMeSiH\}^+$, 26), 197 (21), 183 (100), 181 (13), 105 (21)
* $Ph_4Si_2H_2$, 366 (0.6)	259 (100), 183 (57), 181 (38), 105 (52)
Trisilanes	
* $Ph_4Me_2Si_3H_2$, 424 (4.0)	303 ($Ph_3MeSi_2H^+$, $\{P-PhMeSiH\}^+$, 59), 302 ($\{P-PhMeSiH_2\}^+$, 33), 226 ($Ph_2MeSi_2H^+$, $\{P-Ph_2MeSiH\}^+$, 86), 224 (45), 197 (Ph_2MeSi^+, 100), 183 (15), 181 (19), 121 (21), 105 (74)
* $Ph_4Me_2Si_3H_2$, 424 (0.4)	303 (22), 259 (20), 241 ($Ph_2Me_2Si_2H^+$, 26), 240 (32), 226 (49), 225 (27), 224 (23), 197 (71), 195 (13), 181 (19), 164 ($PhMe_2Si_2H^+$, 13), 135 (21), 121 (23), 105 (100)
$Ph_3Me(C_8H_{15})Si_3H$, 414 (5.0)	303 (44), 197 (24), 183 (100), 105 (22)
$Ph_3Me(C_8H_{15})Si_3H$, 414 (1.1)	303 (20), 259 (13), 197 (13), 121 (100)
* $Ph_5MeSi_3H_2$, 486 (0.94)	365 {$(P-PhMeSiH)^+$, 18}, 303 (36), 302 (29), 288 ($\{P-Ph_2MeSiH\}^+$, 66), 286 (12), 259 (94), 226 (38), 210 ($Ph_2Si_2^{\dot{+}}$, 26), 197 (55), 183 (28), 181 (35), 105 (100)
* $Ph_5MeSi_3H_2$, 486 (3.0)	303 (87), 302 (76), 288 (28), 259 (69), 226 (66), 224 (47), 197 (83), 183 (29), 181 (30), 121 (10), 105 (100)
Tetrasilanes	
$Ph_6Me_2Si_4H_2$, 606 (0.60),	485 ($\{P-PhMeSiH\}^+$, 5.4), 408 ($\{P-Ph_3SiH\}^+$, 37), 346 ($Ph_3Me_2Si_3H^+$, 14), 330 ($Ph_3MeSi_3^{\dot{+}}$, 13), 303 (45), 302 ($Ph_3MeSi_2^{\dot{+}}$, 50), 301 (36), 286 (17), 285 (12), 224 (48), 197 (93), 195 (20), 183 (32), 181 (27), 121 (24), 105 (100)

[a] Suggested assignments for *m/e* values are given the first time the value appears. For series of *m/e* values that differ by hydrogen content, only one assignment is shown. Data given are at least 10% of the base peak and are uncorrected. [b] All components listed were found in the $Cp_2ZrCl_2/^nBuLi$ catalyzed reactions. Components that are designated with an asterisk were found in the $Cp_2TiCl_2/^nBuLi$ catalyzed reactions.

Table 3
Products from the condensation of $HPhMeSiSiMe_2H$ and C_8H_{14} in the presence of $Cp_2ZrCl_2/{}^nBuLi$ identified by mass spectroscopy [a,b]

Molecular ion (% base peak)	Fragment ions (assignment; % base peak)
Monosilanes	
* $PhMeSiH_2$ [c]	
* $PhMeBuSiH$ [c]	
Disilanes	
$PhMe_3Si_2H_2$, 180 (6.0)	135 ($PhMe_2Si^+$, 100), 121 ($PhMeSiH^+$, 43), 120 (13), 105 ($PhSi^+$, 35)
* $Ph_2Me_2Si_2H_2$ [c]	
Trisilanes	
$PhMe_5Si_3H_2$, 238 (5.9)	179 ($\{P-Me_2SiH\}^+$, 31), 178 ($\{P-Me_2SiH_2\}^+$, 38), 177 (15), 163 ($PhMe_2Si_2^+$, 28), 135 ($PhMe_2Si^+$, 100), 121 (25), 116 ($Me_4Si_2^+$, 100), 105 (42), 102 ($Me_3Si_2H^+$, 30)
* $Ph_2Me_4Si_3H_2$, 300 (3.2)	241 ($Ph_2Me_2Si_2H^+$, 21), 225 ($Ph_2MeSi_2^+$, 10), 197 (37), 179 ($PhMe_3Si_2H^+$, 29), 178 ($PhMe_3Si_2^+$, 32), 177 (12), 164 ($PhMe_2Si_2H^+$, 45), 163 (37), 149 ($PhMe_2Si_2H^+$, 10), 121 (42), 119 (12), 105 (100), 102 (13)
* $Ph_3Me_3Si_3H_2$, 362 (3.3)	241 (79), 240 (68), 239 (15), 225 (37), 164 (71), 163 (25), 135 (61), 121 (39), 119 (10), 105 (100)
Tetrasilanes	
$PhMe_7Si_4H_2$, 296 (1.8)	237 ($\{P-Me_2SiH\}^+$, 28), 236 ($\{P-Me_2SiH_2\}^+$, 16), 191 ($PhMe_3Si_2^+$, 12), 179 (27), 178 (25), 177 (46), 163 ($PhMe_2Si_2^+$, 52), 162 (21), 161 (37), 160 ($Me_5Si_3H^+$, 100), 145 ($Me_4Si_3H^+$, 15), 135 (100), 121 (25), 116 ($Me_4Si_3^+$, 61), 115 (11), 107 ($PhSiH_2^+$, 16), 105 (46), 101 ($Me_3Si_2^+$, 13)
$PhMe_7Si_4H_2$, 296 (12)	237 (100), 236 (26), 235 (18), 221 ($PhMe_4Si_3^+$, 11), 191 (13), 179 (33), 178 (55), 177 (52), 176 ($Me_6Si_3H_2^+$, 21), 175 (77), 174 (43), 173 (20), 163 (48), 159 ($Me_5Si_3^+$, 15), 135 (70), 131 (14), 121 (22), 117 ($Me_4Si_2H^+$, 29), 116 (59), 115 (12), 105 (24), 101 (27)
* $Ph_2Me_6Si_4H_2$, 358 (1.8)	299 ($Ph_2Me_4Si_3H^+$, 11), 239 (11), 225 (12), 224 (12), 223 (25), 222 ($PhMe_4Si_3H^+$, 73), 221 (17), 207 ($PhMe_3Si_3H^+$, 10), 197 (16), 179 (43), 178 (53), 177 (37), 163 (54), 162 (33), 161 (15), 135 (100), 121 (30), 107 (14), 105 (51)
* $Ph_2Me_6Si_4H_2$, 358 (0.7)	237 (13), 222 (69), 221 (13), 197 (10), 179 (32), 178 (43), 177 (39), 163 (56), 162 (30), 161 (17), 135 (100), 107 (12), 105 (42)
* $Ph_2Me_6Si_4H_2$, 358 (5.5)	237 (100), 236 (33), 235 (19), 197 (26), 163 (35), 162 (13), 161 (13), 160 (15), 135 (55), 121 (16), 105 (20)
* $Ph_3Me_5Si_4H_2$, 420 (3.8) [d]	299 (44), 298 (11), 241 (18), 240 (16), 239 (21), 225 (23), 222 (73), 221 (26), 207 (11), 178 (27), 177 (30), 163 (46), 162 (25), 161 (16), 135 (100), 121 (44), 107 (14), 105 (72)
Pentasilanes	
$PhMe_9Si_5H_2$, 354 (6.4)	295 ($PhMe_7Si_4H^+$, 84), 237 ($PhMe_5Si_3H^+$, 56), 235 (35), 233 ($Me_8Si_4H^+$, 100), 221 (23), 219 (18), 179 (22), 178 (26), 177 (29), 175 ($Me_6Si_3H^+$, 26), 163 (25), 159 (44), 135 (59), 121 (20), 116 (21), 105 (16)
$Ph_2Me_8Si_5H_2$, 416 (8.6)	357 ($Ph_2Me_6Si_4H^+$, 68), 299 (26), 298 (12), 297 (12), 295 (13), 281 (44), 280 (21), 239 (24), 237 (61), 236 (26), 235 (21), 225 (13), 221 (48), 220 (36), 219 (24), 207 (25), 206 (31), 205 (11), 197 (19), 191 (18), 179 (26), 178 (43), 177 (49), 175 (18), 163 (51), 162 (21), 161 (27), 160 (12), 135 (100), 121 (27), 116 (18), 107 (11), 105 (37)
$Ph_2Me_8Si_5H_2$, 416 (2.8)	357 (18), 299 (23), 297 (15), 295 (53), 281 (15), 239 (12), 237 (21), 235 (11), 221 (38), 219 (22), 197 (13), 191 (15), 177 (41), 175 (21), 163 (38), 162 (15), 161 (23), 160 (12), 159 (10), 135 (100), 121 (31), 117 (13), 116 (22), 107 (11), 105 (37)
$Ph_2Me_8Si_5H_2$, 416 (2.9)	357 (30), 295 (66), 281 (20), 280 (11), 237 (70), 236 (16), 235 (25), 221 (42), 220 (26), 219 (23), 191 (19), 179 (22), 178 (28), 177 (48), 175 (19), 163 (45), 161 (22), 159 (12), 135 (100), 121 (28)
* $Ph_3Me_7Si_5H_2$, 478 (3.3) [e]	419 ($Ph_3Me_5Si_4H^+$, $\{P-Me_2SiH\}^+$, 10), 357 (31), 283 ($Ph_2Me_3Si_3^+$, 24), 281 (56), 280 (16), 267 ($\{Ph_2Me_2Si_3-H\}^+$; 14), 241 (20), 239 (23), 237 (38), 236 (13), 225 (27), 221 (18), 220 (22), 207 ($PhMe_3Si_3H^+$, 100), 206 (24), 197 (35), 195 (10), 193 (10), 191 (23), 177 (32), 175 (10), 163 (30), 162 (13), 161 (18), 135 (82), 133 (11), 121 (30), 116 (12), 107 (11), 105 (41)

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[a] Suggested assignments for m/e values are given the first time the value appears. For series of m/e values that differ by hydrogen content, only one assignment is shown. Data given are at least 10% of the base peak and are uncorrected. [b] All components listed were found in the $Cp_2TiCl_2/{}^nBuLi$ catalyzed reactions. Components that are designated with an asterisk were also found in the $Cp_2ZrCl_2/{}^nBuLi$ catalyzed reactions. [c] m/e data are listed under condensation of $Ph_3MeSi_2H_2$. [d] One of two isomers observed. [e] Three additional isomers observed.

oligomers in an oligomeric mixture. In some cases the ratios could also be measured by GC and were consistent with those obtained by NMR spectroscopy. All of the condensation reactions with the catalyst system $Cp_2TiCl_2/^nBuLi$ were conducted in the presence of *cis*-cyclooctene since condensation occurred more rapidly than in the absence of an olefin. Cyclooctane was formed during the course of the reaction. Selected condensation reactions with the catalyst system $Cp_2MCl_2/^nBuLi$ (M = Zr, Hf) were run both in the presence and the absence of *cis*-cyclooctene.

2.3.1. $HPh_2SiSiPhMeH$

The reaction of $HPh_2SiSiPhMeH$ and *cis*-cyclooctene in the presence of $Cp_2TiCl_2/^nBuLi$ produced 10 different products which included monosilanes, disilanes and trisilanes. The molecular weights of the products could be assigned from GCMS (Table 2). Distillation of the product mixture removed the monosilanes and disilanes leaving the two sets of trisilanes $Ph_4Me_2Si_3H_2$ and $Ph_5MeSi_3H_2$. Fractional distillation provided center cuts which were utilized for spectroscopic characterization, although the $Ph_4Me_2Si_3H_2$ sample was contaminated with the disilane $H(Ph_2Si)_2H$ and additional minor impurities (8% by GC).

The two possible monosilanes, $PhMeSiH_2$ and Ph_2SiH_2, that could be generated from $HPh_2SiSiPhMeH$ were both observed in the reaction mixture. Also observed were the two symmetrical disilanes, $H(PhMeSi)_2H$ and $H(Ph_2Si)_2H$, that could be generated from Si–H dehydrocoupling of these monomers. The disilanes were confirmed by GC and GCMS and by comparison with authentic samples. The major isomer of $Ph_4Me_2Si_3H_2$, $HPh_2SiSiPhMeSiPhMeH$, exhibits a characteristic singlet at δ 5.47 ppm (HPh_2Si) and a pseudo-quintet at δ 4.75 ppm (HPhMeSi) which results from the overlap of the quartets of the two diastereomers. The minor isomer $HPhMeSiSiPh_2SiPhMeH$ exhibits a pseudo-quintet at δ 4.93 ppm (HPhMeSi) which results from the overlap of the quartets of the two diastereomers. Both of these trisilanes have been characterized previously [6]. The $HPh_2SiSiPh_2H$ contaminant exhibits a singlet at δ 5.47 ppm. Integration of the SiH region showed that the ratio of the major to minor trisilane isomers was 2.0: 1.0. The isomers of $Ph_5MeSi_3H_2$, $HPh_2SiSiPhMeSiPh_2H$ (major) and $HPh_2SiSiPh_2SiPhMeH$ (minor) also exhibited characteristic resonances in the Si–H region of the NMR spectrum. A singlet at δ 5.55 and a quartet at δ 4.93 were assigned to the minor isomer and the singlet at δ 5.36 was assigned to the major isomer. Additional minor SiH impurities were evident in the spectrum. Integration of the SiH region indicated that the ratio of the major to minor isomers was approximately 3.0: 1.0.

Initial experiments with $Cp_2ZrCl_2/^nBuLi$ and $HPh_2SiSiPhMeH$ were attempted in the absence of olefin but no reaction occurred. However, when *cis*-cyclooctene was added the reaction of the disilane produced 17 different products (including structural isomers) formed within 24 h. The products were identified by GC/GCMS and include all those listed in Table 2. In addition to the products observed with the titanium system, PhMeBuSiH and $Ph_3MeBuSi_2H$ appear in the product mixture and are probably produced during removal of the butene coordinated to the zirconium complex and produced from reaction of Cp_2ZrCl_2 and ^nBuLi. The remaining new products produced with the zirconium catalyst result from CH/SiH dehydrocoupling with *cis*-cyclooctene [$PhR(C_8H_{13})SiH$ (R = Me, Ph)] and hydrosilylation of *cis*-cyclooctene by the starting disilane [$Ph_3Me(C_8H_{15})Si_2H$]. We have demonstrated previously that $Cp_2ZrCl_2/^nBuLi$ is an effective hydrosilylation catalyst and also promotes CH/SiH coupling [8]. In addition, two isomers of the tetrasilane $Ph_6Me_2Si_4H_2$ (a "dimer" of the starting disilane), were identified. The GC ratio between these groups of products, monosilanes/disilanes/trisilanes + tetrasilane/hydrosilylation + CH/SiH dehydrocoupling, was approximately 1: 1.3: 2.4: 1. When $Cp_2HfCl_2/^nBuLi$ was reacted with a mixture of $HPh_2SiSiPhMeH$ and *cis*-cyclooctene, less than 10% of the disilane was consumed within 1 h to give two isomers of the hydrosilylation product $Ph_3MeSi_2(C_8H_{15})H$. No subsequent change in the product mixture was observed.

2.3.2. $HPhMeSiSiMe_2H$

The reaction of $Cp_2TiCl_2/^nBuLi$ with $HPhMeSiSiMe_2H$ and *cis*-cyclooctene provided at least 21 products that were identified by GC/GCMS and data are summarized in Table 3. In addition to the starting disilane (4.2%), trisilanes [$PhMe_5Si_3H_2$ (two isomers), $Ph_2Me_4Si_3H_2$ (two isomers), total 27%], tetrasilanes [$PhMe_7Si_4H_2$ (two isomers), $Ph_2Me_6Si_4H_2$ (three isomers), $Ph_3Me_5Si_4H_2$ (two isomers), total 45%] and pentasilanes [$PhMe_9Si_5H_2$ (one), $Ph_2Me_8Si_5H_2$ (four isomers), $Ph_3Me_7Si_5H_2$ (three isomers), total 21%] were observed (six minor products were also present in the GC traces ranging from 0.5 to 0.9%). Two sets of trisilanes and one set of tetrasilanes were isolated by preparative gas chromatography and characterized spectroscopically.

Two isomers of the trisilane $PhMe_5Si_3H_2$ were observed, both of which have been previously characterized [6]. In the Si–H region of the ^1H NMR spectrum for the isomer $HPhMeSiSiMe_2SiMe_2H$ (major), a characteristic quartet at δ 4.60 ppm and a septet at δ 4.04 were present, whereas $HMe_2SiSiPhMeSiMe_2H$ (minor) exhibited a septet at δ 4.18. From integration of the Si–H region, the ratio of the major to the minor isomer was 1.2: 1.0. The two isomers of $Ph_2Me_4Si_3H_2$ have been previously characterized [6]. The major isomer $HPhMeSiSiPhMeSiMe_2H$ exhibits a quartet at δ 4.73

and a septet at δ 4.17 and the minor isomer HPhMeSiSiMe$_2$SiPhMeH exhibits two overlapping quartets at δ 4.58 in the SiH region. The integrated ratio of major to minor isomers was 9.4: 1.0 (GC ratio 9.6: 1.0). Two isomers of PhMe$_7$Si$_4$H$_2$, H$_a$Me$_2$SiSiPhMeSiMe$_2$SiMe$_2$H$_b$ (major) and H$_c$PhMeSiSiMe$_2$SiMe$_2$SiMe$_2$H$_d$, were also obtained. An apparent septet at δ 4.04 ppm has been assigned to the terminal SiH$_b$ of the major isomer and SiH$_d$ of the minor isomer. The two septets appear to be coincident. A septet at δ 4.21 is assigned to SiH$_a$ of the major isomer and a quartet at δ 4.6 ppm is assigned to SiH$_c$ of the minor isomer. The presence of an impurity is indicated by overlapping resonances at δ 4.62. The ratio of the major to the minor isomers from integration of the multiplets at 4.04 and 4.21 ppm is 1.2: 1.0.

The reaction of HPhMeSiSiMe$_2$H with Cp$_2$ZrCl$_2$/^{n}BuLi at 80°C (no olefin) for 60 h gave PhMeSiH$_2$, trisilanes [PhMe$_5$Si$_3$H$_2$ (two isomers), Ph$_2$Me$_4$Si$_3$H$_2$ (two isomers), Ph$_3$Me$_3$Si$_3$H$_2$ (two isomers), Ph$_3$Me$_3$BuSi$_3$H and Ph$_4$Me$_2$Si$_3$H$_2$], tetrasilanes [Ph$_2$Me$_6$Si$_4$H$_2$ (three isomers), Ph$_3$Me$_5$Si$_4$H$_2$ (two isomers), Ph$_4$Me$_4$Si$_4$H$_2$] and the pentasilane Ph$_3$Me$_7$Si$_5$H$_2$ (four isomers) and minor products (Table 3). The reaction of HPhMeSiSiMe$_2$H and *cis*-cyclooctene with Cp$_2$HfCl$_2$/^{n}BuLi at 80°C provided only small amounts of monosilane and trisilane and no hydrosilylation products after 3 h, after which time no further reaction occurred. Only 9% (by GC) of the starting disilane reacted.

2.3.3. *HMePhSiSiMePrH*

The reaction of HMePhSiSiMePrH and *cis*-cyclooctene with Cp$_2$TiCl$_2$/^{n}BuLi provided the hydrosilylation product (C$_8$H$_{15}$SiPrMeH, 4.2%), two trisilanes [PhPr$_2$Me$_3$Si$_3$H$_2$ (two isomers, 7.1%), Ph$_2$PrMe$_3$Si$_3$H$_2$ (two isomers), total 52%] and a tetrasilane (Ph$_3$PrMe$_4$Si$_4$H$_2$, 5.9%) in the mixture isolated after 23 h at 50°C (Table 4). In the initial phases of the reaction only PhMeSiH$_2$ and the trisilanes were observed.

2.3.4. *HPh$_2$SiSiPhH$_2$*

The reaction of HPh$_2$SiSiPhH$_2$ and *cis*-cyclooctene (Cp$_2$TiCl$_2$/^{n}BuLi) showed consumption of starting disilane within 1 h. The only products that could be observed in the GC traces were Ph$_2$SiH$_2$, Ph$_4$Si$_2$H$_2$ and Ph$_4$Si$_3$H$_4$. After removal of the volatile material a ^{1}H NMR spectrum showed two sets of broad resonances

Table 4
Products from the condensation of HPhMeSiSiPrMeH and C$_8$H$_{14}$ in the presence of Cp$_2$TiCl$_2$/^{n}BuLi identified by mass spectroscopy [a]

Molecular ion (% base peak)	Fragment ions (assignment; % base peak)
Monosilanes	
PrMe(C$_8$H$_{15}$)SiH, 198 (4.0)	155 [(C$_8$H$_{15}$)MeSiH$^+$, 13], 127 (15), 113 (18), 110 (45), 109 (17), 101 (11)
Disilanes	
HPhMeSiSiPrMeH, 208 (3.37)	163 (PhPrMeSi$^+$, 48), 121 (PhMeSiH$^+$, 100), 105 (PhSi$^+$, 28)
Trisilanes	
PhPr$_2$Me$_3$Si$_3$H$_2$, 294 (3.2)	209 (10), 206 (PhPrMe$_2$Si$_2$H$^+$, 21), 165 (PhMe$_2$Si$_2$H$_2^+$, 100), 164 (49), 163 (33), 149 (PhPrSiH$^+$, 13), 135 (PhMe$_2$Si$^+$, 43), 130 (PrMe$_2$Si$_2$H$^+$, 70), 121 (PhMeSiH$^+$, 67), 105 (44)
Ph$_2$PrMe$_3$Si$_3$H$_2$, 328 (4.9)	241 (Ph$_2$Me$_2$Si$_2$H$^+$, 38), 240 (15), 206 (31), 197 (Ph$_2$MeSi$^+$, 44), 165 (81), 164 (100), 163 (35), 149 (15), 135 (PhMe$_2$Si$^+$, 51), 130 (17), 121 (55), 107 (PhSiH$_2^+$, 11), 105 (81)
Ph$_2$PrMe$_3$Si$_3$H$_2$, 328 (2.0)	206 (41), 197 (12), 165 (100), 164 (70), 163 (25), 135 (43), 130 (18), 121 (47), 105 (60)
Tetrasilanes	
Ph$_3$PrMe$_4$Si$_4$H$_2$, 448 (3.4)	361 (Ph$_3$Me$_3$Si$_3$H$^+$, 16), 285 (Ph$_2$Me$_3$Si$_3$H$_2^+$, 53), 284 (49), 283 (17), 253 (11), 250 (45), 241 (36), 240 (45), 239 (40), 238 (15), 225 (42), 224 (23), 208 (30), 207 (36), 206 (37), 197 (44), 195 (16), 165 (43), 164 (46), 163 (34), 162 (19), 161 (11), 149 (11), 135 (80), 121 (53), 107 (14), 105 (100)
Ph$_3$PrMe$_4$Si$_4$H$_2$, 448 (1.8)	327 (Ph$_2$PrMe$_3$Si$_3$H$^+$, 12), 285 (100), 283 (12), 250 (85), 241 (21), 240 (18), 239 (17), 225 (Ph$_2$MeSi$_2^+$, 22), 208 (28), 207 (37), 206 (23), 197 (29), 165 (30), 164 (30), 163 (27), 162 (14), 149 (12), 147 (10), 135 (62), 121 (48), 105 (62)

[a] Suggested assignments for *m/e* values are given the first time the value appears. For series of *m/e* values that differ by hydrogen content, only one assignment is shown. Data given are at least 10% of the base peak and are uncorrected.

with some fine structure centered about 4.8 and 5.3 ppm, consistent with the formation of cyclic $(PhSiH)_x$ and linear $H(PhSiH)_yH$ [9].

3. Discussion

Dehydrocoupling of hydrosilanes is one of two synthetic routes to polysilanes, the other being a Wurtz-type coupling of chlorosilanes [1]. Both electron-rich and electron-poor transition metals have been utilized as catalysts for dehydrocoupling. The condensation rate for monosilanes follows the order primary ≫ secondary with little evidence for the coupling of tertiary silanes. However, a feature peculiar to Group 4 catalysts is that the coupling of disilanes of type $H_2RSiSiRH_2$ occurs at a faster rate than the coupling of the corresponding monosilane $RSiH_3$. Since primary silanes react rapidly, slow catalysts such as $Cp_2^*HfH_2$ have been utilized for the study of the condensation of both $PhSiH_3$ and $H_2PhSiSiPhH_2$ to allow the observation by ^1H NMR spectroscopy of the stepwise nature of the dehydrocoupling reaction [3]. The Si–H signals for $PhSiH_3$ and for each of the low molecular weight oligomers $H_2PhSi(SiPhH)_xSiPhH_2$ ($x = 0, 1, 2$) were distinguished in the spectrum and thus the formation or disappearance of these species could be monitored for limited chain lengths [2,3]. The signals of the higher oligomers merge with that of the tetramer [2]. The reaction of neat $H(PhSiH)_2H$ with Cp_2TiMe_2 was monitored by GPC and that of $H(PhSiH)_2H$ in C_6D_6 with Cp_2ZrMe_2 by ^1H NMR spectroscopy [3]. No trisilane was observed with Cp_2MMe_2 (M = Ti, Zr) but this was not the case for $CpCp^*HfH_2$, although the timescale for the former precatalyst was in minutes (at least 50% consumption of starting material in less than 30 min) and in days for the latter (at least 50% consumption of starting material in 1 to 2 days). Products were not isolated in these studies [2,3].

The reaction of the related lower molecular weight 1,2-diorganodisilane $H_2MeSiSiMeH_2$ with Cp_2MMe_2 (M = Ti, Zr) was studied by Hengge and Weinberger and the course of the reaction could be monitored to longer chain lengths by gas chromatography [4d]. With Cp_2ZrMe_2 the reaction is fast even at 0°C and after 3 min Si_3 to Si_{11} chains (linear and branched) were observed although the extent of conversion of the starting disilane was not specified. The ratio of linear/branched isomers decreases with time. Branched isomers have not been reported in the condensation of any monosilane nor in the condensation of $H_2PhSiSiPhH_2$ [1]. With Cp_2TiMe_2, the catalyzed condensation of $H_2MeSiSiMeH_2$ takes place slowly, and after 2 h linear $H(MeSiH)_nH$ ($n = 3$–9) and the branched isomers are observed in GC traces. In that study a mixture of trisilane, tetrasilane (as two diastereomers) and pentasilane was isolated, as was a mixture of three hexasilanes. The ^{29}Si NMR spectra confirmed the presence of $Si(Si{\equiv})_3$ units, indicative of branched chains. Solid polymers of composition $[MeSiH_{0.58}]$ were produced with Cp_2ZrMe_2 but oily liquids were formed with Cp_2TiMe_2 [4d]. No information was provided for the molecular weight of the polymers obtained.

The condensation of the monosilane $MeSiH_3$ has been described and, in principle, should provide the same (or similar) products as the reaction of $H_2MeSiSiMeH_2$ [10]. The polymethylsilanes produced from $MeSiH_3$ in cyclohexene (or toluene) with Cp_2MMe_2 exhibit an average M_w in excess of 10000, with higher polydispersities than observed in the condensation of other monosilanes and, in addition, a low percentage of cyclics. The ^{29}Si-DEPT spectra were consistent with the presence of SiH (major) and SiH_2 (minor) groups and *no* quaternary Si centers indicating, at least at this stage, no branching (at least to the extent detectable by ^{29}Si NMR spectroscopy). If the reaction was run for too long a period, an insoluble product was obtained which was believed to be cross-linked. Since the initial stages of the reaction of $MeSiH_3$ were not monitored, the properties of the polymer isolated from the disilane were not determined; the two systems $MeSiH_3$ and $H_2MeSiSiMeH_2$ are difficult to compare. The higher M_w values observed in the condensation of $MeSiH_3$ vs. $PhSiH_3$ with the same catalysts, as well as the branching and/or cross-linking observed in $H_2MeSiSiMeSiH_2$ compared with $H_2PhSiSiPhH_2$, involve the steric requirement of the organic substituent.

Once the condensation of the disilanes $H_2PhSiSiPhH_2$ occurs past the tetrasilane stage, the products cannot be monitored by either GC or ^1H NMR spectroscopy. An advantage in the reaction of methylated disilanes $H_yMe_{3-y}SiSiMe_{3-x}H_x$ ($y = 0$, $x = 1$; $x = y = 1, 2$) was that it could be followed though longer chain lengths by GC [4d]. A feature of the methyl-substituted disilanes, however, is the potential loss of nearly half of the silicon centers due to a disproportionation. The methyl-substituted monosilanes are gaseous at room temperature and not observed in the GC traces, and the fate of these monosilanes cannot be determined. We therefore decided to study the reaction of disilanes of the type $HR^1R^2SiSiR^3R^4H$, where $R^1, R^2 = R^3, R^4$ (symmetrical disilanes) and $R^1, R^2 \neq R^3, R^4$ (unsymmetrical disilanes) where the monosilanes, if produced, could be observed (at least in some cases). In addition, with unsymmetrical disilanes it would be possible, in principle, to determine whether one monosilane is produced in preference to another and also whether certain trisilanes or tetrasilanes were preferentially produced, and thus reveal details of the mechanism of the reaction. When possible, individual products were isolated and purified (separated) by preparative gas chromatography so that isomeric ratios of the oligomers could be determined by ^1H NMR spectroscopy. In some examples the trisilanes had been synthesized by other routes in previously reported work, and thus data could be compared with those of authentic samples.

3.1. Reaction of symmetrical oligomers $H(RMeSi)_xH$ ($R = Ph, Bu$)

The reaction of $H(PhMeSi)_xH$/*cis*-cyclooctene with $Cp_2TiCl_2/^nBuLi$ provided both $PhMeSiH_2$ and $H(PhMeSi)_3H$ in the early stages of the reaction. The data support the equivalent of a disproportionation of the disilane to monosilane and trisilane with the titanium system followed by chain growth through reaction of the monosilane with the disilane and the trisilane. The disproportionation must involve reaction of the silicon–silicon bond of the disilane. However, with zirconium it is probable that an Si–H dehydrocoupling of the disilane to tetrasilane competes with the disproportionation that provides the trisilane. This is supported by smaller amounts of monosilane in comparable time periods relative to the titanium system, as well as a higher tetrasilane/trisilane ratio for the zirconium catalyst in the initial phases of the reaction. That Si–H dehydrocoupling, in general, competes with Si–Si bond cleavage is suggested by the formation of cyclooctane from the cyclooctene.

With the titanium catalyst HBuMeSiSiMeBuH (butyl group replacing the phenyl substituent), trisilane and tetrasilane are formed at the same time. The formation of significant quantities of tetrasilane at the early stages of the reaction suggests coupling of two disilanes.

The reactions of oligomers higher that the disilane were remarkably slow when compared with those of the disilane. Only in the reaction of the trisilane was any monosilane observed. It appears that even though there are additional silicon–silicon bonds in the higher oligomers these do not result in an increase in the reaction rate. These results are in significant contrast to the reactions of $H(MeSiH)_3H$ and $H(MeSiH)_4H$ which, in the presence of Cp_2ZrMe_2, rapidly formed insoluble $(MeSiH_x)_n$ and showed the formation of branched hexasilane and octasilane respectively as the major initial products (within 30 s) as well as isomerization of the tetrasilane [4b]. The branched oligomer appeared to be the major product at this stage.

3.2. Condensation of unsymmetrical disilanes

The reaction of $HR^1R^2SiSiR^3R^4H$ could, in principle, provide three tetrasilanes through coupling of SiH bonds ($HR^1R^2SiSiR^3R^4SiR^1R^2SiR^3R^4H$, $HR^1R^2SiSiR^3R^4SiR^3R^4SiR^1R^2H$ and $HR^3R^4SiSiR^1R^2SiR^1R^2RSiR^3R^4H$). However, if reaction occurred through the Si–Si bond, two different monosilanes, $R^1R^2SiH_2$ and $R^3R^4SiH_2$, would form. Subsequent dehydrocoupling of the monosilane with the starting disilane would provide two sets of isomeric trisilanes, $HR^1R^2SiSiR^1R^2SiR^3R^4H$ and $HR^1R^2SiSiR^3R^4SiR^1R^2H$ as well as $HR^3R^4SiSiR^1R^2SiR^3R^4H$ and $HR^1R^2SiSiR^3R^4SiR^1R^2H$.

When $HPh_2SiSiPhMeH$ and *cis*-cyclooctene were reacted in the presence of $Cp_2TiCl_2/^nBuLi$, both Ph_2SiH_2 and $PhMeSiH_2$ were observed in a ratio of 1 : 1.4 after 22 h. In addition, two sets of the trisilanes $Ph_4Me_2Si_3H_2$ and $Ph_5MeSi_3H_2$ were formed with the $Ph_5MeSi_3H_2$ isomers slightly favored over those of $Ph_4Me_2Si_3H_2$ by a ratio of 1.3 (GC). No tetrasilanes could be detected by GC and are probably absent in this system.

The reaction of $HPhMeSiSiMe_2H$ could give $PhMeSiH_2$ and Me_2SiH_2, the latter of which would be masked in GC traces by the solvent. After 1 h at 80°C ($Cp_2TiCl_2/^nBuLi$, *cis*-cyclooctene) $HPhMeSiSiMe_2H$ and $PhMeSiH_2$ are each 21% (GC) of the silicon-containing products that can be measured. The remainder includes $Ph_xMe_{6-x}Si_3H_2$ ($x = 1, 2$) and $Ph_xMe_{8-x}Si_4H_2$ ($x = 1, 2$). After 22 h, the reaction products contained residual starting material and $PhMeSiH_2$ (each around 4% by GC) as well as trisilanes, tetrasilanes and pentasilanes which are found in a ratio of 1.3 : 2.2 : 1.0 ($Si_3/Si_4/Si_5$). The trisilanes included $PhMe_5Si_3H_2$ and $Ph_2Me_4Si_3H_2$, both of which were isolated by PGC. The tetrasilanes included isomers of $Ph_xMe_{8-x}Si_4H_2$ ($x = 1, 2, 3$), of which only $PhMe_7Si_4H_2$ could be isolated by PGC. Pentasilanes included $Ph_xMe_{10-x}Si_5H_2$ ($x = 1, 2, 3$), which were identified by GCMS. The oligomers appear to be rich in Me_2Si groups, as expected if Me_2SiH_2 undergoes faster coupling than $PhMeSiH_2$ with the disilane (or other oligomers) or if the silylene Me_2Si is produced preferentially.

With $Cp_2ZrCl_2/^nBuLi$ after 24 h in the presence of *cis*-cyclooctene, the same monosilanes, disilanes and trisilanes were observed from $HPh_2SiSiMePhH$ as in the titanium promoted reactions (GC and GCMS). In addition, the tetrasilane $Ph_6Me_2Si_4H_2$ and five hydrosilylation products were also identified. The one tetrasilane observed was that which would result from direct SiH dehydrocoupling of the starting disilane and is formed in the early stages of the reaction.

In constrast to $HPh_2SiSiMePhH$, the reaction of $HPhMeSiSiMe_2H$ could be conducted in the absence of olefin with $Cp_2ZrCl_2/^nBuLi$. The reaction takes about 60 h to consume 95% of the starting disilane, whereas with the titanium system 23 h were required to reach this point. The products are similar with the two catalysts, except that with zirconium the phenyl-rich oligomers $Ph_nMe_nSi_nH_2$ ($n = 3, 4$) were also formed, whereas the methyl-rich oligomers $PhMe_{2n-1}Si_nH_2$ ($n = 4, 5$) and $Ph_2Me_8Si_5H_2$ observed with the use of the titanium catalyst were absent in the zirconium promoted reaction.

The reaction of two other disilanes in the presence of $Cp_2TiCl_2/^nBuLi$ and olefin was briefly examined. From HMePrSiSiMePhH, conducted at 50°C to prevent loss of $PrMeSiH_2$ (b.p. 54°C [11]), two sets of trisilanes (two isomers each) were observed after 23 h. The ratio of $Ph_2PrMe_3Si_3H_2$ to $PhPr_2Me_3Si_3H_2$ was 7.6:1. The only tetrasilane present, $Ph_3PrMe_4Si_4H_2$ (two isomers), does not correspond to the direct dehydrocoupling of the disilane.

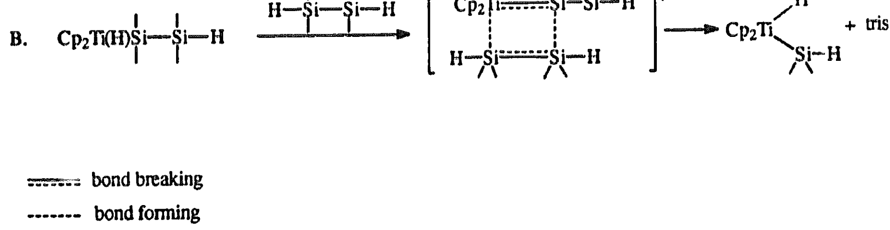
The disilane $HPh_2SiSiPhH_2$ contains a tertiary SiH and a secondary SiH_2 center. Not unexpectedly it reacts much faster than the tetraorganodisilane $HR^1R^2SiSiR^3R^4H$. Consumption of the starting material is essentially complete at room temperature within 1 h. Of the two monosilanes that could be produced, Ph_2SiH_2 and $PhSiH_3$, only the former was observed. At the initial stages of the reaction two isomers of $Ph_4Si_3H_4$ (a product that would form between the starting disilane and $PhSiH_3$) are observed but are eventually consumed. The primary silane produced, $PhSiH_3$, reacted rapidly under these conditions to provide cyclic and linear polysilanes $(PhSiH)_x$ and $H(PhSiH)_yH$, as indicated by the ^1H NMR spectrum.

3.3. Mechanistic implications

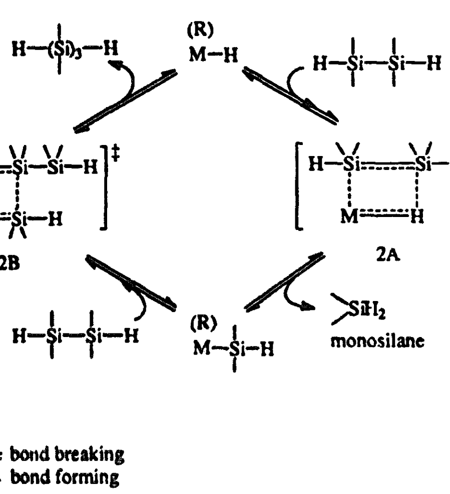
The reactions of both symmetrical and unsymmetrical disilanes show that monosilanes were produced, and the production of measurable monosilanes in the initial phases of the reaction decreased through the catalysts in the order Ti ≫ Zr ≫ Hf. Trisilanes were subsequently formed from the equivalent of the dehydrocoupling of the monosilane at either Si–H bond of the starting disilane. The reaction data support two processes leading to the tetrasilane: successive addition of monosilane to the disilane and Si–H dehydrocoupling of two disilanes.

There are at least two stages in the reaction leading to the observed oligomeric products. The first stage involves the production of the catalytically active metal species. The nature of the product produced from the reaction of Cp_2TiCl_2 and ^nBuLi (or other active RM reagents) has not been unequivocally established. It is probable that lower valent titanium species are formed and different products have been claimed, including Cp_2TiH [12] and $Cp_2Ti(PMe_3)_2$ [13a] when the phosphine was present and $Cp_2Ti(olefin)_2$ [14] when the olefin was present. An adduct of Ph_2SiH_2 and $Cp_2Ti(PMe_3)$ which appears to contain a three-center interaction between the silicon, titanium and hydride has also been reported [13b]. A metal hydride was proposed by Tilley and coworkers to be the catalytically active species for the $CpCp^*M[Si(SiMe_3)_3]R$ (M = Zr, Hf) promoted reactions of $PhSiH_3$, although the oxidation state of the hydride was not specified [3]. If Cp_2TiBu is produced, a σ-bond metathesis reaction with $HSiR^1R^2SiSiR^3R^4H$ would give $Cp_2Ti(SiR^1R^2SiSiR^3R^4H)$ and butane. If followed by a second σ-bond metathesis (Scheme 1A) Cp_2TiH and tetrasilane would be formed. If the Ti(II) complex $Cp_2Ti(olefin)$ was generated, oxidative addition of $HSiR^1R^2SiSiR^3R^4H$ would produce $Cp_2TiH(SiR^1R^2SiSiR^3R^4H)$ [or $Cp_2TiH(SiR^3R^4SiR^1R^2H)$]. Reaction of the disilanyltitanium(IV) produced with a second mole of disilane would lead to $Cp_2TiH(SiR^1R^2H)$ and trisilane (Scheme 1B).

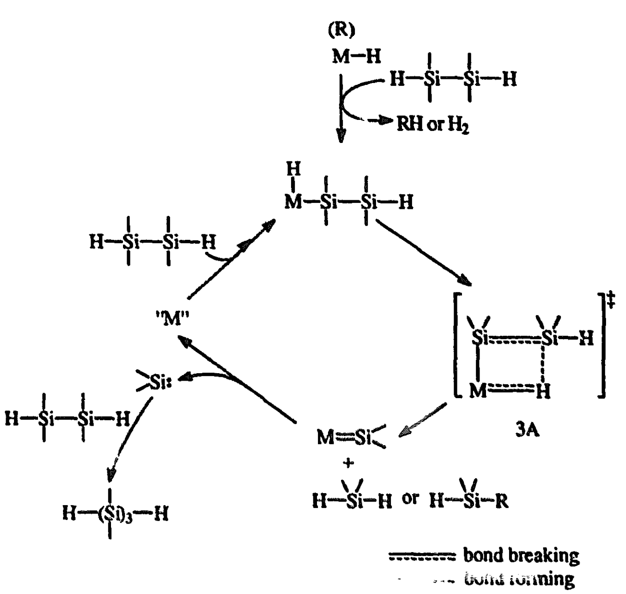
Two different mechanisms to odd-numbered oligomers have been proposed: σ-bond metathesis (Tilley) and β-bond elimination (Hengge). These mechanisms are illustrated for a general disilane in Schemes 2 and 3, which are adapted from published schemes [1a,3,4b]. MH represents the transition metal unit and may be either Cp_2MH or Cp_2MHR. As can be seen by a comparison of the two schemes, the transition states 2A and 3A that would be required to obtain monosi-



Scheme 1.



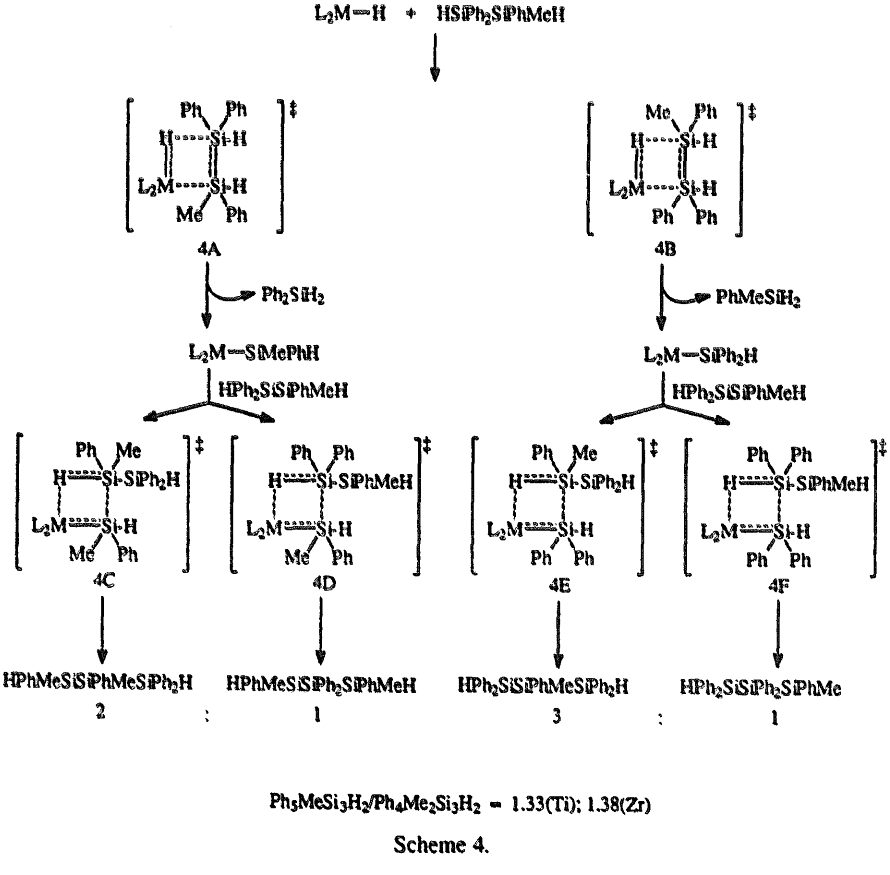
Scheme 2.



Scheme 3.

lanes (and trisilanes) are quite similar. In Scheme 2, the first step leading to 2A is simply the reverse of the Si–Si bond forming process in the reaction of a monosilane. Both silicon centers become pentacoordinate in the transition state 2A. In 3A (Scheme 3) one of the silicon centers is tetracoordinate, the other pentacoordinate. It might be expected that both transition states 2A and 3A would exhibit similar steric constraints.

Tilley has argued persuasively that the least sterically hindered transition state in silicon–silicon bond formation arises from the placement of the bulkiest silicon center in the position that is β to the metal center [1a]. The various transition states are shown in Fig. 1 for the reaction of a primary silane and the energy increases from I to II to III. When a H is replaced by an organic substituent to give the secondary silane $RR'SiH_2$, a similar order should be expected. If σ-bond metathesis



$Ph_5MeSi_3H_2/Ph_4Me_2Si_3H_2$ = 1.33(Ti); 1.38(Zr)

Scheme 4.

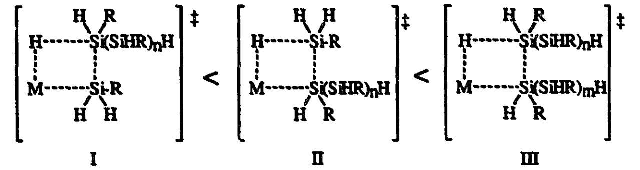


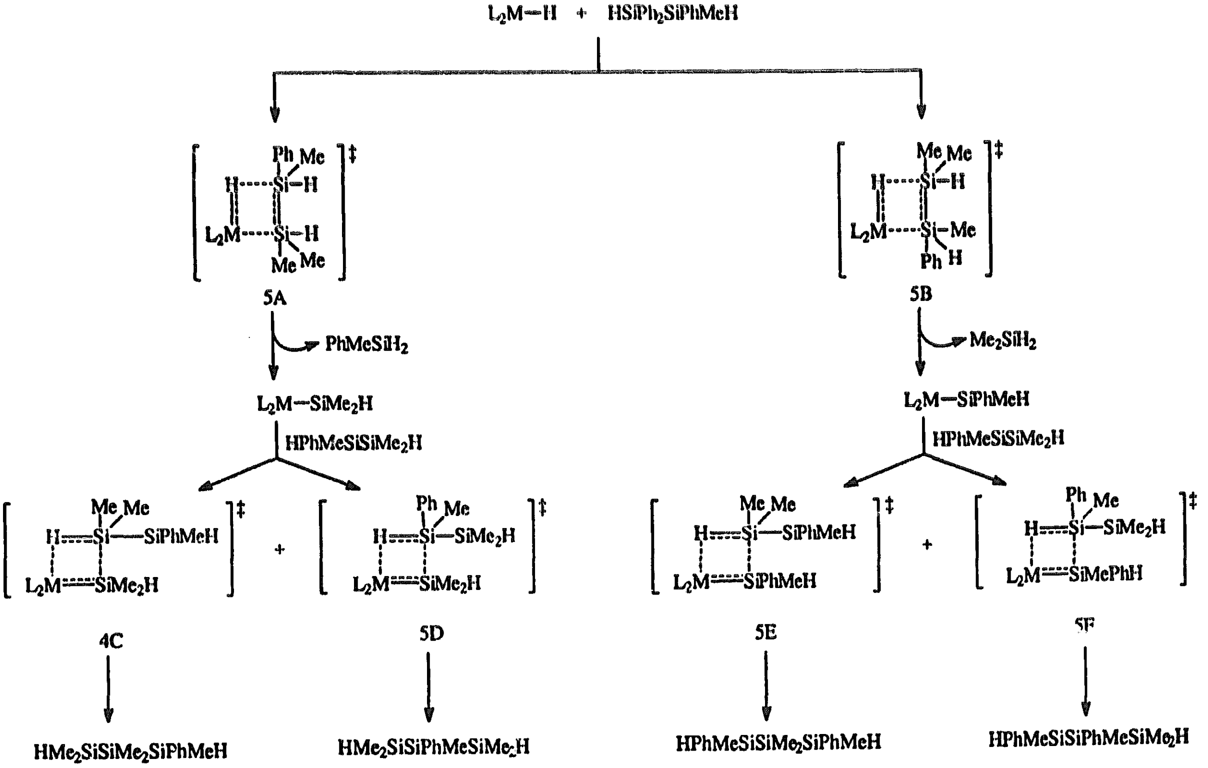
Fig. 1. Presumed transition states for chain growth from a primary silane. Energy increases I < II < III.

is still the operative mechanism, steric hindrance to chain growth must occur even in transition state I since only short oligomers are produced from $RR'SiH_2$. For a tertiary silane, all the H not in the metallocycle that forms the transition state must be organic groups, and it is in this case that Si–Si bond formation is not observed.

The sequence of σ-bond metathesis steps leading to two monosilanes and two sets of trisilanes is illustrated for the unsymmetrical disilane $HPh_2SiSiPhMeH$ in Scheme 4. The two sets of trisilanes occur through a partitioning in the reaction of MH with the two different silicon centers depicted in 4A and 4B, which then results in the production of two different metal silyls. Formation of the trisilane occurs through reaction of the metal silyls with the disilane, which is initially in large excess, through the transition states depicted in 4C through 4F. The second transition state (4C–4F) should be higher in energy than 4A and 4B since the small H-substituent has been replaced with an $SiPh_2H$ or an SiPhMeH group. By a similar argument, 4C and 4E should be lower in energy than 4D and 4F respectively, accounting for the major trisilane isomer that is observed. The ratio of the isomers of $Ph_4Me_2Si_3H_2$ and $Ph_5MeSi_3H_2$ is essentially invariant throughout the reaction period.

In the silylene mechanism the H on the silicon α to the metal center is absent and elimination of the monosilane gives $L_2M{=}SiMePh$ (from 4A′) and $L_2M{=}SiPh_2$ (from 4B′). It was speculated by Hengge that free silylene was delivered by the metal and then the trisilane formed from the insertion of the silylene into the Si–H bond (or the Si–Si bond) of the disilane. Thus, the only influence that the metal center could have on the oligomer distribution would be through the early transition states 4A or 4B or in the strength of the M=Si interaction which would then determine the release of free silylene. A free silylene would be expected to be a very reactive species and may not discriminate between the different SiH bonds. Unfortunately, to our knowledge there are no studies that reveal the effect of the size of substituents on silicon in $RR'R''SiH$ on the insertion of a silylene into an SiH bond. If silylene insertion accounts for the formation of oligomers then the major isomer would be predicted on the basis of preferential insertion into the SiH bond of the silicon center that has the smaller set of substituents (and in highest concentration).

The reaction of $HPhMeSiSiMe_2H$ with Cp_2TiCl_2/ ^nBuLi (in the presence of cyclooctene) gave monosilanes through tetrasilanes within 1 h with 21% of the



Scheme 5.

starting material remaining. After an additional 19 h the starting material had been reduced to about 8%, and pentasilanes had also formed. For an unsymmetrical starting disilane of the type HABH (A = PhMeSi and B = Me_2Si in this case), if one considers the possible oligomers that differ in composition and connectivity then there are six different trisilanes, 10 different tetrasilanes and 20 pentasilanes. Many of these exist as diastereomers, but diastereomers have not been distinguishable on the columns utilized for the GC analyses except in the case of some disilanes. Of the possible oligomers that differ in composition, four of the six trisilanes, seven of the 10 tetrasilanes, and 11 of the 20 pentasilanes could be distinguished by GCMS. The oligomers missing tended to be of the type HA_xH or HB_xH, although $H(PhMeSi)_3H$ and $H(Me_2Si)_4H$ were observed (about 0.5% each by GC). The formation of trisilanes from $HPhMeSiSiMe_2H$ is outlined in Scheme 5. On the basis of previous arguments, the lower energy transition states should be 5A < 5B, 5C < 5D and 5E < 5F and would predict $HMe_2SiSiMe_2SiPhMeH$ to be the major $PhMe_5Si_3H_2$ isomer and $HPhMeSiSiMe_2SiPhMeH$ the favored isomer of $Ph_2Me_4Si_3H_2$. The ratio of the two isomers of $Ph_2Me_4Si_3H_2$ changes from 1.7 after 1 h to 9.4 (GC measurement) after 22 h, but the major isomer was that which would be formed through 5F. The major isomer of $PhMe_5Si_3H_2$ after 22 h is that predicted from 5C. Since the two isomers of $PhMe_5Si_3H_2$ are coincident in the GC traces, a change in isomer ratio in this case was not readily determined. Unlike $HPh_2SiSiPhMeH$, continued chain growth was observed in the reactions of $HPhMeSiSiMe_2H$. Therefore the distinction between 5E and 5F (5C and 5D), as reflected by the isomer ratio after time has elapsed, may not be an adequate (although indirect) indication of the difference in transition states as one of the isomers or one set of oligomers may react preferentially to form a higher oligomer. As an example, after 1 h of reaction the ratio of $PhMe_5Si_3H_2/Ph_2Me_4Si_3H_2$ is 1.2 : 1, falling to 0.21 : 1 (GC measurement) after 22 h.

A related case involves the condensation of HPhMeSiSiPrMeH which was conducted at 50°C to avoid the loss of $PrMeSiH_2$. The product distribution is simpler and includes two sets of trisilanes and, in the later stages of the reaction, two isomers of the tetrasilane $Ph_3PrMe_4Si_4H_2$. A minor product of hydrosilylation, $HPrMeSi(C_8H_{15})$, was also observed. The major trisilane was $Ph_2PrMe_3Si_3H_2$ which would be related to $Ph_2Me_4Si_3H_2$ in the previously discussed case. The ratio of the two isomers of $Ph_2PrMe_3Si_3H_2$ varied only from 1.3 (1 h) to 1.4 (23 h) and the ratio of $Ph_2PrMe_3Si_3H_2/PhPr_2Me_3Si_3H_2$ varied only slightly through the reaction period (7.8 to 7.6). The tetrasilane must be formed stepwise since direct SiH dehydrocoupling would give a tetrasilane of the composition $Ph_2Pr_2Me_4Si_4H_2$.

The reaction of $HPh_2SiSiPhH_2$ occurred quite rapidly in the presence of $Cp_2TiCl_2/^{n}BuLi$. The formation of Ph_2SiH_2 is evident at the beginning stages, and although $PhSiH_3$ could be detected under the conditions utilized for collection of the GC data, it was not present. Although the trisilane $Ph_4Si_3H_4$ (coupling of the starting disilane with $PhSiH_3$) as well as the disilane $Ph_4Si_2H_2$ (coupling of Ph_2SiH_2) were identified within minutes of the start of the reaction, both were eventually consumed. The end product of the condensation of the monomer $PhSiH_3$ would be cyclic and linear polysilanes [15] and the ^1H NMR data obtained for the products was consistent with the formation of cyclic and linear $(PhSiH)_x$ and $H(PhSiH)_yH$ respectively.

4. Summary

On the basis of the study of the oligomer series $H(PhMeSi)_xH$ ($x = 2, 3, 4$), disilanes appear to be unique in the rapid reaction of the Si–Si bond. The product distribution from 1,1,2,2-tetraorganodisilanes shows initial formation of monosilanes and trisilanes followed by slow build up of higher oligomers. The SiH coupling of the disilane to give tetrasilane is an additional process that occurs simultaneously in some cases. The rate of reaction in the presence of $Cp_2TiCl_2/^{n}BuLi$ and *cis*-cyclooctene at 80°C, as indicated by the consumption of the phenyl-substituted disilanes after 1 h, was similar for $HPhMeSiSiMe_2H$, HPhMeSiSiPhMeH and $HPh_2SiSiPhMeH$ (all about 75%). Subsequent reactions are slow.

The formation of monosilane and trisilane infers reaction of the metal center with the silicon–silicon bond. This process may occur either through the interaction of M–H (formed from the transition metal precursors) with the disilane or through $M(H)SiR^1R^2SiR^3R^4H$ (Scheme 1) which subsequently forms the monosilane and MSiRR′H (σ-bond metathesis) or $M{=}SiR^1R^2$ ($\beta^{\prime}$-elimination). The transition states for these two processes originally proposed by Tilley and by Hengge suggest that steric effects involved in the silicon–silicon bond cleavage would be similar for the two mechanisms. The formation of trisilanes involves the coupling of the resultant metal silyl (or metal silylene) with the starting disilanes. This was demonstrated through the reaction of unsymmetrical disilanes which must generate two different metal silyls (or metal silylenes) as inferred by the presence of two different monosilanes from $HPh_2SiSiPhMeH$.

Reaction of the metal silyl (or metal silylene) with the starting disilane would give two sets of trisilanes, both of which are observed. Since transfer of the silicon unit from the metal to the disilane can occur in two different ways, structural isomers of the trisilane are generated. In each case studied, the isomer ratio exceeded one. If the formation of the trisilane occurs through σ-bond metathesis, then by analogy to arguments presented for chain growth in the reactions of monosilanes the most sterically hindered silicon center should be β to the metal center. If no subsequent reaction of the trisilane takes place and substituents at silicon are sufficiently different, the isomer ratio obtained should reflect the placement of the most bulky silicon center in the β-position. The major isomers of the trisilanes produced from $HPh_2SiSiPhMeH$ could be rationalized through this argument, as could the major isomer of one of the two sets of trisilanes from $HPhMeSiSiMe_2H$. However, in this latter case chain growth continues throughout the reaction period and the ratio of the two isomers as well as the ratio of the two trisilanes changes with time. The appearance of the tetrasilane that corresponds to the coupling of two starting disilanes in the early stages of the reaction suggests that Si–H dehydrocoupling competes with Si–Si cleavage of the disilane. Other tetrasilanes must form either through successive Si–H coupling of monosilane to the disilane or of monosilane to trisilane. Other evidence that supports Si–H dehydrocoupling was the formation of symmetrical disilanes in the reaction mixtures that started with an unsymmetrical disilane.

If chain growth occurs through insertion of silylene into Si–H bonds (or Si–Si bonds) then some discrimination in the silylene insertion must occur to account for the fact that the trisilane isomers are not formed in a 1 : 1 ratio. In this case, reaction must be slightly more favored for insertion of the silylene into the SiH bond with the smaller substituents at silicon. Since free silylenes react very rapidly it is unlikely that much discrimination between SiH bonds would occur in the types of disilane that were the subject of this study.

Whether or not a metal silylene complex can be formed from the Group 4 triad metals is still a major question. Although metal–silylene complexes have been isolated, in general these have primarily involved more electron-rich metals such as iron and ruthenium [16]. That low molecular weight $(SiR_2)_n$ polymers can be formed from the thermal decomposition of the silylene complex has been demonstrated. As an example, $(Me_2Si)_x$ was observed in the thermal decomposition of $(CO)_4Fe{=}SiMe_2(HMPA)$ [17], although how formation of the polysilane takes place is unknown.

The initial reaction of 1,2-dihydrodisilanes is rapid but levels off before starting material is consumed. Continued reaction of the disilane occurs but is slow. Similar observations were also reported by Tilley and coworkers [3] for reactions of $H_2PhSiSiPhH_2$. The first products observed in the reaction of $RR'SiH_2$ with $Cp_2TiCl_2/{}^nBuLi$ (with added cyclooctene) are disilanes followed more slowly by trisilanes and then tetrasilanes, although significant amounts of tetrasilane are difficult to obtain. In the condensation of $RR'SiH_2$, the disilane that is produced must also be recycled into monosilanes and thus the formation of trisilane does not occur, in this case, until there is a significant build up of disilane. Chain growth starting from the trisilane or the tetrasilane of $H(PhMeSi)_xH$ was very slow, as observed in the experiments reported here, although this could also involve a problem in the step that generates the catalytically active species from the precursors employed. If continued chain growth occurs through a transition state similar to 2A (Scheme 2), then replacing a hydrogen substituent with an –SiPhRH group may introduce steric interactions that result in an increase in the barrier to Si–Si bond formation. This was not observed for $H(MeSiH)_xH$ ($x = 3, 4$) which contains the smallest possible organic substituent [4b]. That steric interactions are important in dehydrocoupling is indicated by the considerable decrease in the rate of condensation of primary vs. secondary silanes and the fact that coupling is not generally observed for tertiary silanes. That tertiary silanes oxidatively add to Group 4 metallocenes has been demonstrated at least in the case of hafnium [18]. Therefore, it is the formation of the Si–Si bond that is the problem. Only with methyl-substituted disilanes $Me_{6-x}Si_2H_x$ were branched chains observed in the initial phases of the condensation reaction. Formation of branched chains requires the reaction of an internal SiH (a type of tertiary silane) bond. It is the apparent sensitivity to steric effects and the competition between Si–H bonds and Si–Si bonds for the metal center that currently limits the utility of dehydrocoupling as a synthetic method for the formation of polysilanes.

5. Experimental

5.1. General considerations

All reactions were carried out under an inert atmosphere of dry nitrogen. Glassware and solvents were dried before use: ether (Na/benzophenone); toluene (CaH_2); CH_2Cl_2 (P_2O_5 after pretreatment with sulfuric acid and drying over CaH_2). The GC data were collected on a Shimadzu GC-14A with a 12 m DB-5 capillary column programmed for the range 60–320°C (20°C min^{-1}) unless otherwise specified. Preparative GC was performed on a Varian Aerograph Model 700 with 5% SE-30 on a Chrom G 40/60 column (10 ft × 3/8 in). The temperature settings for the column, collector, injector, and detector were 150, 90, 115 and 100°C. The GCMS data were collected on a Hewlett-Packard 5988A instrument with an RTE-A data system and GC separation in split injection mode using a 12.5 m (HP-1) capillary column. Other than the parent ion, peaks in the mass spectrum are reported that are greater than 10% of the base peak with m/e at least 10%

and are uncorrected. All NMR data, ^1H, ^{13}C, ^{29}Si, were collected on either a Varian XL-300 multinuclear spectrometer or on a Bruker ARX-500 multinuclear spectrometer. The solvent was C_6D_6 in all cases and was employed as an internal standard, unless otherwise specified. The aromatic regions in the ^1H NMR spectra are not diagnostic and thus are not included. Commercial reagents, ^nBuLi (in hexanes), MeMgCl (in ether), PhMgBr (in ether), PrMgCl (in ether), HOTf and $LiAlH_4$ were used as supplied. The monosilanes, $PhMeSiH_2$ [19] and Ph_2SiH_2 [20] were prepared by reduction of the commercial chloride with $LiAlH_4$. The preparation of $HPh_2SiSiPh_2H$ [6], $H(PhMeSi)_xH$ ($x = 2, 3, 4$) [6], $H(BuMeSi)_xH$ ($x = 2, 3$) [6], $HPh_2SiSiPhMeH$ [6], $HPhMeSiSiMe_2H$ [6] and $HPh_2SiSiPhH_2$ [7] have been previously described.

5.2. Synthesis of HMePrSiSiPhMeH

To a solution of $H(PhMeSi)_2H$ (2.5 g, 10 mmol) in CH_2Cl_2 (20 ml) which had been cooled to −40°C was added HOTf (0.92 ml, 10 mmol). The solution was warmed to 0°C and stirred for 30 min. Subsequently, the mixture was cooled to −40°C, a solution of PrMgCl in ether (5.1 ml, 20.0 M) was added slowly, followed by warming to room temperature and stirring for 1 h. After aqueous work-up and removal of the volatiles the residue was distilled to give a fraction, b.p. 45–50°C/0.1 mmHg, which contained HMePrSiSiPhMeH (1.3 g, 60%; 95% by GC). Mass spectrum, see Table 4.

The sample was eluted through a 1 in × 4 in column of silica gel with a 50:50 mixture of hexane/toluene before further purification by preparative gas chromatography. Spectroscopic and analytical data were obtained from the sample isolated by preparative gas chromatography. ^1H NMR (δ, ppm; TMS): 0.111, 0.114 [(2d, $J_{CHSiH} = 5.6$ Hz (av), (CH_3, SiPrH)], 0.386, 0.391 [(2d, $J_{CHSiH} = 5.2$ Hz (av), (CH_3SiPhH)], 0.63 (m, $CH_3CH_2CH_2SiH$), 0.89 (two overlapping t, $CH_3CH_2CH_2$), 1.35 (m, $CH_3CH_2CH_2SiH$). ^{29}Si (δ, ppm; TMS): −31.38, −31.43, (PhSiMeH), −32.04 and −32.28 (PrSiMeH). Anal. Found: C, 62.46; H, 10.05. $C_{16}H_{22}Si_2$ Calc.: C, 63.38; H, 9.67%.

5.3. Condensation of $H(PhMeSi)_2H$ at 80°C in the presence of Cp_2MCl_2/^nBuLi

A mixture of Cp_2TiCl_2 (20 mg, 0.08 mmol) in toluene (1 ml) was cooled to 0°C and ^nBuLi (0.1 ml, 2.5 M) was added to produce a dark brown solution. After 5 min at 0°C *cis*-cyclooctene (0.5 ml) and $H(PhMeSi)_2H$ (0.60 g, 2.5 mmol) were added. The mixture was allowed to warm to room temperature and then heated in an oil bath to 80°C. Aliquots were taken after 1 h and after 3.5 h. The reaction was quenched by addition of hexanes after 4 days. The composition of the product mixture as determined by GC is presented in Table 1.

In a similar manner, ^nBuLi (0.14 ml, 2.3 M) was added to Cp_2ZrCl_2 (0.030 g, 1.1×10^{-4}) in toluene (1.0 ml) followed by *cis*-cyclooctene (0.5 ml) and $H(PhMeSi)_2H$ (0.80 g, 3.3×10^{-3}) and the reaction mixture placed in an 80°C bath. After 1 h, monosilane (10%), disilane (69%), trisilane (6.3%) and tetrasilane (12.2%) were present. The solution decolorized within 15 h when the disilane was present at 56%, monosilane, trisilane and tetrasilane were 10%, 15% and 15% respectively.

5.4. Condensation of $H(PhMeSi)_3H$ at 80°C in the presence of Cp_2TiCl_2/^nBuLi

In a similar manner, ^nBuLi (0.06 ml, 2.5 M) was added to Cp_2TiCl_2 (10 mg, 0.04 mmol) in toluene (1 ml) at 0°C followed by *cis*-cyclooctene (0.5 ml) and $H(PhMeSi)_3H$ [0.56 g, 1.6 mmol; contains $H(PhMeSi)_2H$ (5.3%)]. The mixture was heated in an oil bath at 80°C for 1 day. Aliquots were taken at 1 and 2 h and showed the presence of $H(PhMeSi)_2H$, $H(PhMeSi)_3H$ and $H(PhMeSi)_4H$ (see Table 1). Only minor changes occurred after 2 h.

5.5. Reaction of $H(PhMeSi)_4H$ at 90°C in the presence of Cp_2TiCl_2/^nBuLi

In a similar manner, ^nBuLi (0.09 ml, 2.5 M) was added to Cp_2TiCl_2 (20 mg, 0.06) followed by *cis*-cyclooctene (1.0 ml) and $H(PhMeSi)_4H$ [1.0 g, 1.9 mmol containing 7.3% of $H(PhMeSi)_3H$]. The mixture reacted for 1 h at room temperature and was then heated in an oil bath at 90°C for 4 h then at room temperature for 12 h. Only minor changes occur in the percentages of the components after 2 h, see Table 1. No oligomers higher than the tetrasilane were observed in an HPLC analysis.

5.6. Condensation of HBuMeSiSiMeBuH at 80°C in the presence of Cp_2TiCl_2/^nBuLi

In a similar manner, ^nBuLi (0.12 ml, 2.5 M) was added to Cp_2TiCl_2 (2.5 mg, 8.5×10^{-3} mmol) in toluene (1 ml) followed by *cis*-cyclooctene (0.5 ml) and HBuMeSiSiMeBuH (0.6 g, 3 mmol). The mixture was heated in an oil bath at 80°C for 3 days. After a hexane quench, GC analysis of the reaction mixture showed the presence of $H(BuMeSi)_2H$ (20%), $H(BuMeSi)_3H$ (51%) and $H(BuSiMe)_4H$ (25%). Mass spectrum [*m/e*, relative intensities]: 202 ($Bu_2Me_2Si_2H_2$, 12), 101 ($BuMeSiH^+$, 24), 100 ($BuMeSi^+$, 31); 302 ($Bu_3Me_2Si_3H_2^+$, 0.1), 200 ($Bu_2Me_2Si_2^+$, 48), 145 ($BuMe_2Si_2H_2^+$, 70), 144 ($BuMe_2Si_2H^+$, 100), 133 (41), 131 (12), 129 ($BuMeSi_2H^+$, 17), 117 (21), 115 (21), 113 (20), 103

(65); 402 ($Bu_4Me_4Si_4H_2$, 1.7), 301 ($Bu_3Me_3Si_3H^+$, 21), 300 (23), 245 ($Bu_2Me_3Si_3H_2^+$, 64), 244 (21), 200 ($Bu_2Me_2Si_2^+$, 75), 189 (100), 177 (35), 145 (39), 144 (76), 143 (22), 133 (89), 132 (19), 131 (32), 130 (14), 129 (33), 127 (12), 117 (17), 115 (27), 113 (21), 103 (33), 101 (21).

5.7. *Condensation of $HPh_2SiSiMePhH$ at 80°C in the presence of Cp_2TiCl_2 / ^nBuLi*

In a similar manner, ^nBuLi (0.39 ml, 2.5 M) was added to a slurry of Cp_2TiCl_2 (81 mg, 0.32 mmol) in toluene (1.5 ml) followed by *cis*-cyclooctene (1.5 ml) and $HPh_2SiSiMePhH$ (2.6 g, 8.7 mmol) in toluene (2 ml). The mixture was heated to 80°C for 22 h before the reaction was quenched by the addition of hexanes. After filtering the solution through Celite the solvent was removed and flash distillation of the oily residue from 120–230°C/0.05 mmHg provided an oil, 2.13 g (81% weight recovery) and a residue, 0.19 g, which was not investigated further. The GC trace showed the presence of four monosilanes [$PhMeSiH_2$ (23%), PhMeBuSiH (1.8%), Ph_2SiH_2 (16%) and Ph_2SiBuH (1.8%)], disilanes [HPhMeSiSiMePhH (6.8%), $HPh_2SiSiPhMeH$ (21%), $Ph_3BuMeSi_2H$ (1.8%), $HPh_2SiSiPh_2H$ (6.8%)] and trisilanes [$Ph_4Me_2Si_3H_2$ (two isomers; 9.0%) and $Ph_5MeSi_3H_2$ (two isomers, 12%)] each of which was assigned from the molecular weight determined by GCMS (Table 2).

Redistillation provided 10 fractions from which the isomers of $Ph_4Me_2Si_3H_2$ (b.p. 158–180°C/0.1 mmHg; GC ratio of the two isomers 1.9 : 1.0) contaminated with $HPh_2SiSiPh_2H$ and of $Ph_5MeSi_3H_2$ (b.p. 170–175°C/0.05 mmHg; GC ratio of the two isomers 3.0 : 1.0) were isolated.

$Ph_4Me_2Si_3H_2$ was a mixture of $HPh_2SiSiPhMeSiPhMeH$ (major isomer; two diastereomers) and $HPhMeSiSiPh_2SiPhMeH$ (minor isomer; two diastereomers). $HPh_2SiSiPhMeSiPhMeH$. ^1H NMR (δ, ppm; 500 MHz): 0.31 (d, CH_3SiPhH), 0.34 (d, CH_3SiPhH), 0.51 (s, CH_3SiPh), 0.52 (s, CH_3SiPh), 4.75 (q, *H*SiMePh), 5.35 (s, *H*Ph_2Si). ^{13}C NMR (δ, ppm): −6.64 ($PhSiCH_3$), −7.12, −7.20 ($HSiPhCH_3$). ^{29}Si NMR (δ, ppm): −33.6, −33.7 (H*Si*Ph_2), −35.5, −35.7 (H*Si*PhMe), −42.0, −42.1 (Ph*Si*Me). Mass spectrum, see Table 2. $HPhMeSiSiPh_2SiPhMeH$. ^1H NMR (δ, ppm; 500 MHz): 0.41, 0.42 (two d, CH_3SiPhH), 4.93 (q, *H*SiMePh). ^{13}C NMR (δ, ppm): −7.23, −7.27 ($HSiPhCH_3$). ^{29}Si NMR (δ, ppm): −30.6, −30.8 (H*Si*PhMe), −46.0, −46.5 (*Si*Ph_2). Mass spectrum, see Table 2. The ratio of the two $Ph_4Si_3Me_2H_2$ isomers was 2 : 1 by integration of the SiH region. A ^1H–^1H COSY verified that the multiplet at 4.93 ppm is coupled to the multiplets at 0.41 and 0.42 ppm.

$Ph_5MeSi_3H_2$ is a mixture of $HPh_2SiSiPhMeSiPh_2H$ and $HPh_2SiSiPh_2SiPhMeH$ in a 3 : 1 ratio. Major isomer. ^1H NMR (δ, ppm; 500 MHz): 0.59 (s, CH_3SiPh), 5.36 (s, *H*$SiPh_2$). ^{13}C NMR (δ, ppm): −6.75 (s, $PhSiCH_3$). ^{29}Si NMR (δ, ppm): −30.18 (s, Ph_2*Si*H), −46.7 (s, Ph*Si*Me). Mass spectrum, see Table 2. Minor isomer. ^1H NMR (δ, ppm; 500 MHz): 0.38 (d, CH_3SiPhH), 4.93 (q, *H*SiPhMe), 5.55 (s, *H*$SiPh_2$). ^{13}C NMR (δ, ppm): −6.65 (s, $HSiPhCH_3$). ^{29}Si NMR (δ, ppm): −32.67 (s PhMe*Si*H), −35.06 (s, Ph_2*Si*H), −41.9 (s, Ph_2*Si*). Mass spectrum, see Table 2.

5.8. *Condensation of $HPh_2SiSiMePhH$ in the presence of Cp_2ZrCl_2 / ^nBuLi*

In a similar manner, ^nBuLi (0.07 ml, 2.5 M) was added to a slurry of Cp_2ZrCl_2 (20 mg, 0.068 mmol) in toluene (1.0 ml) followed by *cis*-cyclooctene (0.5 ml) and $HPh_2SiSiMePhH$ (0.52 g, 1.6 mmol). The mixture was heated to 80°C for 24 h before the reaction was quenched with hexanes and the resultant slurry filtered through Celite. On the basis of GCMS data (Table 3), in addition to the starting material (36% by GC) 15 products were identified which included four monosilanes ($PhMeSiH_2$, PhMeBuSiH, Ph_2SiH_2, Ph_2BuSiH, total 12%), two additional disilanes [$Ph_3MeBuSi_2H$, $Ph_4Si_2H_2$, total 6.3%], four trisilanes [$Ph_4Me_2Si_3H_2$ (two isomers), $Ph_5MeSi_3H_2$ (two isomers), total 19%], one tetrasilane [$Ph_6Me_2Si_4H_2$, 11%] and five products of hydrosilylation of or dehydrocoupling with cyclooctene [$C_8H_{13}SiPhMeH$, $C_8H_{15}SiPhMeH$, $C_8H_{13}SiPh_2H$, total 11%; $C_8H_{15}Si_2Ph_3MeH$ (two isomers), total 16%].

When the reaction was conducted with Cp_2ZrCl_2 (20 mg, 0.068 mmol), ^nBuLi (0.07 ml, 2.5 M) and $HPh_2SiSiPhMeH$ (0.51 g, 1.6 mmol) in toluene (1.0 ml) in the absence of olefin for 22 h at 80°C, no reaction occurred.

5.9. *Condensation of $HPh_2SiSiMePhH$ in the presence of cis-cyclooctene and Cp_2HfCl_2*

A mixture of Cp_2HfCl_2 (20 mg, 0.053 mmol) in toluene (1.0 ml) was cooled to 0°C before addition of ^nBuLi (0.07 ml, 2.5 M). After 5 min, *cis*-cyclooctene (0.50 ml) was added followed by $HPh_2SiSiMePhH$ (0.52 g, 1.7 mmol). The mixture was allowed to warm to room temperature and then heated in an oil bath for 1.5 h. Hexanes were added to the cooled mixture and the slurry was filtered through Celite. GC analysis showed starting disilane and two isomers of the hydrosilylation product $C_8H_{15}Si_2Ph_3MeH$ (9.0%).

5.10. *Condensation of $HPhMeSiSiMe_2H$ in the presence of cis-cyclooctene and Cp_2TiCl_2 / ^nBuLi*

To a slurry of Cp_2TiCl_2 (0.14 g, 0.56 mmol) in toluene (4.0 ml) at 0°C was added ^nBuLi (0.67 ml, 2.5

M) followed by *cis*-cyclooctene (2.0 ml) and $HPhMeSiSiMe_2H$ (3.0 g, 17 mmol) and the mixture heated at 80°C for 22 h. GCMS analysis provided detailed information about the products (Table 3). After quenching with hexanes the resultant slurry was filtered through Celite. The solvents were removed and flash distillation provided an oil, b.p. 90–240°C/1.0 mmHg, 2.24 g (75% weight recovery) and a residue, 0.22 g, which was not investigated further. Redistillation provided a fraction, b.p. 70–140°C/0.1 mmHg, GC analysis of which indicated the presence of starting material (4.2%), trisilanes [$PhMe_5Si_3H_2$, $Ph_2Me_4Si_3H_2$ (two isomers), total 27%], tetrasilanes [$PhMe_7Si_4H_2$ (two isomers), $Ph_2Me_6Si_4H_2$ (four isomers), $Ph_3Me_5Si_4H_2$ (two isomers), total 46%] and pentasilanes [$PhMe_9Si_5H_2$, $Ph_2Me_8Si_5H_2$ (two isomers), $Ph_3Me_7Si_5H_2$ (four isomers), total 21%]. Additional components were revealed as small peaks in the GCMS trace: $H(Me_2Si)_4H$, $Ph_2Si_2Me_2H_2$, $Ph_2Me_3Si_2H$, $Ph_2Me_5Si_3H$, $Ph_3Me_3Si_3H_2$.

Preparative gas chromatography resulted in the isolation of two of the trisilanes and one of the tetrasilanes. Two structural isomers were observed for $PhMe_5Si_3H_2$ according to ^1H NMR data. The ratio for $HPhMeSiSiMe_2SiMe_2H/HMe_2SiSiPhMeSiMe_2H$ was 1.2:1.0 from integration of the Si–H region.

$HPhMeSiSiMe_2SiMe_2H$ (major). ^1H NMR (δ, ppm; 500 MHz): 0.086, 0.095 [two overlapping d, $(CH_3)_2SiH$], 0.16, 0.17 [2s, $(CH_3)_2Si$], 0.41 (d, CH_3SiPhH), 4.04 (septet, HMe_2Si), 4.60 (q, $HMePh$). Mass spectrum, see Table 3. $HMe_2SiSiPhMeSiMe_2H$. ^1H NMR (δ, ppm; 500 MHz): 0.16, 0.18 [two overlapping d, $(CH_3)_2SiH)$], 0.43 (s, CH_3SiPh), 4.18 (septet, HMe_2Si). ^{13}C NMR (δ, ppm; mixture of isomers, TMS): −5.8, −6.1, −6.1, −6.2, −6.3, −7.3, −8.4 (Si*Me* region). ^{29}Si NMR (δ, ppm; mixture of isomers, TMS): −33.4, −36.4, −37.0, −45.2, −47.4. Mass spectrum, see Table 3.

Two structural isomers of $PhMe_7Si_4H_2$, $HMe_2SiSiPhMeSiMe_2SiMe_2H$ and $HPhMeSiSiMe_2SiMe_2SiMe_2H$, were isolated in a 1.2:1.0 ratio.

$HMe_2SiSiPhMeSiMe_2SiMe_2H$. ^1H NMR (δ, ppm): 0.08 [d, $(CH_3)_2SiH)$], 0.21 [2d, $(CH_3)_2SiH$], 0.24, 0.25 [2s, $(CH_3)_2Si$], 0.48 (s, CH_3SiPh), 4.05 (septet, $HSi(CH_3)_2$, 4.2 [septet, $HSi(CH_3)_2$]. Mass spectrum, see Table 3. $HPhMeSiSiMe_2SiMe_2SiMe_2H$. ^1NMR (δ, ppm): 0.14, 0.15 [2s, $(CH_3)_2Si$], 0.22 [d, $(CH_3)_2SiH$], 0.44 (d, CH_3SiPhH), 4.04 [septet, $HSi(CH_3)_2$], 4.6 (q, $HPhSiMe$). Mass spectrum, see Table 3. ^{13}C NMR (δ, ppm; mixture of isomers): −5.44, −5.46, −5.53, −5.55, −5.72, −5.83, −5.89, −5.96, −5.97, −7.03, −7.45, −7.67, −7.92. ^{29}Si (δ, ppm; mixture of isomers): −21.1, −33.2, −35.99, −36.25, −36.47, −36.83, −36.84, −42.83, −44.14, −44.18.

The isomers of $Ph_2Me_4Si_3H_2$, $HMe_2SiSiPhMeSiPhMeH$ and $HPhMeSiSiMe_2SiPhMeH$, were isolated in a ratio of 9.4:1.0. $HMe_2SiSiPhMeSiPhMeH$ (two diastereomers). ^1H NMR (δ, ppm): 0.09, 0.11, 0.12 [3d, $^2J = 4.4$ (av), $(CH_3)_2SiH$], 0.41, 0.44 [2s, (CH_3SiPh)], 0.43 [d, $^2J = 4.4$, (CH_3SiPhH)], 4.2 (septet, $HSiMe_2$), 4.7 (q, $HSiPhMe$). Mass spectrum, see Table 3. $HPhMeSiSiMe_2SiPhMeH$ (two diastereomers). ^1H NMR (δ, ppm): 0.17 [s, $(CH_3)_2Si$], 0.34 (d, CH_3SiPhH), 4.58 (q, $HSiPhMe$). ^{13}C NMR (δ, ppm; mixture of isomers, TMS): −5.89, −5.91, −5.94, −7.08, −7.12, −7.44, −8.01, −8.17 (Si*Me* region). ^{29}Si NMR (δ, ppm; TMS): −33.2, −33.3, −36.7, −36.8, −45.4, −45.6 (signals correspond to major isomer); −34.0, −34.1, −47.31 (signals of minor isomer).

5.11. Condensation of $HPhMeSiSiMe_2H$ in the presence of Cp_2ZrCl_2 / ^nBuLi

In a similar fashion, ^nBuLi (0.46 ml, 2.3 M) was added to a slurry of Cp_2ZrCl_2 (0.11 g, 0.38 mmol) in toluene (2.0 ml) followed by $HPhMeSiSiMe_2H$ (1.9 g, 11 mmol) and the mixture heated in an oil bath at 80°C for 60 h. After quenching with hexane and filtering through Celite, GC and GCMS data indicated the presence of starting material (5.1%) as well as monosilanes [$PhMeSiH_2$, PhMeBuSiH, total 4.0%], disilanes [$PhMe_3Si_2H$ (two), $Ph_2Me_2Si_2H_2$ (two), total 10%], trisilanes [$PhMe_5Si_3H_2$ (two), $Ph_2Me_4Si_3H_2$ (two isomers), $Ph_3Me_3Si_3H_2$ (two isomers), $Ph_3Me_3BuSi_3H$, total 37%], tetrasilanes [$Ph_2Me_6Si_4H_2$ (three isomers), $Ph_3Me_5Si_4H_2$ (two isomers), $Ph_4Me_4Si_4H_2$, total 35%] and the pentasilane $Ph_3Me_7Si_5H_2$ (four isomers, 7.8%). Five minor peaks are also observed in the GC traces ranging from 0.5 to 1.8%. Aliquots removed after 1 and 19 h of reaction showed the ratio monosilane/disilane (including the starting material)/tetrasilane/pentasilane to change from 5.0 : 72 : 10 : 13 : 0 (1 h) to 8.0:28:37:28:2.4 (19 h).

5.12. Condensation of $HPhMeSiSiMe_2H$ in the presence of Cp_2HfCl_2 / ^nBuLi

In a similar fashion, ^nBuLi (0.20 ml, 2.5 M) was added to Cp_2HfCl_2 (50 mg, 0.10 mmol) in toluene (1 ml) followed by $HPhMeSiSiMe_2H$ (0.70 g, 3.9 mmol) and the mixture heated to 80°C for 1 day. After quenching with hexanes and filtering through Celite, GC (and GCMS) analysis indicated starting material (90%), PhMeBuSiH (4.0%) and an unidentified component (4.7%).

5.13. Condensation of HPhMeSiSiPrMeH in the presence of cis-cyclooctene and Cp_2TiCl_2 / ^nBuLi

In a similar fashion, ^nBuLi (0.2 ml, 2.5 M) was added to Cp_2TiCl_2 (40 mg, 0.16 mmol) in toluene (1 ml) followed by cis-cyclooctene (1 ml) and HPhMe-

SiSiPrMeH (0.52 g, 2.5 mmol; 4% PhPrMeSiH). The mixture was heated at 50°C and aliquots were withdrawn periodically for 23 h. After quenching with hexanes and filtering through Celite, the residue was distilled to give 0.23 g of oil, b.p. 70–170°C/0.1 mmHg and 0.05 g of non-volatile residue. The product mixture was characterized by GCMS to determine molecular formulas. GC analysis showed starting material (31%) and the PhPrMeSiH impurity (3.6%), monosilane (C_8H_{15}SiPrMeH, 3.6%), trisilanes [$PhPr_2Me_3Si_3H_2$ (two isomers, 5.9%), $Ph_2PrMe_3Si_3H_2$ (two isomers), total 45%] and tetrasilane [$Ph_3PrMe_4Si_4H_2$ (two isomers), 6.2%]. After 1 and 9 h the ratio starting material/monosilane/trisilanes/tetrasilane was 55 : 3.2 : 36 : 0 and 34 : 3.8 : 46 : 5.9 respectively. No detectable $PhMeSiH_2$ was observed.

5.14. Condensation of $HPh_2SiSiPhH_2$ at 80°C in the presence of cis-cyclooctene and Cp_2TiCl_2/ ^{n}BuLi

In a similar fashion, ^{n}BuLi (0.08 ml, 2.5 M) was added to Cp_2TiCl_2 (20 mg, 0.080 mmol) in toluene (1 ml) followed by cis-cyclooctene (0.5 ml) and $HPh_2SiSiPhH_2$ (0.56 g, 1.9 mmol) and the mixture heated in an oil bath at 80°C for 3 h. After quenching with hexanes and filtering through Celite the solvent was removed and flash distillation at 100–250°C/0.05 mmHg provided an oil, 0.21 g (36% weight recovery) and a residue, 0.25 g, which showed cyclic components presumed to be $(PhSiH)_x$ and $H(PhSiH)_xH$. ^1H NMR (δ, ppm): 5.2 (broad massif).

5.15. Condensation of $HPh_2SiSiPhH_2$ at room temperature in the presence of cis-cyclooctene and Cp_2TiCl_2/ ^{n}BuLi

In a similar fashion, ^{n}BuLi (0.08 ml, 2.5 M) was added to a slurry of Cp_2TiCl_2 (20 mg, 0.08 mmol) in toluene (1 ml) followed by addition of cis-cyclooctene (0.5 ml) and $HPh_2SiSiPhH_2$ (0.56 g, 1.9 mmol) and the mixture stirred at room temperature for 3 days. Hexanes were added and the slurry filtered through Celite. The solvent was removed and flash distillation at 100–250°C/0.05 mmHg provided an oil, 0.23 g (41% weight recovery) and a residue, 0.23 g. ^1H NMR (δ, ppm): 4.8 (broad massif), 5.3 (broad massif).

Acknowledgements

Acknowledgement is made to the National Science Foundation (CHE-921[illegible]688) for partial support of this work. Additional support was provided by a Research Incentive Award from the University of Missouri-St. Louis.

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