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Dehydrogenative silation, isomerization and the control of *syn- vs. anti*-addition in the hydrosilation of alkynes

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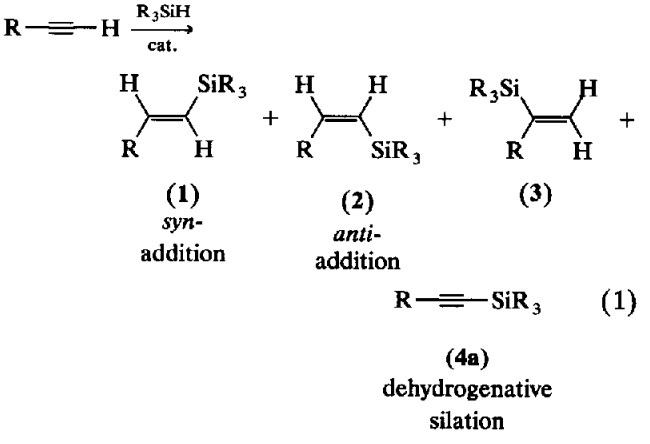
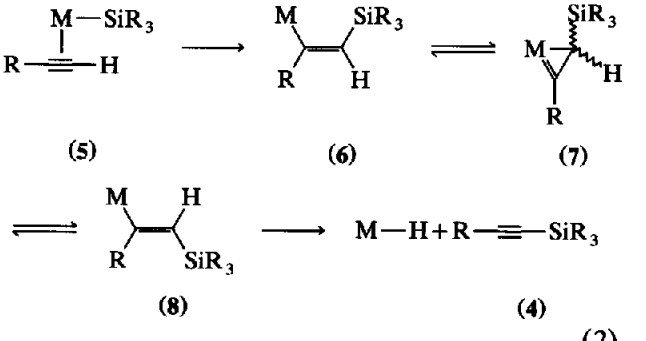
Abstract

Alkyne hydrosilation has been examined in detail for the catalysts $[IrH(H_2O)(bq)L_2]SbF_6$ (L = PPh_3, bq = 7,8-benzoquinolinato) and $RhCl(PPh_3)_3$. Factors that favor the normal *syn-* or the unusual *anti*-silane addition to the alkynes are examined. Two other unusual products are noted: the dehydrogenative silation product $RC{\equiv}CSiR'_3$, formed by β-elimination in a vinylmetal intermediate and allylsilane products of vinylsilane isomerization. The iridium catalyst is advantageous in that it does not give fast vinylsilane isomerization, as does $RhCl(PPh_3)_3$, so allowing formation and isolation of the thermodynamically less stable *cis-*, rather than the more stable *trans*-vinylsilane isomer $RCH{=}CH(SiR'_3)$.

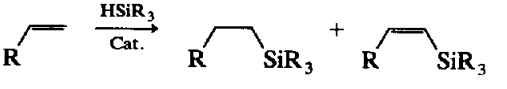
In the hydrosilation of alkynes, both the normal *syn-* (1) and the unusual *anti*-addition products (2) are found, as well as α-isomers (3) (eqn. (1)) [1], but the ratio



of products can vary dramatically depending on the catalyst and conditions [2]. There has been some disagreement about how the unexpected *anti*-addition product is formed. A related longstanding problem in hydrosilation is whether initial insertion of the unsaturated ligand, alkene or alkyne, takes place into an M–Si or an M–H bond [3]. Both we [4] and Ojima [5a] have proposed that the *anti*-addition product is formed by initial insertion of the unsaturated substrate into the M–Si bond. This is followed by isomerization of the intermediate vinyl complex, **6**, to the less sterically congested isomer **8**. We have suggested an η^2-vinyl species, **7**, as the most likely intermediate for this isomerization (eqn. (2)), but Ojima [5] and Nile [2d] prefer an alternative zwitterionic carbene formulation, $M^-{=}CR{-}CH^+{-}SiR_3$.



In the hydrosilation of alkenes, an unsaturated by-product is sometimes observed, for example **9** in eqn. (3) [6]. This dehydrogenative silation is thought to arise



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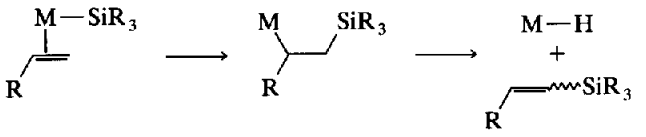
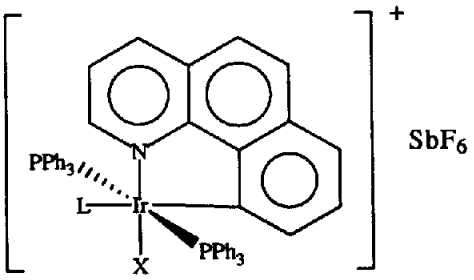
by initial insertion of the unsaturated substrate into the M–Si bond, followed by β-elimination of the intermediate shown in eqn. (4). In the hydrosilation of alkynes,



(4)

RC≡CH, the corresponding dehydrogenative silation product, RC≡CSiR′$_3$ (**4**) had not been reported when we started our work. Very recently, Doyle *et al.* [7] briefly noted that a small amount (6%) of this product was formed in one case using a Rh^{II} perfluorobutyrate catalyst. The same product has also been obtained by a dehydrocondensation reaction of silane with monosubstituted alkynes in the presence of H_2PtCl_6/I_2 but an entirely different mechanism involving R′$_3$SiI as intermediate was proposed; only normal hydrosilation was observed without additives [8a]. Liu and Harrod [8b] have reported coupling with CuCl/amine at 100°C but the rates were slow for 3° silanes; a sigma bond metathesis mechanism was proposed.

We now report studies on alkyne hydrosilation catalyzed by [IrH(H_2O)bqL$_2$]SbF_6 (L = PPh_3, bq = 7,8-benzoquinolinato) (**10**), and by $RhCl(PPh_3)_3$. We have identified the unusual dehydrogenative silation product **4**, and have found conditions where it becomes the major (84%) product. We also report other conditions which favor *syn*- (**1**) or *anti*- (**2**) addition to give vinylsilanes, so that the ratio of **1** to **2** can be made to vary from 94:6 to 0:100.



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1. Results and discussion

1.1. Choice of catalyst

In this paper we have tried to simplify the mechanistic situation by looking at a catalyst, [IrH(H_2O)(bq)L$_2$]-SbF_6 (**10**) in which only two *cis* sites are available [9], one of which (denoted X in **10**) normally binds an anionic ligand such as H or SiR_3 and the other (de-

TABLE 1. Some results of alkyne hydrosilation with **10** as catalyst

Entry	Reactants [a]		Conditions: temperature (°C), time (h)	Product ratio		Vinylsilane product ratios			Ratio of *anti* / *syn* [b]	Yield and turnovers [c]
	R	R′$_3$		Alkynyl silane	Vinyl silane	*cis* (*anti*)	*trans* (*syn*)	α		
1	1-Butyl	Ph_2Me	r.t., 24	2	98	97	2	1	98/2	89
2	Cy	Ph_2Me	r.t., 24	7	93	74	4	22	95/5	87
3	t-Butyl	Ph_2Me	r.t., 24	65	35	47	50	3	48/52	7
4	Phenyl	Ph_2Me	r.t., 48	3	97	95	3	2	97/3	85
5	Phenyl	$PhMe_2$	r.t., 48	3	97	87	2	9	97/3	95
6	Phenyl	Et_3	r.t., 48	5	95	91	5.5	3.5	94/6	85
7	Phenyl	$(MeO)_3$	r.t., 48	5	95	57	39	4	60/40	20
8	1-Butyl	Ph_2Me	65, 24	6	94	85	5	10	94/6	85
9	1-Butyl	$PhMe_2$	65, 24	10	90	80	6	14	93/7	89
10	1-Butyl	Et_3	65, 24	18	82	81	13	6	86/14	80
11	Phenyl	Ph_2Me	65, 24	4	96	91	6	3	94/6	93
12	Phenyl	$PhMe_2$	65, 24	2	98	82	4	14	95/5	91
13	Phenyl	Et_3	65, 24	10	90	80	16	4	83/17	77
14	Cy	Ph_2Me	65, 24	15	85	44	45	11	49/51	88
15	Cy	$PhMe_2$	65, 24	13	87	29	59	12	33/67	96
16	Cy	Et_3	65, 24	44	56	42	40	18	51/49	82
17	t-Butyl	Ph_2Me	65, 24	52	48	29	56	15	34/66	62
18	t-Butyl	$PhMe_2$	65, 24	43	57	32	52	16	38/62	54
19	t-Butyl	Et_3	65, 24	61	39	32	56	12	36/64	62

Ratios are mole ratios determined by GC-MS and NMR. [a] R is the alkyne substituent and R′$_3$ are the silane substituents. [b] Of silane addition to give the vinylsilanes. [c] Isolated yields based on silane. Since the catalyst was 1 mol%, these numbers also represent total turnovers. r.t., room temperature.

noted L) binds a neutral ligand, such as water or an unsaturated species such as alkyne or alkene. We had hoped to be able to isolate or spectroscopically observe potential intermediates in this system, but this did not prove successful. The reactions were studied at temperatures ranging from 20°C to 90°C in dichloromethane with 1 mol% catalyst. The reactions were usually complete after 24 h and the products were identified by NMR and GC-MS. We will consider the stereochemistry of silane addition first, because the isomerization step required to account for the *anti*-addition product is also required for the new dehydrogenative silation reaction.

1.2. Syn- vs. anti-silane addition to the alkyne

The major product in almost all cases is the *cis* species, resulting from *anti*-addition of silane to the alkyne. This is surprising, because the *cis* species is thermodynamically less stable than the *trans* isomer. In our previous work on a very similar iridium catalyst [5a], we also found predominant *anti*-addition of silane to an alkyne. In this case, we were able to rule out all other mechanisms except initial insertion into the M–Si bond and isomerization of the intermediate vinyl **6** [10] to the stabler form **8**, in which the bulky metal and silyl groups are *trans* (eqn. (2)).

If the R group in RC≡CH is very bulky, we might expect an equilibrium between **6** and **8**, which would translate to a mixture of *syn*- and *anti*-addition products in the resulting vinylsilanes. Entries 1–3 in Table 1 show that a large effect of this sort is seen only for the very bulky t-butyl group and to a lesser extent the cyclohexyl group. The steric bulk of the silyl group has only a marginal influence, slightly favoring *syn*-addition for small R'_3Si groups (Table 1, entries 4–6). Since **6** lacks an *endo*-β-hydrogen, β-elimination is not possible, but once **8** has been formed, β-elimination can lead to the dehydrogenative silation product **4** (eqn. (2)).

Raising the temperature favors *syn*-addition resulting in *trans*-isomers, as seen in Table 2. This is probably because higher temperature favors reductive elimination of the product before equilibration of **6** and **8** is complete. The simplest way for this to be true is for $\Delta S^{\ddagger}$ of the reductive elimination to be much more positive than $\Delta S^{\ddagger}$ for the vinyl equilibration step. This is reasonable, because $\Delta S^{\ddagger}$ for reductive elimination is expected to be positive and $\Delta S^{\ddagger}$ for the equilibration is likely to be negative for the following reasons. Going from the sterically congested *cis*-vinyl (**6**) to the proposed η^2-vinyl species, **7**, is likely to be the difficult and therefore rate-determining step for the isomerization of **6** to **8**. This step must have a negative $\Delta S^{\ddagger}$ because free rotation of the M–C bond is restricted in the more ordered η^2-vinyl species, **7**.

1.3. Effect of change of silane on rate

$(MeO)_3SiH$ is normally [5] found to be a very reactive silane in hydrosilation, because the Si–H bond of the silane is unusually weak, and the M–Si bond of the oxidative addition product is unusually strong, both of which favor oxidative addition. In our system, this silane is one of the least reactive; we see only 20% conversion (= 20 turnovers) over 48 h with PhC_2H as substrate as opposed to the 85% and 95% conversions noted for Et_3SiH and $PhMe_2SiH$, respectively (Table 1, entries 5–7). This implies that oxidative addition of the silane is not the turnover limiting (rate determining) step in this system.

The α-vinylsilane, $R(R'_3Si)C{=}CH_2$ (**3**), was never an important product in any case, although with the very bulky $CyC_2H/PhMe_2SiH$ system, the α-isomer constituted as much as 22% of the vinylsilanes (Table 1, entry 2).

1.4. Dehydrogenative silation

In studying the reaction of a variety of 1-alkynes RC_2H with various silanes, R'_3SiH, we saw a substantial amount of the alkyne hydrogenation product, $RCH{=}CH_2$, but were not able at first to identify the source of the H_2 required. If dehydrodimerization of the silane was responsible, $R'_3SiSiR'_3$ should appear in

TABLE 2. Results of alkyne hydrosilation of phenylacetylene and triethylsilane with **10** as catalyst at different temperatures

Entry	Conditions: temperature (°C), time (h)	Product ratio		Vinylsilane ratio			*Anti / syn* ratio [a]	Yield and turnovers [b]
		Alkynyl silane	Vinyl silane	*cis*	*trans*	α		
1	r.t., 48	6	94	91	5.5	3.5	94/6	96
2	40, 17	7	93	88	8.5	3.5	91/9	90
3	65, 18	10	90	80	16	4	83/17	94
4	93, 13	20	80	75	21	4	78/22	100

Ratios are mole ratios. [a] Of silane addition to give the vinylsilanes. [b] Yields based on silane and determined by NMR. Since the catalyst was 1 mol%, these numbers also represent total turnovers. r.t., room temperature.

TABLE 3. Product ratio of alkynylsilane, vinylalkane and vinylsilane in hydrosilation of alkynes and silanes with $[IrH(H_2O)(bq)L_2]^+$ (**10**) as catalyst

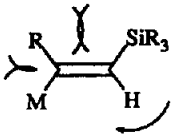
Entry	Reactants		Conditions: temperature (°C), time (h)	Mole ratio of products		
	Silane	Alkyne		Alkynyl silane	$RCH{=}CH_2$ [a]	Vinyl silane
1	Ph_2MeSiH	1-Hexyne	r.t., 24	2	Trace	98
2	Ph_2MeSiH	CyCCH	r.t., 24	6.5	9	84.5
3	Et_3SiH	^{t}BuCCH	65, 24	40	35	24
4	Et_3SiH	PhCCH	r.t., 48	5	12	83
5	Et_3SiH	PhCCH	40, 17	6	9	85
6	Et_3SiH	PhCCH	65, 18	9	12	79
7	Et_3SiH	PhCCH	96, 13	15.5	14.5	70

[a] Determined by NMR. r.t., room temperature.

the products, but it was absent. Close inspection revealed that the dehydrogenative silation product, $R'_3SiC{\equiv}CR$, was also present. Each mole of this product formed should supply 1 mole of H_2 and indeed we find that $R'_3SiC{\equiv}CR$ and $RCH{=}CH_2$ are formed in approximately equimolar amounts (Table 3). Equation (2) shows how **4** can be formed; the resulting metal hydride can then lead to alkene hydrogenation to give $RCH{=}CH_2$.

Voronkov [8] has observed in his H_2PtCl_6/I_2 system that $R'_3SiC{\equiv}CR$ formation was accompanied by H_2 evolution but not formation of hydrogenated products. This system is thought to be mechanistically unrelated to our own, however.

We find that the selectivity for the dehydrogenative silation product is largest when both R and R′ are sterically demanding. For example, at 20°C, as much as 65% of the product is the silylalkyne with ^{t}BuC$_2$H and Ph_2MeSiH (Table 1, entry 3), but only 2% is seen for ^{n}BuC$_2$H and Ph_2MeSiH (Table 1, entry 1). Table 1 also shows the dependence of dehydrogenative silation on the steric size of R (Table 1, entries 8–19). For sterically demanding alkyne R groups like t-butyl, over half of the products come from dehydrogenative silation (Table 1, entries 17–19). A large amount of *trans*-isomer (*syn*-addition product) is also obtained. For less sterically demanding alkyne R groups such as cyclohexyl, less dehydrogenative silation product is obtained than with t-butyl. With relatively sterically unhindered alkyl groups like n-butyl or phenyl, the formation of alkynyl silanes is essentially suppressed. Mechanistically, this finding is reasonable, because β-elimination is likely to be accelerated by sterically demanding substituents that cause the vinyl C–H bond to approach the metal as a result of congestion between R and SiR_3, as shown in **11**.



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Surprisingly, this dehydrogenative silation product has not been reported before, apart from the small amounts found by Doyle [7]. We have therefore looked at classical catalysts to see if the product is also formed in these cases but had been missed. As shown in Table 4, for Wilkinson's complex, the silylalkyne dehydrogenative silation product constitutes as much as 6%, 10%, 22% and 26% of the hydrosilated product with PhC_2H, ^{n}BuC$_2$H, CyC$_2$H and ^{t}BuC$_2$H at 65°C for 4 h; the corresponding figures for the Ir catalyst are 10%, 18%, 44% and 61%, respectively, after 24 h.

Dehydrogenative silation is strongly favored by increasing the alkyne/silane ratio as shown for

TABLE 4. Results of alkyne hydrosilation with Wilkinson's complex as catalyst with Et_3SiH [a]

Entry	R	Product ratio		Vinylsilane ratio			*Anti / syn*	Yield (%)
		Alkynyl silane	Vinyl silane	*cis*	*trans*	α		
1	^{n}Bu	10	90	62	36	2	63/47	84
2	Ph	6	94	44	55	1	44/56	88
3	Cy	22	78	9.5	80	10.5	11/89	80
4	^{t}Bu	26	74	Trace	100	0	0/100	73

[a] Reactions were carried out at 70°C for 4 h.

TABLE 5. Results of hydrosilation of t-butylacetylene and triethylsilane with $[IrH(H_2O)(bq)L_2]^+$ (10) as catalyst using different ratios of alkyne to silane

Entry	Mol ratio alkyne/silane	Conditions: temperature (°C), time (h)	Product ratio		Vinylsilane ratio			Alkyl silane [a]	*Anti/syn*	Yield (%)
			Alkynyl silane	Vinyl silane	*cis*	*trans*	α			
1	1.2/1	65, 24	61	39	32	56	12	0	36/64	62
2	8/1	80, 40	84	16	12	77	11	0	14/86	76
3	1/4	70, 24	59	41	37	41	0	22	47/53	80

[a] $^tBuCH_2CH_2SiEt_3$.

$^tBuC_2H/Et_3SiH$ (Table 5). The reason may be that the formation of $RC_2SiR'_3$ requires a hydrogen acceptor to remove the hydrogen liberated, and so having a high concentration of alkyne is favorable. Where the alkyne/silane ratio is reversed, the alkyne is no longer able to act as hydrogen acceptor. In this case the vinylsilane seems to take over this role, because 22% of $^tBuCH_2CH_2SiEt_3$ is now observed in the products (Table 5, entry 3).

1.5. Identification of silanes

The molecular weight of the silane isomers was determined from the molecular ion peak in the GC-MS. The regiochemistry and stereochemistry of **1–3** were determined from the ^1H NMR criteria discussed by Watanabe [2c] and by Nile [2d] and as also used by subsequent investigators [2]. The two CH=CH′ or =CHH′ vinyl resonances at 5–7.5 δ show characteristic coupling: $^3J(H, H')$ for **1**, where these protons are mutually *trans*, is in the range 18–20 Hz and for **2**, where the protons are *cis*, is in the range 12–16 Hz. In the α-isomer **3**, the vinylic protons are *geminal* and the $^2J(H, H')$ found in this case is much smaller, *ca.* 3 Hz.

We identified these alkynylsilanes, **4**, from their molecular weight, determined by GC-MS and by comparison of the MS fragmentation pattern and ^1H NMR spectra with the authentic compounds. These were made by a standard procedure: treatment of RC_2H with ^{n}BuLi in THF at 0°C to generate RC_2Li, followed by reaction with R'_3SiCl and warming to room temperature (see Experimental section).

1.6. Isomerization of the initial vinylsilane to allylsilanes

Doyle *et al.* [7] have recently studied alkyne hydrosilation with rhodium(II) perfluorobutyrate or chloroplatinic acid as catalyst, and shown that the vinylsilanes initially formed are subsequently isomerized to allylsilanes. We also see this in our system and for Wilkinson's catalyst. Our catalyst is much less isomerizing, however, and this is a great advantage in that it allows us to obtain large quantities of *cis*-vinylsilanes, largely uncontaminated by isomers. The vinylsilane isomerization seems to require excess silane, and for this reason we prefer to run the reactions with an excess of alkyne, typically 1.2 mol alkyne per mol of silane.

1.7. Isomerization of cis-vinylsilane with Wilkinson's catalyst

The accessibility of the *cis*-vinylsilanes with our iridium catalyst has allowed us to obtain this material in sufficient amount and purity to look at the $RhCl(PPh_3)_3/R'_3SiH$ system for the isomerization of *cis*-{^{n}Bu–CH=CHSiPh$_2$Me}. Table 6 shows that the initially largely *cis*-β-vinylsilane is rapidly isomerized at 75°C, first to the *trans*-β-vinylsilanes, and then to the *cis*- and *trans*-allylsilanes. After 43 h, the reaction is

TABLE 6. Isomerization of vinylsilane of *cis*-1-(diphenylmethylsilyl)-1-hexene to allylsilanes by Wilkinson's complex in the presence of silane

Conditions: temperature (°C), total elapsed time (h)	Product ratio				*Cis/trans* ratio [a]	Vinyl/allyl ratio	Nonvinyl [b]		
	cis	*trans*	α	Allyl			*cis*-allyl	*trans*-allyl	Other [c]
Starting material [d]	88	2	10	0	98/2	100/0			
75, 4 [e]	7	44.4	9.1	39.5	14/86	61/39	51.5	33.5	15.0
75, 21	2	41.2	6.3	50.5	5/95	50/50	51.4	34.1	14.5
82, 25 [e]	2	34.7	5.6	57.8	5/95	42/58	48.5	36.9	14.6
82, 43	1	28.7	4.8	65.4	4/96	35/65	40.9	41.3	17.8

These figures refer to a single experiment followed for 43 h and indicate the product composition after the time noted. [a] Of vinylsilanes. [b] Unsaturated isomers other than vinylsilanes. [c] A mixture of homoallyl and other unsaturated silanes. [d] Composition of initial mixture before addition of isomerization catalyst. [e] 0.5 equiv. of silane per Rh added (otherwise, no additive).

largely over and the major product is a mixture of *cis*- and *trans*-allylsilanes.

1.8. Reactions of 10 with alkenes and alkynes

Unfortunately, all efforts to observe identifiable organometallic species by separate addition of 1-alkyne or silane to the catalyst were unsuccessful and gave unidentifiable mixtures. We do know that unsaturated species such as alkenes add to the precursor to give stable alkene hydrides, however. Albeniz *et al.* [11] found that ethylene reacts with the Ir catalyst **10** to give a stable alkene hydride complex $[IrH(C_2H_4)(bq)L_2]SbF_6$ which does not appear to undergo insertion.

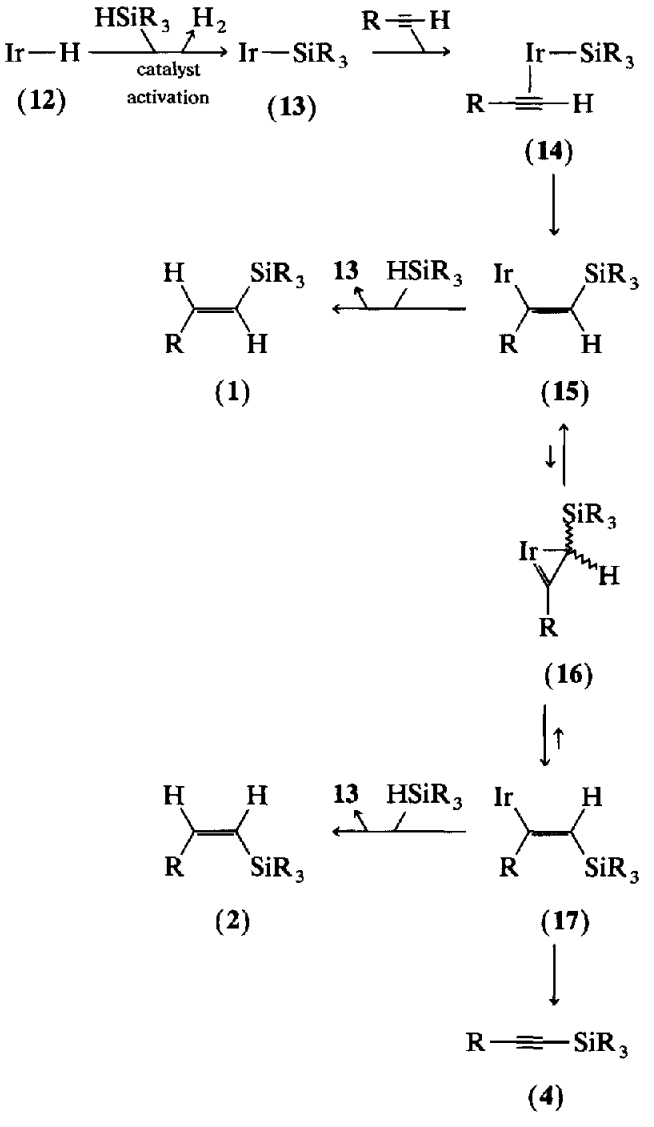
1.9. Mechanism

We know that the alkyne must first insert into an M–Si bond rather than an M–H bond in order to see predominant *anti*-addition [4b]. The simplest mechanistic hypothesis is therefore the one shown in Scheme 1. We can now see why the iridium system is particularly favorable for the rearrangement of the vinyl intermediate (**15** → **17**), and therefore for catalyzing *anti*-addition, because no hydride is present on the metal for a reductive elimination, and so **15** has time to rearrange to **17** before the hydride required for cleaving the vinyl group from the metal is supplied by an incoming silane.

Once **15** has rearranged to **17**, two scenarios can be envisaged for the reductive elimination. If silane oxidative addition takes place to give an Ir^V species, reductive elimination gives the vinylsilane product. On the other hand, cationic Ir^V species are very rare [12] and an alternative is formation of a sigma complex, known to occur in very similar systems [9,13], followed by proton transfer to the vinyl group (eqn. (5)). This pathway is most consistent with the low reactivity of the normally very reactive $(MeO)_3SiH$. The electron accepting $(MeO)_3Si$ group disfavors the formation of a sigma bond complex because the SiH bond is less basic and therefore retards the reaction.

$$M\text{–}CR{=}CH(SiR'_3) + R'_3Si\text{–}H \longrightarrow R'_3Si\text{–}H\text{–}M\text{–}CR{=}CH(SiR'_3) \longrightarrow R'_3Si\text{–}M + HCR{=}CH(SiR'_3) \quad (5)$$

High temperatures favor the formation of *trans*-vinylsilanes (*syn*-addition) and of dehydrogenative silation products, especially for sterically hindered alkyl substituted alkynes such as t-butylacetylene. This can be rationalized on the basis that high temperature accelerates β-elimination of **17** to give alkynylsilane **4**. The unisomerized intermediate **15**, which, having no *cis*-β-hydrogen, cannot β-eliminate, instead reductively eliminates to give *trans*-vinylsilane **1**.



Scheme 1.

As the steric influence of R increases, it must eventually equal that of the L_nM fragment, at which point the *cis*- and *trans*-vinyliridium intermediates should have similar free energies and *syn*- and *anti*-addition should become comparable. Table 1 shows that this is the case for C = Cy and ^{t}Bu, where the proportion of *syn*-addition is significantly higher than for the smaller R groups, where the highest tendency for *anti*-addition is seen.

2. Conclusion

The iridium complex **10** is a good catalyst for the *anti*-addition of silanes to alkynes, largely because it has a low tendency to isomerize the products. In this

way, the *cis*-vinylsilane isomer can be obtained in good yield. This is interesting because the *cis* isomer is thermodynamically less stable than the *trans* isomer. Excess hydrosilane leads to isomerization, so using a slight excess of alkyne is beneficial. Wilkinson's catalyst proves to be more active in isomerization, accounting for its poorer selectivity for *anti*-addition. Especially with this catalyst, further isomerization of the vinylsilane to the allylsilanes is also seen.

Bulky R groups lead to dehydrogenative silation to give the alkynylsilane, $RC{\equiv}CSiR'_3$, a reaction not previously studied. A mechanism is suggested involving initial alkyne insertion into an M–Si bond and isomerization of the vinylmetal intermediate via an η^2-vinyl species. The same rearrangement is required before dehydrogenative silation can take place, because this places the β-H *endo* to the metal. A sigma bond complex of the incoming silane is proposed for the cleavage of the vinylmetal intermediate from the catalyst.

3. Experimental details

^{1}H NMR spectra were recorded on a Bruker WM 250 spectrometer and are reported in ppm from TMS as internal standard. Mass spectra (GC-MS) were obtained on a Hewlett Packard HP 5971A mass spectrometer equipped with an HP 5890 series II Gas Chromatograph. Column chromatography was performed on Merck Silica Gel 60 (230–400 mesh). The iridium catalyst, (η^2-7,8-benzoquinolinato)aquahydridobis(triphenylphosphine)iridium(III) hexafluoroantimonate (**10**), was prepared according to the literature method [9]. Wilkinson's complex, and all alkynes, hydrosilanes and chlorosilanes, were purchased from Aldrich Chemical Co., Inc., and used without further purification.

Caution: $(MeO)_3SiH$ can contain small amounts of the toxic $(MeO)_4Si$.

3.1. General procedure

3.1.1. Hydrosilation of 1-alkynes with silanes

A screw-capped pressure vial was charged with the iridium catalyst **10** (8.8×10^{-3} mmol) dissolved in CD_2Cl_2 (0.1 ml) and the solution flushed with nitrogen, and a hydrosilane (0.88 mmol) added. After 15 min stirring at room temperature, alkyne (1.06 mmol) was added dropwise. The reaction vial was kept at the required reaction temperature by immersion in a hot oil bath. The progress of the reaction was monitored by ^{1}H NMR and GC-MS. After the reaction was complete, the products were separated and purified by column chromatography with hexane as an eluent. The yield and product ratios were determined by ^{1}H NMR and GC-MS. The alkynylsilanes were identified by comparison with authentic samples prepared as shown below.

3.1.2. Synthesis of silylalkynes

A dry Schlenk vessel was charged with 1.85 mmol of the terminal alkyne dissolved in 2 ml of THF, flushed with nitrogen, and ^{n}BuLi in hexane added (1.5 ml, 1.6 N) at 0°C. The mixture was allowed to warm to room temperature and stirred for 30 min. To this solution was added 1.85 mmol of the appropriate chlorosilane, during which time a white precipitate formed, and stirring was continued for an additional 5 h at room temperature. Addition of water and extraction with ether gave the silylalkynes in 50–60% yield after purification by column chromatography.

3.2. Identification of products

1-(Diphenylmethylsilyl)-1-hexyne

^{1}H NMR ($CDCl_3$): δ 0.66 (s, 3H, SiMe); 0.92 (t, $J = 7.2$ Hz, 3H, Me in ^{n}Bu); 1.4–1.6 (m, 4H, 4,5-CH_2 groups in hexynyl); 2.32 (t, $J = 7.0$ Hz, 2H, 3-CH_2 in hexynyl); 7.3–7.7 (m, 10H, Ph). MS: *m/e* 278 (M^+, 4), 263(100), 236(10), 221(14), 207(11), 181(7), 143(9), 105(24).

cis-1-(Diphenylmethylsilyl)-1-hexene

^{1}H NMR ($CDCl_3$): δ 0.64 (s, 3H, Me); 0.7–2.1 (m, 9H, ^{n}Bu); 5.80 (d, $J = 13.9$ Hz, 1H, SiCH=); 6.57 (dt, $J = 13.9$, 7.5 Hz, 1H, ^{n}Bu–*CH*=); 7.2–7.7 (m, 10H, Ph). MS: *m/e* 280 (M^+, 11), 265(43), 223(91), 197(61), 183(100), 145(59), 121(68), 105(66).

trans-1-(Diphenylmethylsilyl)-1-hexene

^{1}H NMR ($CDCl_3$): δ 0.92 (s, 3H, Me); 0.7–2.3 (m, 9H, ^{n}Bu); 5.94 (d, $J = 18.5$ Hz, 1H, SiCH=); 6.16 (dt, $J = 18.5$, 6.1 Hz, 1H, ^{n}Bu*CH*=); 7.3–7.7 (m, 10H, Ph). MS: *m/e* 280 (M^+, 10), 265(43), 223(84), 197(39), 183(100), 145(94), 121(65), 105(59).

2-(Diphenylmethylsilyl)-1-hexene

^{1}H NMR ($CDCl_3$): δ 0.65 (s, 3H, Me); 0.7–2.3 (m, 9H, ^{n}Bu); 5.38, 5.83 (d, $J = 2.9$ Hz, 1H, =CH_2); 7.2–7.7 (m, 10H, Ph). MS: *m/e* 280 (M^+, 15), 265(11), 223(9), 197(100), 183(25), 121(16), 105(26).

1-(Dimethylphenylsilyl)-1-hexyne

^{1}H NMR ($CDCl_3$): δ 0.38 (s, 6H, $SiMe_2$); 0.9 (t, 3H, Me in ^{n}Bu); 1.3–1.6 (m, 4H, 4,5-CH_2 groups in hexynyl); 2.26 (t, $J = 6.9$ Hz, 2H, 3-CH_2 in hexynyl); 7.3–7.7 (m, 5H, Ph). MS: *m/e* 216 (M^+, 2), 201(100), 174(22), 145(18), 135(8), 121(7), 105(12).

cis-1-(Dimethylphenylsilyl)-1-hexene [2d,2e,5]

^{1}H NMR ($CDCl_3$): δ 0.38 (s, 6H, $SiMe_2$); 0.8–2.2 (m, 9H, ^{n}Bu); 5.6 (d, J = 14 Hz, 1H, SiCH=); 6.4 (dt, J = 14 Hz, 7.4 Hz, 1H, ^{n}Bu*CH*=); 7.3–7.7 (m, 5H, Ph). MS: *m/e* 218 (M^+, 4) 203(46), 161(42), 145(25), 135(52), 121(100), 105(27).

trans-1-(Dimethylphenylsilyl)-1-hexene [2d,2e,5]

^{1}H NMR ($CDCl_3$): δ 0.3 (s, 6H, $SiMe_2$); 0.8–2.2 (m, 9H, ^{n}Bu); 5.7 (d, J = 18.6 Hz, 1H, SiCH=); 6.1 (dt, J = 18.6, 6.2 Hz, 1H, ^{n}Bu*CH*=); 7.3–7.6 (m, 5H, Ph). MS: *m/e* 218 (M^+, 6), 203(60), 161(40), 145(19), 135(33), 121(100), 105(19).

2-(Dimethylphenylsilyl)-1-hexene [2d,2e,5]

^{1}H NMR ($CDCl_3$): δ 0.38 (s, 6H, $SiMe_2$); 0.8–2.2 (m, 9H, ^{n}Bu); 5.38 and 5.67 (each: d, J = 2.9 Hz, 1H, =CH*H*); 7.3–7.7 (m, 5H, Ph). MS: *m/e* 218 (M^+, 10), 203(15), 174(7), 161(21) 135(100), 121(51), 105(18).

1-(Triethylsilyl)-1-hexyne [8]

^{1}H NMR ($CDCl_3$): δ 0.57 (q, J = 7.9 Hz, 6H, $SiCH_2$); 0.91 (t, 3H, Me of ^{n}Bu); 0.96 (t, J = 7.8 Hz, 9H, $SiCH_2CH_3$); 1.5 (m, 4H, 4,5-CH_2 groups in hexynyl); 2.24 (t, J = 6.9 Hz, 2H, 3-CH_2 in hexynyl). MS: *m/e* 196 (M^+, 2), 167(100), 139(54), 111(29), 97(16), 83(14).

cis-1-(Triethylsilyl)-1-hexene [2d,2e,5,8]

^{1}H NMR ($CDCl_3$): δ 0.6 (q, 6H, $SiCH_2$); 0.92 (t, 9H, $SiCH_2CH_3$); 0.9–2.2 (m, 9H, ^{n}Bu); 5.39 (d, J = 14.1 Hz, 1H, SiCH=); 6.39 (dd, J = 14.1, 7.3 Hz, 1H, ^{n}Bu*CH*=). 198 (M^+, 1), 169(100), 156(8), 141(90), 113(28), 99(10), 85(22), 59(24).

trans-1-(Triethylsilyl)-1-hexene [2d,2e,5,8]

^{1}H NMR ($CDCl_3$): δ 0.6 (q, 6H, $SiCH_2$); 0.92 (t, 9H, $SiCH_2CH_3$); 0.9–2.2 (m, 9H, ^{n}Bu); 5.53 (d, J = 18.7 Hz, 1H, SiCH=); 6.03 (dt, J = 18.7, 6.3 Hz, 1H, ^{n}Bu*CH*=). MS: *m/e* 198 (M^+, 3), 169(86), 141(100), 113(26), 97(6), 85(15), 59(23).

2-(Triethylsilyl)-1-hexene [2d,2e,5,8].

^{1}H NMR ($CDCl_3$): δ 0.6 (q, 6H, $SiCH_2$); 0.92 (t, 9H, $SiCH_2CH_3$); 0.9–2.2 (m, 9H, ^{n}Bu); 5.28 and 5.62 (each: d, J = 3.0 Hz, 1H, CH_2). MS: *m/e* 198 (M^+, 7), 169(10), 141(10), 115(89), 87(100), 59(30).

Diphenylmethyl(phenylethynyl)silane

^{1}H NMR ($CDCl_3$): δ 0.76 (s, 3H, Me); 7.2–7.6 (m, 15H, Ph). MS: *m/e* 298 (M^+, 31), 283(100), 221(11), 181(8), 129(15), 105(20).

cis-β-(Diphenylmethylsilyl)styrene

^{1}H NMR ($CDCl_3$): δ 0.46 (s, 3H, Me); 6.2 (d, J = 15.2 Hz, 1H, SiCH=); 7.2–7.4 (m, 15H, Ph); 7.6 (d, J = 15.2 Hz, 1H, Ph*CH*=). MS: *m/e* 300 (M^+, 15), 285(36), 222(43), 207(100), 197(21), 183(37), 145(27), 105(54).

trans-β-(Diphenylmethylsilyl)styrene

^{1}H NMR ($CDCl_3$): δ 0.70 (s, 3H, Me); 6.75 (d, J = 19.1 Hz, 1H, SiCH=); 6.97 (d, J = 19.1 Hz, 1H, Ph*CH*=); 7.2–7.6 (m, 15H, Ph). MS: *m/e* 300 (M^+, 15), 285(35), 222(40), 207(100), 183(46), 145(25), 105(57).

α-(Diphenylmethylsilyl)styrene

^{1}H NMR ($CDCl_3$): δ 0.66 (s, 3H, Me); 5.58 (d, J = 2.87 Hz, 1H, =CH*H*); 7.2–7.6 (m, 15H, Ph). MS: *m/e* 300 (M^+, 17), 285(13), 222(10), 197(100), 105(12).

Dimethylphenyl(phenylethynyl)silane

^{1}H NMR ($CDCl_3$): δ 0.42 (s, 6H, Me); 7.1–7.6 (m, 10H, Ph). MS: *m/e* 236 (M^+, 18), 221(100), 178(4), 129(9), 105(9).

cis-β-(Dimethylphenylsilyl)styrene [2]

^{1}H NMR ($CDCl_3$): δ 0.26 (s, 6H, Me); 6.0 (d, J = 15.2 Hz, 1H, SiCH=); 7.5 (d, J = 15.2 Hz, 1H, Ph*CH*=); 7.2–7.6 (m, 10H, Ph). MS: *m/e* 238 (M^+, 23), 223(44), 179(6), 145(100), 121(23), 105(16).

trans-β-(Dimethylphenylsilyl)styrene [2c]

^{1}H NMR ($CDCl_3$): δ 0.36 (s, 6H, Me); 6.6 (d, J = 19.1 Hz, 1H, SiCH=); 7.0 (d, J = 19.1 Hz, 1H, Ph*CH*=); 7.2–7.6 (m, 10H, Ph). MS: *m/e* 238 (M^+, 36), 223(57), 179(5), 145(100), 121(31), 105(20).

α-(Dimethylphenylsilyl)styrene [2c]

^{1}H NMR ($CDCl_3$): δ 0.41 (s, 6H, Me); 5.66 and 5.98 (each: d, J = 2.9 Hz, 1H, =CH*H*); 7.3–7.6 (m, 10H, Ph). MS: *m/e* 238 (M^+, 24), 223(31), 197(13), 145(13), 135(100), 121(8), 105(13).

Triethyl(phenylethynyl)silane [8]

^{1}H NMR ($CDCl_3$): δ 0.68 (q, J = 7.8 Hz, 6H, =CH_2); 1.05 (t, J = 7.8 Hz, 9H, CH_3); 7.2–7.5 (m, 5H, Ph). MS: *m/e* 216 (M^+, 4), 187(76), 159(78), 131(100), 105(29).

cis-β-(Triethylsilyl)styrene [2b,3a,3b,8]

^{1}H NMR ($CDCl_3$): δ 0.6 (q, 6H, =CH_2); 0.9 (t, 9H, CH_3; 5.76 (d, J = 15.2 Hz, 1H, SiCH=); 7.2–7.4 (m, 5H, Ph); 7.45 (d, J = 15.2 Hz, 1H, Ph*CH*=). MS: *m/e* 218 (M^+, 12), 189(100), 161(94), 131(100), 105(62).

trans-β-(Triethylsilyl)styrene [2b,3a,3b,8]

^{1}H NMR ($CDCl_3$): δ 0.65 (q, 6H, =CH_2); 0.98 (t, 9H, CH_3); 6.4 (d, J = 19.2 Hz, 1H, SiCH=); 6.9 (d,

J = 19.2 Hz, 1H, PhC*H*=); 7.2–7.4 (m, 5H, Ph). MS: *m/e* 218 (M^+, 12), 189(100), 161(67), 131(52), 105(23).

α-(Triethylsilyl)styrene

^{1}H NMR ($CDCl_3$): δ 0.6 (q, 6H, =CH_2); 0.9 (t, 9H, CH_3); 5.58 and 5.86 (each: d, J = 0.8 Hz, 1H, =CH*H*). MS: *m/e* 218 (M^+, 4), 190(63), 161(100), 133(53), 107(46).

Trimethoxy(phenylethynyl)silane

^{1}H NMR ($CDCl_3$); δ 3.65 (s, 9H, MeO); 7.2–7.7 (m, 6H, Ph). MS: *m/e* 222 (M^+, 100), 207(47), 191(51), 177(7), 161(53), 147(7), 131(28), 115(37), 102(26), 90(48).

cis-β-(Trimethoxysilyl)styrene [3b]

^{1}H NMR ($CDCl_3$): δ 3.47 (s, 9H, MeO); 5.55 (d, J = 15.5 Hz, 1H, SiCH=); 7.2–7.7 (m, 6H, PhCH=). MS: *m/e* 224 (M^+, 46), 209(5), 194(37), 162(100), 147(7), 131(23), 121(41), 107(53), 91(82).

trans-β-(Trimethoxysilyl)styrene [3b]

^{1}H NMR ($CDCl_3$): δ 3.62 (s, 9H, MeO); 6.13 (d, J = 19.3 Hz, 1H, SiCH=); 7.24 (d, J = 19.3 Hz, 1H, PhC*H*=); 7.2–7.7 (m, 5H, Ph). MS: *m/e* 224 (M^+, 54), 209(6), 194(40), 162(100), 147(7), 131(18), 121(40), 107(41), 91(75).

α-(Trimethoxysilyl)styrene [3b]

^{1}H NMR ($CDCl_3$): δ 3.57 (s, 9H, MeO); 5.94 and 6.15 (each: d, J = 2.8 Hz, 1H, J = CH*H*); 7.2–7.7 (m, 5H, Ph). MS: *m/e* 224 (M^+, 19), 209(18), 194(65), 162(16), 121(100), 107(32), 91(82).

Diphenylmethylsilyl(cyclohexylethynyl)silane

^{1}H NMR ($CDCl_3$): δ 0.68 (s, 3H, Me); 0.8–1.9 (m, 10H, cyclohexyl); 2.5 (m, 1H, CH of cyclohexyl); 7.2–7.6 (m, 10H, Ph). MS: *m/e* 304 (M^+, 4), 289(100), 221(17), 207(30).

cis-1-Diphenylmethylsilyl-2-cyclohexyl ethylene

^{1}H NMR ($CDCl_3$): δ 0.62 (s, 3H, Me); 0.8–2.1 (m, 11H, cyclohexyl); 5.7 (d, J = 13.8 Hz, 1H, SiCH=); 6.35 (dd, J = 13.8, 10.2 Hz, 1H, R*CH*=); 7.2–7.6 (m, 10H, Ph). MS: *m/e* 306 (M^+, 2), 291(4), 228(60), 197(100), 183(63), 145(28), 121(48), 105(46).

trans-1-Diphenylmethylsilyl-2-cyclohexyl ethylene

^{1}H NMR ($CDCl_3$): δ 0.68 (s, 3H, Me); 0.8–2.1 (m, 11H, cyclohexyl); 5.9 (d, J = 18.7 Hz, SiCH=); 6.15 (dd, J = 18.7, 5.7 Hz, 1H, R*CH*=); 7.2–7.6 (m, 10H, Ph). MS: *m/e* 306 (M^+, 8), 291(10), 223(48), 197(100), 183(68), 145(27), 121(45), 105(42).

1-Diphenylmethylsilyl-1-cyclohexyl ethylene

^{1}H NMR ($CDCl_3$): δ 0.68 (s, 3H, Me); 0.8–2.1 (m, 11H, cyclohexyl); 5.37, 5.86 (d, J = 2.5 Hz, 1H, =CH*H*); 7.2–7.6 (m, 10H, Ph). MS: *m/e* 306 (M^+, 4), 291(1), 228(10), 184(13), 197(100), 121(9), 105(14).

Dimethylphenylsilyl(cyclohexylethynyl)silane

^{1}H NMR ($CDCl_3$): δ 0.37 (s, 6H, Me); 1.2–1.9 (m, 11H, cyclohexyl); 2.4 (m, 1H, CH of cyclohexyl); 7.2–7.7 (m, 5H, Ph). MS: *m/e* 242 (M^+, 2), 227(100), 145(26), 121(8), 105(8).

cis-1-Dimethylphenylsilyl-2-cyclohexyl ethylene

^{1}H NMR ($CDCl_3$): δ 0.31 (s, 6H, Me); 1.0–2.1 (m, 11H, cyclohexyl); 5.5 (d, J = 13.9 Hz, 1H, SiCH=); 6.2 (dd, J = 13.9, 10.0 Hz, R*CH*=); 7.3–7.6 (m, 5H, Ph). MS: *m/e* 244 (M^+, 2), 229(9), 185(13), 166(42), 161(28), 135(100), 121(63), 105(17).

trans-1-Dimethylphenylsilyl-2-cyclohexyl ethylene

^{1}H NMR ($CDCl_3$): δ 0.37 (s, 6H, Me); 1.0–2.1 (m, 11H, cyclohexyl); 5.7 (d, J = 18.8 Hz, 1H, SiCH=); 6.1 (dd, J = 18.8, 6.0 Hz, 1H, R*CH*=); 7.3–7.6 (m, 5H, Ph). MS: *m/e* 244 (M^+, 7), 229(17), 185(15), 166(2), 161(30), 135(100), 121(63), 105(15).

1-Dimethylphenylsilyl-1-cyclohexyl ethylene

^{1}H NMR ($CDCl_3$): δ 0.32 (s, 6H, Me); 1.0–2.1 (m, 11H, cyclohexyl); 5.40 and 5.72 (each: d, J = 2.6 Hz, 1H, =CH_2); 7.3–7.6 (m, 5H, Ph). MS: *m/e* 224 (M^+, 6), 166(8), 151(6), 135(100), 121(18), 105(6).

Triethylsilyl(cyclohexylethynyl)silane

^{1}H NMR ($CDCl_3$): δ 0.6 (s, 6H, $SiCH_2$); 0.95 (t, 9H, $SiCH_2CH_3$); 1.2–2.2 (m, 10H, cyclohexyl); 2.41 (m, 1H, CH of cyclohexyl). MS: *m/e* 222 (M^+, 1), 193(100), 165(43), 137(17), 109(15), 81(17).

cis-1-Triethylsilyl-2-cyclohexyl ethylene

^{1}H NMR ($CDCl_3$): δ 0.6 (q, 6H, $SiCH_2$); 0.95 (t, 9H, $SiCH_2CH_3$); 1.0–2.2 (m, 11H, cyclohexyl); 5.28 (d, J = 13.9 Hz, 1H, SiCH=); 6.18 (dd, J = 13.9, 10 Hz, 1H, R*CH*=). MS: *m/e* 224 (M^+, 3), 195(100), 167(58), 139(20), 113(15), 87(30), 59(29).

trans-1-Triethylsilyl-2-cyclohexyl ethylene

^{1}H NMR ($CDCl_3$): δ 0.6 (q, 6H, $SiCH_2$); 0.95 (t, 9H, $SiCH_2CH_3$); 1.0–2.2 (m, 11H, cyclohexyl); 5.5 (d, J = 18.9 Hz, 1H, SiCH=); 6.0 (dd, J = 18.9, 6.0 Hz, 1H, R*CH*=). MS: *m/e* 224 (M^+, 3), 195(100), 167(53), 139(16), 111(14), 87(14), 59(18).

1-Triethylsilyl-1-cyclohexyl ethylene

^{1}H NMR ($CDCl_3$): δ 0.6 (q, 6H, $SiCH_2$); 0.95 (t, 9H, $SiCH_2CH_3$); 1.0–2.2 (m, 11H, cyclohexyl); 5.29 and

5.66 (each: d, $J = 2.6$ Hz, 1H, $=CH_2$). MS: m/e 224 (M^+, 6), 195(49), 167(100), 139(25), 115(28), 87(57), 59(45).

3,3-Dimethyl-1-(diphenylmethylsilyl)-1-butyne

^{1}H NMR ($CDCl_3$): δ 0.64 (s, 3H, Me); 1.28 (s, 9H, ^{t}Bu); 7.3–7.7 (m, 10H, Ph). MS: m/e 278 (M^+, 22), 263(100), 221(42), 159(13), 105(14).

cis-3,3-Dimethyl-1-(diphenylmethylsilyl)-1-butene

^{1}H NMR ($CDCl_3$): δ 0.62 (s, 3H, SiMe); 1.03 (s, 9H, ^{t}Bu); 5.70 (d, $J = 15.6$ Hz, 1H, SiCH=); 6.60 (d, $J = 15.6$ Hz, 1H, ^{t}Bu*CH*=); 7.3–7.6 (m, 10H, Ph). MS: m/e 280 (M^+, 10), 265(30), 223(78), 197(100), 183(43), 145(43), 121(24), 105(38).

trans-3,3-Dimethyl-1-(diphenylmethylsilyl)-1-butene

^{1}H NMR ($CDCl_3$): δ 0.62 (s, 3H, SiMe); 1.01 (s, 9H, ^{t}Bu); 5.84 (d, $J = 18.9$ Hz, 1H, SiCH=); 6.20 (d, $J = 18.9$ Hz, 1H, ^{t}Bu*CH*=); 7.3–7.7 (m, 10H, Ph). MS: m/e 280 (M^+, 15), 265(26), 223(94), 197(100), 183(73), 145(74), 121(42), 105(67).

3,3-Dimethyl-2-(diphenylmethylsilyl)-1-butene

^{1}H NMR ($CDCl_3$): δ 0.73 (s, 3H, SiMe); 0.92 (9H, ^{t}Bu); 5.30 and 5.95 (each: d, $J = 1.88$ Hz, 1H, $=CH_2$); 7.3–7.6 (m, 10H, Ph). MS: m/e 280 (M^+, 10), 265(7), 223(5), 197(100), 105(10).

3,3-Dimethyl-1-(dimethylphenylsilyl)-1-butyne

^{1}H NMR ($CDCl_3$): δ 0.36 (s, 6H, $SiMe_2$); 1.25 (s, 9H, ^{t}Bu); 7.3–7.7 (m, 5H, Ph). MS: m/e 216 (M^+, 21), 201(100), 185(5), 159(33), 135(6), 105(9).

cis-3,3-Dimethyl-1-(dimethylphenylsilyl)-1-butene

^{1}H NMR ($CDCl_3$): δ 0.41 (s, 6H, $SiMe_2$); 0.96 (s, 9H, ^{t}Bu); 5.50 (d, $J = 15.6$ Hz, 1H, SiCH=); 6.48 (d, $J = 15.6$ Hz, 1H, ^{t}Bu*CH*=); 7.3–7.6 (m, 5H, Ph). MS: m/e 218 (M^+, 4), 203(15), 161(33), 135(100), 121(16), 105(15), 73(15).

trans-3,3-Dimethyl-1-(dimethylphenylsilyl)-1-butene

^{1}H NMR ($CDCl_3$): δ 0.32 (s, 6H, $SiMe_2$); 1.01 (s, 9H, ^{t}Bu); 5.68 (d, $J = 18.9$ Hz, 1H, SiCH=); 6.14 (d, $J = 18.9$ Hz, 1H, ^{t}Bu*CH*=); 7.3–7.6 (m, 5H, Ph). MS: m/e 218 (M^+, 9), 203(35), 161(83), 135(100), 121(46), 105(19), 73(25).

3,3-Dimethyl-2-(dimethylphenylsilyl)-1-butene

^{1}H NMR ($CDCl_3$): δ 0.44 (s, 6H, $SiMe_2$); 1.02 (s, 9H, ^{t}Bu); 5.41 and 5.80 (each: d, $J = 1.91$ Hz, 1H, $=CH_2$); 7.3–7.6 (m, 5H, Ph). MS: m/e 218 (M^+, 3), 203(8), 161(14), 135(100), 121(11), 105(9), 73(15).

3,3-Dimethyl-1-(triethylsilyl)-1-butyne [8]

^{1}H NMR ($CDCl_3$): δ 0.53 (q, $J = 7.8$ Hz, 6H, $SiCH_2$); 0.96 (t, $J = 7.8$ Hz, 9H, $SiCH_2CH_3$); 1.21 (s, 9H, ^{t}Bu). MS: m/e 196 (M^+, 1), 167(100), 139(65), 111(30), 95(12), 83(19).

cis-3,3-Dimethyl-1-(triethylsilyl)-1-butene [8]

^{1}H NMR ($CDCl_3$): δ 0.54 (q, 6H, $SiCH_2$); 0.92 (t, 6H, $SiCH_2CH_3$); 0.95 (s, 9H, ^{t}Bu); 5.20 (d, $J = 15.8$ Hz, 1H, SiCH=); 6.44 (d, $J = 15.8$ Hz, 1H, ^{t}Bu*CH*=). MS: m/e 198 (M^+, 1), 169(100), 141(28), 113(36), 99(17), 73(28), 59(25).

trans-3,3-Dimethyl-1-(triethylsilyl)-1-butene [8]

^{1}H NMR ($CDCl_3$): δ 0.54 (q, 6H, $SiCH_2$); 0.92 (t, 6H, $SiCH_2CH_3$); 0.98 (s, 9H, ^{t}Bu); 5.4 (d, $J = 19.2$ Hz, 1H, $SiCH_2$=); 6.0 (d, $J = 19.2$ Hz, 1H, ^{t}Bu*CH*=). MS: m/e 198 (M^+, 4), 169(100), 141(61) 113(18), 99(21), 59(24).

3,3-Dimethyl-2-(triethylsilyl)-1-butene [8]

^{1}H NMR ($CDCl_3$): δ 0.54 (q, 6H, $SiCH_2$); 0.92 (t, 6H, $SiCH_2CH_3$); 1.0 (s, 9H, ^{t}Bu); 5.29 and 5.75 (each: d, $J = 1.97$ Hz, 1H, $=CH_2$). MS: m/e 198 (M^+, 2), 169(69), 141(30), 101(100), 87(22), 73(35), 59(19).

3.3. Synthesis of 3,3-dimethylbutyl(triethyl)silane

To a screw-capped vial charged with Wilkinson's complex (0.01 g) and flushed with nitrogen, was added a mixture of triethylsilane (0.102 g) and 3,3-dimethyl-1-butene (0.87 g). The mixture was heated to 100°C for 17 h. Isolation by column chromatography gave 3,3-dimethylbutyl(triethyl)silane (0.168 g, 95%). ^{1}H NMR ($CDCl_3$): δ 0.44 (m, 2H, $SiCH_2CH_2$); 0.50 (q, $J = 7.9$ Hz, 6H, $SiCH_2CH_3$); 0.85 (s, 9H, ^{t}Bu); 0.92 (t, $J = 7.9$ Hz, 9H, $SiCH_2CH_3$); 1.14 (m, 2H, ^{t}Bu). MS: m/e 171 ($M^+ - 29$, 84), 143(6), 115(84), 87(100), 59(31).

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