Journal of Organometallic Chemistry, 161 (1978) 91—95
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ORGANOSILICON CHEMISTRY

XXII *. CHLOROTRIS(TRIPHENYLPHOSPHINE)RHODIUM(I)-CATALYSIS OF THE REACTION BETWEEN HEX-1-YNE AND TRIETHYLSILANE

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(Received May 17th, 1978)

Summary

The reaction of hex-1-yne with triethylsilane is catalysed by $RhCl(PPh_3)_3$ to give *cis*- and *trans*-n-$C_4H_9CH{=}CHSiEt_3$ as major products, the former favoured by decrease in the catalyst concentration, increase in the temperature or increase in the silane/alkyne ratio. The *trans*-product isomerises to the *cis* on treatment with the catalyst, but only in the presence of the silane. Mechanistic schemes are proposed to account for these observations, in which *cis*-addition gives the *trans*-isomer as the initial product of hydrosilation, and the *cis*-compound is formed from this by isomerisation.

Introduction

The mode of addition of a substrate, e.g. R_3MH (M = Si, Ge), has been used as a criterion of mechanism, in that homogeneous catalysis, and many homogeneously catalysed systems, give *cis*-addition whereas other modes of reaction, such as radical processes, may result in *trans*-addition. These differences have been illustrated in the reactions of trichlorosilane with acetylenes [2,3]. The rhodium complex $RhCl(PPh_3)_3$, previously used as a catalyst for the hydrosilation of olefins [4], has now been applied to alkynes. During the course of our work, Ojima et al. reported that this catalyst gave stereoselective *trans*-addition of several tertiary silanes to a variety of alkynes [5]. Our data for the triethylsilane/hex-1-yne system are similar to those of the Japanese workers, but are interpreted in a different way.

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* For part XXI see ref. 1 (no reprints available).

Results

Chlorotris(triphenylphosphine)rhodium(I) catalyses the reaction between triethylsilane and hex-1-yne at room temperature and at 60°C. Four products were always obtained (GLC), the major ones being identified by their NMR spectra and by comparison with authentic samples as *trans*- and *cis*-1-triethylsilylhex-1-ene, n-$C_4H_9CH{=}CHSiEt_3$. The unidentified minor products, one of lower and the other of higher retention time than the major products, were present as only ca. 5% of the total. The data of Table 1 show that, with a 1/1 mol ratio of alkyne/silane, the reaction is complete within the first hour and that there is no substantial change in the ratio of yields of the major products thereafter, apart from a slight decrease in the *trans*/*cis*-isomer ratio with increasing time. Formation of the *cis*-isomer is enhanced by raising the temperature and lowering the catalyst concentration.

The composition of mixtures of the two isomers was not changed by treatment with the catalyst and silane for periods up to 4 h at 60°C or 24 h at room temperature (mol ratio silane/hexenylsilane/catalyst, 6.25/2.00/0.00625). However, the pure *trans*-isomer was partially isomerised to the *cis*-form in 24 h at 60°C in the presence of the silane and the catalyst (mol ratio, 2.25/1.00/0.001), and was completely isomerised when the catalyst concentration was increased (mol ratio, 1.0/1.0/0.01). In both cases some of the higher-boiling compound found in the hex-1-yne reaction was also observed. The *trans*-isomer was unaffected by heating to 60°C over 8 days with either the catalyst alone or the silane alone. When the hydrosilation reaction of hex-1-yne was repeated with a

TABLE 1

REACTIONS OF $HSiEt_3$ AND $C_4H_9C{\equiv}CH$, CATALYSED BY $RhCl(PPh_3)_3$

Molar equivalents			Temperature (°C)	Time (h)	n-BuCH=CHSiEt₃ (%)		
$HSiEt_3$	HC≡CBu-n	Catalyst			*trans*	*cis*	*trans*/(*trans* + *cis*)
1.0	1.0	0.001	20	1	65	20	0.70
				2	84	14	0.86
				4	79	17	0.82
				24	82	16	0.84
		0.0001	20	2	50	50	0.51
				4	44	51	0.46
				24	36	59	0.38
1.0	1.0	0.01	60	24	45	40	0.56
					50	35	0.59
1.0	1.0	0.001	60	1	53	40	0.57
				2	33	55	0.37
				4	46	46	0.50
				24	46	46	0.50
					37	59	0.39
1.1	1.0	0.0011	60	14	58	30	0.66
1.0	1.0	0.0001	60	2	33	63	0.34
				4	25	72	0.26
					18	79	0.19
				24	26	74	0.26
1.0[a]	1.0	0.0005	40	2	35	65	0.35

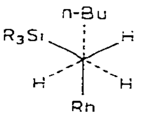
[a] Data from ref. 5.

2/1 mol ratio of triethylsilane: hex-1-yne (60°C, 0.01 molar equivalents of catalyst), only the *cis*-isomer and the higher-boiling compound were obtained.

Discussion

The hydrosilation of hex-1-yne with triethylsilane, catalysed by the complex $RhCl(PPh_3)_3$, leads to the formation of both *cis*- and *trans*-n-$C_4H_9CH{=}CHSiEt_3$. Ojima et al. [5] suggests that *trans*-addition of the silane to the triple bond is occurring, which would imply a process other than normal homogeneous catalysis, since the latter would be expected to give *cis*-addition. Our data show that, at a given temperature, lowering the catalyst concentration or increasing the silane concentration increases the amount of the *cis*-isomer. Raising the temperature also increases the yield of *cis*-isomer. These observations suggest either that there are two hydrosilation processes occurring, one leading to each isomer, or that the hydrosilation reaction forms one isomer but is followed by an isomerisation. If the latter were the case, the initial product would reasonably be expected to be the *trans*-isomer, resulting from *cis*-addition, since this is the product expected from a homogeneously catalysed reaction (cf. catalysis [3] by H_2PtCl_6) *.

Essentially similar results have been reported by Corriu and Moreau for the addition of tertiary germanes, R_3GeH, to phenylacetylene, catalysed by the rhodium complex [6]. The major products were the *cis*- and *trans*-isomers of $PhCH{=}CHGeR_3$, and the yield of the *cis*- isomer was increased by increasing the germane/acetylene ratio and by decreasing the catalyst concentration. A small degree of *cis*- to *trans*-isomerisation was noted when a mixture of the isomers was treated with the germane and the catalyst at room temperature; in the absence of the germane there was no change in the composition of the mixture. Corriu and Moreau concluded that both isomers were the result of direct reaction, and proposed that the *trans*-isomer was formed by *cis*-addition by the normal intramolecular homogeneous catalysis mechanism, i.e. oxidative addition of Ge—H to rhodium and coordination of the acetylene to the resultant rhodium(III) hydride complex. The *cis*-isomer, it was suggested, was formed by attack of a free molecule of the germane on the coordinated acetylene, followed by a hydride transfer to the rhodium to give a *trans*-$R_3GeCH{=}C(Ph)(RhH)$ system and, eventually, the *trans*-germylstyrene. The stereochemical pathway of the hydride transfer is not obvious, however, and this seems an unnecessarily complicated mechanism. This type of scheme does not explain the isomerisation of the isolated *trans*-product which occurred in our work with hexyne in the presence of the catalyst and the silane, and we believe that all the data can be better accom-



(I)

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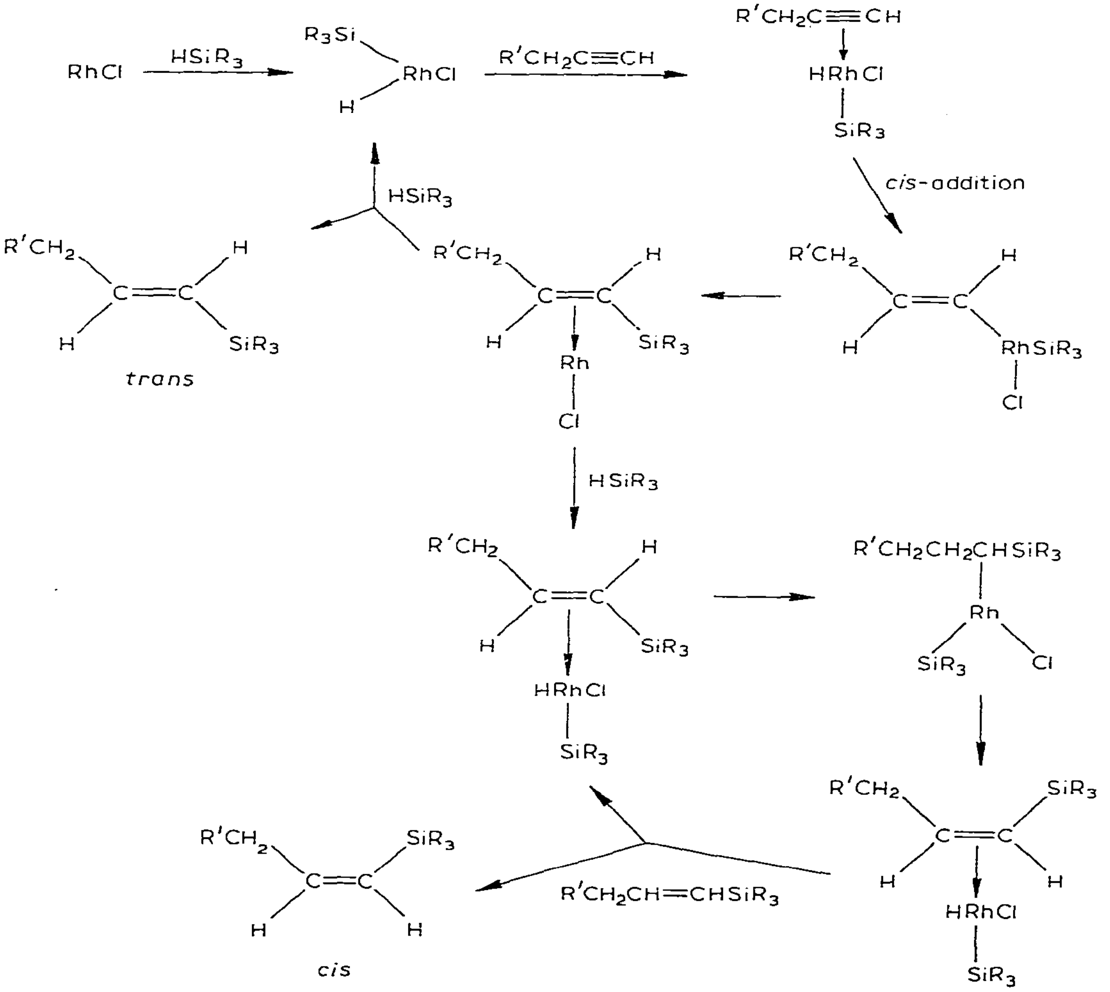
* We find that, contrary to previous reports, a little of the *cis*-isomer is formed in the H_2PtCl_6-catalysed reaction of $HSiEt_3$ with hex-1-yne.

modated by invoking the formation of the *trans*-isomer by the normal catalytic mechanism described above, followed by an isomerisation of this product to the *cis*-form. The reaction intermediate, presumably the known $RhHCl(MR_3)(PPh_3)_2$ (M = Si, Ge) [4], is then a five-coordinate metal hydride which is known to be an effective catalyst for the isomerisation of olefins [4,7]. Insertion of the *trans* isomer into the Rh—H bond would presumably give a n-hexylrhodium species in which the butyl 'tail' would be *anti* to the metal atom (I), to minimise steric interactions. *cis*-Elimination of a β-hydrogen atom and the rhodium would then lead to the *cis*-hexenylsilane.

On this basis, the hydrosilation and the isomerisation are competitive reactions occurring on the same catalyst species. Under conditions when the hydride would have a long lifetime, isomerisation of the slowly forming *trans*-isomer would be more extensive. The lifetime of the hydride depends essentially on the ratio of the concentrations of the reactants. When 1/1 mol ratios of silane(ger-



SCHEME 1. For clarity, the phosphine ligands have been omitted. The starting complex has three phosphine ligands, all other rhodium species have two. R = Et, R' = n-Pr.

mane)/acetylene are used, the greatest extent of isomerisation occurs when the catalyst concentration is lowest, i.e. when the hydrosilation reaction is proceeding slowly and the silane (germane) is present for the longest period. When a ratio of silane/acetylene of 2/1 was used, only the *cis*-isomer was formed since, even when hydrosilation was complete, silane was still present to keep the rhodium complex in the hydride form and allow total isomerisation. This observation is consistent with the finding that isomerisation of the pure *trans*-isomer requires the presence of both the catalyst and the silane, and is also consistent with the increasing *cis*/*trans* ratio found by the French workers on increasing the germane/acetylene ratio. The reactions involved are summarised in Scheme 1.

A minor product of low boiling point may be n-$C_4H_9C{\equiv}CSiEt_3$. The highest boiling component, obtained during the hydrosilation or the isomerisation of the *trans*-isomer, was not identified, but it seems likely that it is either a hex-2-enylsilane, formed by isomerisation of the major products, or, more probably, it is the product of addition of a second molecule of the silane, i.e. a disilylhexane.

Experimental

Triethylsilane and $RhCl(PPh_3)_3$ were prepared by literature methods [8,9]. GLC analyses were performed with Apiezon L columns at 170°C. *trans*-1-Triethylsilylhex-1-ene was prepared by reaction of hex-1-yne (2.05 g) with $HSiEt_3$ (2.90 g) in the presence of H_2PtCl_6 (0.05 cm^3 of 0.1 *M* isopropanol solution) at 60°C for 24 h, followed by distillation at 58—60°C/2 mmHg. GLC separation gave three components, the second of which, the greatest in quantity, was *trans*-1-triethylsilylhex-1-ene. The component with the longest retention time (5—8%) was the *cis*-isomer. The first component (10—20%) showed IR absorption at 2188 cm^{-1} and ^1H NMR resonances at τ 8.28(1), 8.98(2) 9.49(6), and 9.89(3) ppm. The absence of resonances lower than τ 8 ppm eliminates alkenyl species and the product is presumably an alkyne, possibly n-$C_4H_9C{\equiv}CSiEt_3$.

Catalysis reactions were carried out either in sealed, evacuated tubes, or under nitrogen. A typical procedure is as follows: Triethylsilane (1.45 g, 12.5 mmol), hex-1-yne (1.025 g, 12.5 mmol) and $RhCl(PPh_3)_3$ (0.115 g, 0.125 mmol) were stirred under nitrogen at 60°C for 24 h. The IR spectrum of the resulting mixture indicated the consumption of all the silane. The volatile constituents were distilled under vacuum into a cold trap and separated by preparative-scale GLC. Four components were present, the yields in order of increasing retention time being 10, 45, 40, and 5%. The NMR spectra of the major components were consistent with their being *trans*- and *cis*-hex-1-enyltriethylsilane.

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