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HOMOGENEOUS CATALYSIS

VI *. HYDROSILYLATION USING TRIS(PENTANEDIONATO)RHODIUM(III) OR TETRAKIS(μ -ACETATO)DIRHODIUM(II) AS CATALYST **

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Summary

The catalytic activity of tris(pentanedionato)rhodium(III), (or rhodium(III) acetylacetonate) (I) has been investigated for the hydrosilylation of a variety of organic substrates: alkenes, terminal or internal acetylenes, conjugated dienes, or α,β -unsaturated carbonyls or nitriles. With $\text{PhCH}=\text{CH}_2$ or $\text{PhCH}_2\text{CH}=\text{CH}_2$, ω -substitution was unexpectedly observed, as well as addition. Compound I is an active hydrosilylation catalyst in the absence of any added reducing agent, as is tetrakis(μ -acetato)dirhodium(II) (II) which does not, however, show any unusual catalytic activity due to the two metal atom cluster. Possible mechanisms are suggested.

Introduction

Various rhodium(I) complexes have been used successfully as hydrosilylation catalysts [1–3]; however, little work has been done on the catalytic activity of complexes of rhodium with higher oxidation states. In this paper we report on the catalytic activity of tris(pentanedionato)rhodium(III) ($[\text{Rh}(\text{acac})_3]$ or I) and tetrakis(μ -acetato)dirhodium(II) (II). The activity of II was also investigated to see if the close proximity of the two rhodium atoms would impart novel catalytic

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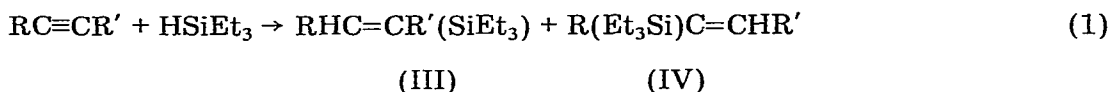
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activity, as has been demonstrated for complexes with clusters of metal atoms [4,5].

Results

Hydrosilylation using tris(pentanedionato)rhodium(III) as catalyst

I. Hydrosilylation of acetylenes. Compound I proved an efficient catalyst for the hydrosilylation of a terminal or internal acetylene using triethylsilane at 60°C, giving 1/1 acetylene/silane adducts (eq. 1), with no accompanying oligomerisation of the terminal acetylene, as had been observed with nickel-based Ziegler systems [6].



(IIIa, IVa: R = CH₃CH₂CH₂, R' = H;

IIIb, IVb: R = (CH₃)₂CHCH₂CH₂, R' = H;

IIIc, IVc: R = CH₃CH₂CH₂CH₂, R' = H;

IIId, IVd: R = R' = Et;

IIIe, IVe: R = CH₃CH₂CH₂, R' = Me)

With RC≡CH, the terminal adducts IIIa—IIIc predominate, as the *trans*-isomers, the products of *cis*-addition of the silanes (Table 1). This was established from the ¹H NMR spectrum of the adduct formed from 1-pentyne, where the resonances in the olefinic region appear as an AB quartet, *J*_{AB} 14 Hz, which is split further by interaction with the allylic hydrogens (*J*_{BC} 7 Hz) *. The minor product was identified by GLC comparison with an authentic sample, as the isomer IVa.

Internal acetylenes are also hydrosilylated in good yields (Table 1) and the products formed are likewise the simple 1/1 acetylene/silane adducts, which were identified by their ¹H NMR spectra (Table 2).

It is probable that the mechanism for the catalysis by tris(pentadionato)-rhodium(III) (I) is similar to that proposed for the catalysis by Ziegler systems [6]. The major difference is that the metal-hydride bond, which is considered to be a prerequisite in hydrosilylations, must be formed by a reduction of [Rh(acac)₃] by the silane, rather than homolysis from an alkylmetal precursor. Such a formation of a metal-hydride species has been proposed [7] and silanes have been used as co-catalysts in Ziegler type polymerizations [8]. A major consideration must also be whether a silyl group is also present on the metal centre, and evidence suggests that this is probable, since Ziegler systems using silanes as co-catalysts afford silicopolymers [8,9] and compound I with a terminal acetylene produces only the substituted olefin. Thus a vital step ((1) in Fig 1) is considered to be insertion of the acetylene into a Rh—H bond to give the σ-alkenylrhodium complexes V or VI. When R = R' = alkyl, compounds V and VI are similar and hence are obtained in comparable proportions, whereas if R or R' = H, then the terminally substituted isomer, i.e. the primary alkenyl-

* Rather different NMR assignments are proposed elsewhere [21,33].

TABLE 1

HYDROSILYLATION OF ACETYLENES WITH TRIETHYLSILANE USING RHODIUM(III) ACETYLACETONATE AS CATALYST AT 60°C^a

Acetylene ^b	Time (h)	Yield (%) ^c	Adduct
1-Pentyne	12	56	Et ₃ SiCH=CHC ₃ H ₇
		9	CH ₂ =C(SiEt ₃)C ₃ H ₇
5-Methyl-1-hexyne	15	62	Et ₃ SiCH=CHC ₅ H ₁₁
		9	CH ₂ =C(SiEt ₃)C ₅ H ₁₁
1-Hexyne	15	80	Et ₃ SiCH=CHC ₄ H ₉
		7	CH ₂ =C(SiEt ₃)C ₄ H ₉
2-Hexyne	18	38	CH ₃ C(SiEt ₃)=CHC ₃ H ₇
		44	CH ₃ CH=C(SiEt ₃)C ₃ H ₇
3-Hexyne	18	74	CH ₃ CH ₂ CH=C(SiEt ₃)C ₂ H ₅

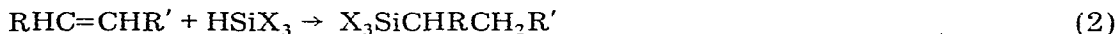
^a [Rh(acac)₃], 0.05 mmol; Et₃SiH, 6.3 mmol; maintained on an oil bath at 60°C. ^b 18 mmol. ^c Based on silane; calculated by quantitative GLC.

rhodium complex, is more stable than the secondary alkenyl complex, resulting in its preponderance.

II. Hydrosilylation of dienes. The 1/1 diene/silane adducts (VII)–(X), obtained by 1,4-addition, are formed predominantly in high yield (Table 3) when a conjugated diene is hydrosilylated using HSiEt₃ or HSi(OEt)₃ with [Rh(acac)₃] as catalyst. NMR data of two of the adducts are included in Table 4.

A possible mechanism is outlined in Fig. 2 for the hydrosilylation of isoprene and involves the formation of a π -allylrhodium complex, by insertion of isoprene into a Rh–H bond formed by reduction by the silane. The 1,4-adduct may arise by 1,2-addition followed by rapid isomerisation.

III. Hydrosilylation of alkenes. Tris(pentadienato)rhodium(III) (I) is an active catalyst for the hydrosilylation of simple olefins, styrene, or allylbenzene using HSiEt₃, or in one case HSi(OEt)₃, invariably to yield the terminal adduct (eq. 2). Results are summarised in Table 5. Products were identified by compara-



- (XI: R = H, R' = n-C₆H₁₃, X = Et;
 XII: R = H, R' = n-C₆H₁₃, X = OEt;
 XIII: R = Me, R' = n-C₅H₁₁, X = Et;
 XIV: R = Me, R' = n-C₃H₇, X = Et;
 XV: R = Me, R' = Et = X)

tive GLC, with authentic samples and analytical GLC showed that isomerisations or internal hydrosilylations do not take place. This is in contrast to the behaviour of terminal olefins when using compound I in the presence of (AlEt₃)₂ as co-catalyst [10].

Tri- or tetra-substituted, or cyclic, olefins are not hydrosilylated using compound I, consistent with results for the systems [Rh(acac)₃]/(AlEt₃)₂ [10] or [RhCl(PPh₃)₃] [11]. Likewise, the yields of adducts are better in the hydro-

TABLE 2

NMR DATA OF SILANE:ACETYLENE ADDUCTS ^a

(i)	1-Pentenyltriethylsilane		
	SiCH=CH—	CH ₃ CH ₂ CH ₂ —	—SiEt ₃
	3.3—4.8 (2H, multiplet)	7.7—9.6 (22 H, complex, overlapping signals)	
(ii)	4-Triethylsilyl-4-octene		
	—CH=C—Si—	CH ₃ CH ₂ CH ₂	—SiEt ₃
	4.38 (1H, triplet, <i>J</i> 7 Hz)	7.8—8.2 (29 H, complex, overlapping signals)	

^a Chemical shift values, τ (ppm).

silylation of terminal olefins than non-terminal olefins and this is attributed to the rate-limiting isomerisation [12–16].

As in the [Rh(acac)₃]/(AlEt₃)₂ system [10], tris(pentadionato)rhodium(III) causes not only addition to styrene or allylbenzene but also substitution (Table 5); this will be discussed elsewhere. The products were identified by GLC-mass spectrometry (GLC-MS) and, for the derivatives from styrene, by NMR; this showed PhCH=CHSiEt₃ to be the *trans*-isomer.

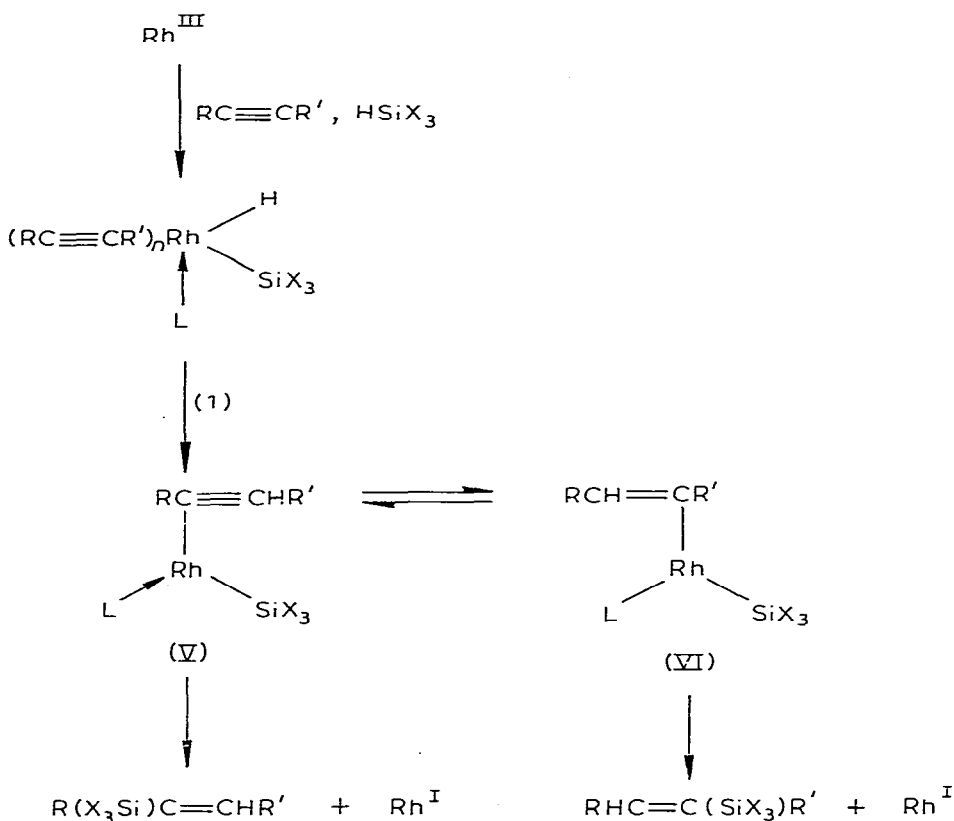


Fig. 1. Proposed mechanism for the hydrosilylation of acetylenes using rhodium(III) acetylacetonate as catalyst (L represents all other ligands, e.g. acac).

TABLE 3

HYDROSILYLATION OF DIENES USING RHODIUM(III) ACETYLACETONATE AS CATALYST ^a

Diene	Silane ^b	Time (h)	Yield (%) ^c	Adduct
	HSiEt ₃	15	94 5	1,4-adduct (VIIa) 1,2-adduct (VIIb)
	HSi(OEt) ₃	12	89	1,4-adduct (VIII)
	HSiEt ₃	12	85	1,4-adduct (IX)
	HSi(OEt) ₃	12	69	1,4-adduct (X)

^a [Rh(acac)₃], 0.05 mmol; maintained on an oil bath at 60°C. ^b HSiEt₃, 6.3 mmol, unsaturate, 18 mmol; HSi(OEt)₃, 5.5 mmol, unsaturate, 15 mmol. ^c Based on silane calculated by quantitative GLC.

IV. Hydrosilylation of α,β -unsaturated carbonyls or nitriles, or of allyl compounds $\text{CH}_2=\text{CHCH}_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{OH}, \text{OCOMe}, \text{or } \text{CH}_2\text{Br}$). The hydrosilylation of an olefin containing a functional group is only possible with a catalyst system which does not react with the substrate. Much work has already been undertaken using H_2 [PtCl₆] [17,18] but little previous work has been attempted using a relatively high oxidation state complex. Of the systems studied, only α,β -unsaturated aldehydes readily undergo hydrosilylation. Corresponding acids or nitriles are completely unreactive, whilst substituted allyl compounds generally undergo reduction, although some hydrosilylation may also occur.

Crotonaldehyde (*trans*-2-butenal) or acrolein (propenal) are each hydrosilylated using [Rh(acac)₃]. In the catalysis of their hydrosilylation using Ziegler systems, polymerisation occurs [19,20] and also alkylation, due to the co-catalyst [21]. Polymers so produced have been shown to contain silyl groups. The use of

TABLE 4

NMR DATA OF SILANE: DIENE ADDUCTS ^a

(i)	$\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{SiEt}_3$ (VIIa) —CH=C— 4.95 (1H, quartet, <i>J</i> 6 Hz)	$\text{CH}_3\text{C}=\text{C}(\text{CH}_3)\text{CH}_2\text{Si}$ 8.3–8.7 (8H, complex)	SiEt ₃ 9.0–9.6 (15H, complex)
(ii)	$\text{CH}_3\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)\text{CH}_2\text{SiEt}_3$ (IX) $\text{CH}_3\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)\text{CH}_2$ 8.1–8.7 (11H, complex)	SiEt ₃ 9.0–9.6 (15H, complex)	

^a Chemical shift values, τ (ppm).

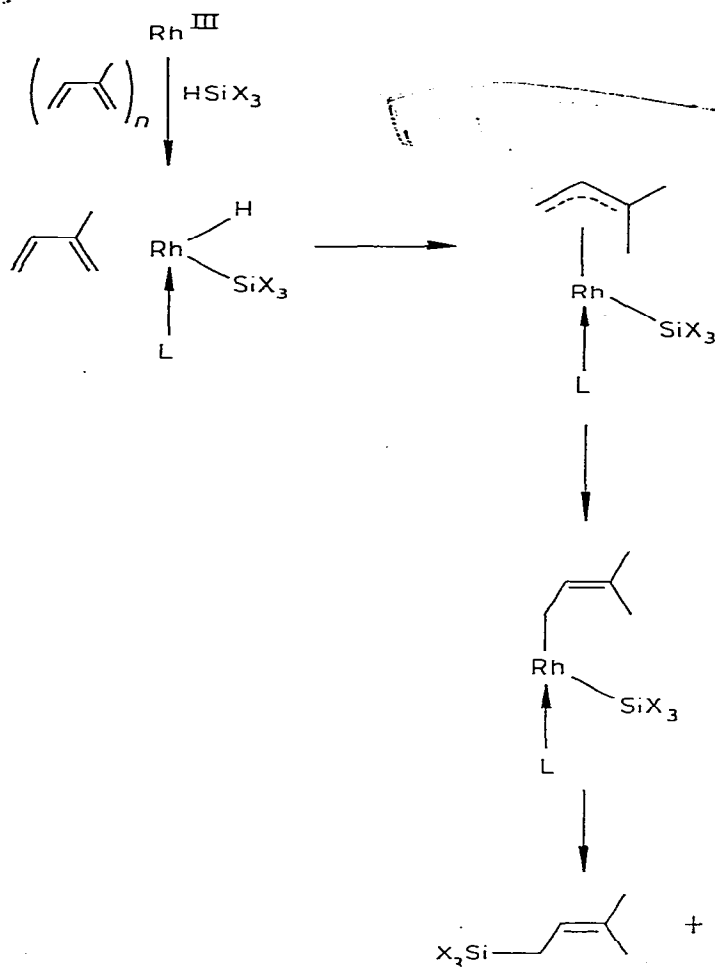


Fig. 2. Proposed mechanism for the hydrosilylation of isoprene using rhodium(III).

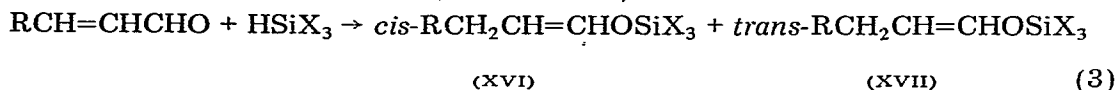
TABLE 5

HYDROSILYLATION OF OLEFINS USING RHODIUM(III) ACETYLACETONATE AS CATALYST^a

Olefin	Silane	Time (h)	Yield ^b (%)	Adduct
1-Octene	HSiEt_3 ^c	17	93	n-octylSiEt_3
1-Octene	HSi(OEt)_3 ^d	20	82	n-octylSi(OEt)_3
<i>cis</i> -2-Octene	HSiEt_3	20	74	n-octylSiEt_3
2-Hexene	HSiEt_3	18	29	n-hexylSiEt_3
<i>cis</i> -2-Pentene	HSiEt_3	20	31	n-pentylSiEt_3
Styrene	HSiEt_3	16	75	$\text{C}_6\text{H}_5\text{CH=CHSiEt}_3$
			24	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{SiEt}_3$
Allylbenzene	HSiEt_3	18	12	$\text{C}_6\text{H}_5\text{CH}_2\text{CHCHSiEt}_3$
			46	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{SiEt}_3$
			2	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{SiEt}_3)\text{CH}_3$

^a $[\text{Rh}(\text{acac})_3]$, 0.05 mmol, maintained at 60°C on an oil bath. ^b Based on silane; calculated by quantitative GLC. ^c Et_3SiH , 6.3 mmol; unsaturate, 18 mmol. ^d $(\text{EtO})_3\text{SiH}$, 5.5 mmol; unsaturate, 15 mmol.

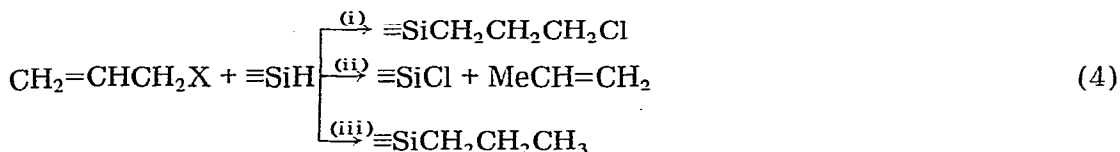
compound I results only in hydrosilylation to give the *cis*- and *trans*-adducts XVI and XVII (eq. 3) (R = Me or H, X = Et or OEt).



A similar 1,4-addition was found using $[\text{RhCl}(\text{PPh}_3)_3]$ as catalyst with trialkylsilanes [22] or trialkoxysilanes [23], but with $[\text{Ni}(\text{COD})_2]$ as catalyst attack occurred at the carbonyl group [23].

Reaction between the three components: compound I, HSiX_3 , and aldehyde, results at ambient temperatures in a dark red-brown solution; a metal-aldehyde complex is probably formed, as has been demonstrated when a nickel(0) complex was used as catalyst [23]. Distillation of the dark brown solution gives the products of eq. 3, identified by ^1H NMR spectroscopy. Only moderate yields (Table 6) of the adducts are obtained, and no attempts were made to optimise these. In each case the ratio of the isomers formed was ca. 3/2, but experiments were not made to establish their identity.

The addition of a silane to several allyl compounds has received considerable attention, not least because in some cases the results are of commercial interest. When either a Group VIII metal [24–27] or metal complex [24,26] is used as catalyst, the hydrosilylation of a substituted allyl compound is complicated, with products ranging from those of hydrosilylation (eq. 4i), reduction (eq. 4 ii), or both reduction and hydrosilylation (eq. 4 iii).



In attempts to hydrosilylate various allyl compounds using $[\text{Rh}(\text{acac})_3]$ as catalyst, only the products due to the reduction reaction (eq. 4ii) were observed, the substituted allyl compound XVI, or a derivative (XVII or XVIII) (Table 7), being isolated. In no case was a hydrosilylation product of propene (see eq. 4ii),

TABLE 6

HYDROSILYLATION OF α,β -UNSATURATED ALDEHYDES USING RHODIUM(III) ACETYLACETONATE AS CATALYST ^a

Aldehyde	Silane ^b	Time (h)	Yield (%)	Adducts
<i>trans</i> -CH ₃ CH=CHCHO	HSiEt ₃	15	31	<i>cis</i> - and <i>trans</i> -CH ₃ CH ₂ CH=CHOSiEt ₃
<i>trans</i> -CH ₃ CH=CHCHO	HSi(OEt) ₃	12	28	<i>cis</i> - and <i>trans</i> -CH ₃ CH ₂ CH=CHOSi(OEt) ₃
CH ₂ =CHCHO	HSiEt ₃	15	42	<i>cis</i> - and <i>trans</i> -CH ₃ CH=CHOSiEt ₃
C ₆ H ₅ CH=CHCHO	HSiEt ₃	20	0	

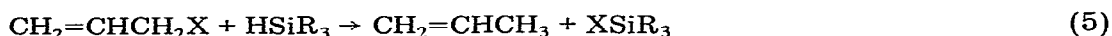
^a $[\text{Rh}(\text{acac})_3]$, 0.05 mmol; maintained on an oil bath at 60°C. ^b HSiEt₃, 6.3 mmol, aldehyde, 18 mmol; HSi(OEt)₃, 5.5 mmol, aldehyde, 15 mmol. ^c Based on silane; calculated by quantitative GLC.

TABLE 7

HYDROSILYLATION OF ALLYL COMPOUNDS $\text{CH}_2=\text{CHCH}_2\text{X}$ USING RHODIUM(III) ACETYLACETONATE AS CATALYST ^a

X	Silane ^b	Time (h)	Yield (%) ^c	Product
Cl	Et_3SiH	3	72	Et_3SiCl
Br	Et_3SiH	2	68	Et_3SiBr
Br	Ph_3SiH	1.5	82	Ph_3SiOH ^d
Br	$(\text{EtO})_3\text{SiH}$	3	61	$[(\text{EtO})_3\text{Si}]_2\text{O}$ ^d
CH_2Br	Et_3SiH	12	22	$\text{Et}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$
			47	Et_3SiBr
OH	Et_3SiH	6	46	$(\text{Et}_3\text{Si})_2\text{O}$
OOCMe	Et_3SiH	3	71	$\text{Et}_3\text{SiOOCCH}_3$
Br^e	Et_3SiH	6	0	
Br^f	—	6	0	

^a $[\text{Rh}(\text{acac})_3]$, 0.05 mmol, heated on an oil bath at 60°C . ^b Et_3SiH , 6.3 mmol, unsaturate, 18 mmol; $(\text{EtO})_3\text{SiH}$, 5.5 mmol, unsaturate, 15 mmol; Ph_3SiH , 5 mmol, unsaturate, 15 mmol. ^c Based on silane, calculated gravimetrically. ^d Hydrolysis products. ^e No $[\text{Rh}(\text{acac})_3]$. ^f No silane.



(XVI)

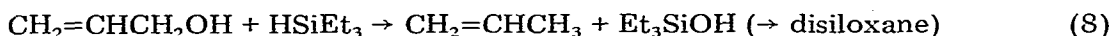


(XVII)

(XVIII)

$\text{MeCH}_2\text{CH}_2\text{SiR}_3$ or $\text{XCH}_2\text{CH}_2\text{CH}_2\text{SiR}_3$, recovered or detected by GLC-MS. However, in the hydrosilylation of $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{Br}$, both Et_3SiBr and $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SiEt}_3$ were observed (Table 7).

Where $\text{X} = \text{Br}$ or Cl and using HSiEt_3 , a substantial quantity of Et_3SiX was recovered. Similarly with HSiPh_3 or $\text{HSi}(\text{OEt})_3$ a high yield of the hydrolysis product Ph_3SiOH or $[(\text{EtO})_3\text{Si}]_2\text{O}$ was recovered. When $\text{X} = \text{OCOMe}$, triethylsilyl acetate was obtained; and for $\text{X} = \text{OH}$, hexaethyldisiloxane was identified (eq. 7 and 8).



Reduction takes place rapidly on warming the three component system, as assessed by evolution of gas, and is apparently complete within 1–2 h. No reaction occurs between the olefin and silane in the absence of catalyst or between the olefin and $[\text{Rh}(\text{acac})_3]$ in the absence of silane.

Hydrosilylation using tetrakis(μ -acetato)dirhodium(II) as catalyst

The concept that clusters of metal atoms might impart unusual catalytic activity has been the focus of much current research [4,5]. The structure of $[\text{Rh}_2(\text{OCOMe})_4]$ (II) in which the two rhodium atoms are close to one another, was therefore considered to be of interest and the activity of this complex for the hydrosilylation of a broad spectrum of organic substrates was investigated.

TABLE 8

HYDROSILYLATION USING DIRHODIUM(II) TETRAACETATE AS CATALYST ^a

Unsaturate	Mmol	Silane	Mmol	Product(s)	Yield (%) ^b
1-Octene	6.4	HSi(OEt) ₃	5.4	CH ₃ (CH ₂) ₇ Si(OEt) ₃	98
1-Octene	6.4	HSiEt ₃	6.3	CH ₃ (CH ₂) ₇ SiEt ₃	71
1-Octene	6.4	HSiMe(OEt) ₂	6.2	CH ₃ (CH ₂) ₇ SiMe(OEt) ₂	53
1-Octene	6.4	HSiMe(OEt) ₂	6.2	CH ₃ (CH ₂) ₇ SiMe(OEt) ₂	63 ^c
1-Octene	13	HSiPhMe ₂	6.5	CH ₃ (CH ₂) ₇ SiPhMe ₂	47
DMBD ^d	8.8	HSi(OEt) ₃	5.4	CH ₂ =C(CH ₃)CH(CH ₃)- CH ₂ Si(OEt) ₃	8
				(CH ₃) ₂ C=C(CH ₃)CH ₂ Si- (OEt) ₂	24
DMBD ^d	8.8	HSiEt ₃	6.3	CH ₂ =C(CH ₃)CH(CH ₃)CH ₂ - SiEt ₃	9
				(CH ₃) ₂ C=C(CH ₃)CH ₂ SiEt ₃	63
Cyclohexanone	9.8	HSi(OEt) ₃	5.4	(CH ₂) ₅ CHOSi(OEt) ₃	58
Cyclohexanone	9.8	HSiEt ₃	6.3	(CH ₂) ₅ CHOSiEt ₃	51
1-Hexyne	8.7	HSiPhMe ₂	6.5	<i>cis</i> - and <i>trans</i> -C ₄ H ₉ CH=CHSiPhMe ₂	71
1-Hexyne	8.7	HSiEt ₃	6.3	<i>cis</i> - and <i>trans</i> -C ₄ H ₉ CH=CHSiEt ₃	47

^a Rh₂(OOCCH₃)₄: 0.022 g, 0.010 mmol; 100°C, 8 h. ^b Based on silane; calculated by quantitative GLC.^c 1.0 cm³ CH₃CN added as solvent. ^d 2,3-Dimethyl-1,3-butadiene.

The results (Table 8) show that although II is a good catalyst for the hydrosilylation of terminal olefins, dienes, cyclic ketones, or terminal acetylenes, the yields and overall product distribution vary little from those obtained with [Rh(acac)₃] (I). This similarity is probably due to reductive fragmentation of the dirhodium aggregate by the silane and the relatively forcing conditions (100°C, 8 h) used. As complex II is initially insoluble in the mixture of reactants, an experiment was carried out using the polar solvent acetonitrile for the hydrosilylation of 1-octene by diethoxymethylsilane. This modification offers a slight improvement, the yield of 1-diethoxymethylsilane increasing from 53%, with no solvent, to 63% in acetonitrile.

Experimental

General procedures

All reactions were carried out under pure argon or nitrogen gas, using freshly distilled, dry degassed solvents. ¹H NMR spectra were recorded on a Varian Associates T60 or A60 spectrometer. IR spectra were obtained with a Perkin-Elmer 457 grating spectrophotometer as thin films. Mass spectrum-GLC analyses were carried out on a machine constructed from an Edwards E606 fast scanning mass spectrometer and a Pye-Unicam Model 104 Series 64 gas chromatograph. Preparative GLC separations were carried out using a Pye-Unicam Model 105 preparative GLC or a Varian Aerograph A-700 "Autoprep" gas chromatograph. The GLC analysis of the reaction products was carried out on a Pye Series 104 or on a Varian Aerograph A-700 gas chromatograph, using a 6 ft column of 10% SE30 on 100-120 mesh Chromosorb G. The usual conditions

and standards were employed [6,31,32]. All the unsaturated compounds were commercial products, dried over molecular sieves and distilled prior to use, with the exception of 2,3-dimethyl-1,3-butadiene, which was prepared by the dehydration of pinacol, by the literature method [28]. The pentanedionatorrhodium(III) [29] and tetrakis(μ -acetato)dirrhodium(II) [30] were prepared by standard procedures. The silanes were purchased or prepared according to literature methods [6]. Some typical experiments are described below. Spectroscopic characterisation is as described in the Tables, and GLC analysis was routinely performed on volatile products. Comparisons were invariably made with literature data, in particular from refs. 33 and 34. Identification of the products obtained from hydrosilylation of styrene or allylbenzene rested on GLC and NMR data and was identical to that observed in the $[\text{Rh}(\text{acac})_3]/(\text{AlEt}_3)_2$ system [10].

Hydrosilylation of 1-pentyne with triethylsilane

1-Pentyne (5.4 g, 80 mmol), triethylsilane (3.6 g, 31.5 mmol), and $[\text{Rh}(\text{acac})_3]$ (100 mg, 0.25 mmol) were heated, with stirring, at 60°C for 15 h under an inert atmosphere. Volatiles were then removed under reduced pressure and the residue distilled to give $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CHSiEt}_3$ (5.5 g, 94.8%), b.p. 92°C/15 mmHg. (Found: C, 71.9; H, 13.0. $\text{C}_{11}\text{H}_{24}\text{Si}$ calcd.: C, 71.7; H, 13.0%).

Hydrosilylation of isoprene with triethylsilane

$[\text{Rh}(\text{acac})_3]$ (50 mg, 0.125 mmol), isoprene (3.1 g, 45 mmol), and triethylsilane (1.75 g, 15 mmol) were heated together, with stirring, for 12 h at 60°C. Distillation under reduced pressure gave $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{SiEt}_3$ (1.87 g, 67.8%), b.p. 71°C/5 mmHg. (Found: C, 71.8; H, 13.2. $\text{C}_{11}\text{H}_{24}\text{Si}$ calcd.: C, 71.7; H, 13.0%). GLC showed this to contain ~5% of an isomeric impurity.

Hydrosilylation of 1-octene by triethoxysilane

1-Octene (8.4 g, 75 mmol), triethoxysilane (4.5 g, 27.5 mmol), and $[\text{Rh}(\text{acac})_3]$ (100 mg, 0.25 mmol) were heated at 60°C under an inert atmosphere for 15 h. Vacuum distillation, after removal of volatiles, gave $\text{C}_8\text{H}_{17}\text{Si}(\text{OEt})_3$ (5.5 g, 72.5%), b.p. 120°C/10 mmHg. (Found: C, 59.4; H, 11.7. $\text{C}_{14}\text{H}_{32}\text{O}_3\text{Si}$ calcd.: C, 59.4; H, 11.6%).

Hydrosilylation of allyl bromide by triphenylsilane

Allyl bromide (1.8 g, 15 mmol), triphenylsilane (1.25 g, 5 mmol), and $[\text{Rh}(\text{acac})_3]$ (20 mg, 0.05 mmol) were heated at 60°C, with stirring, for 8 h. Volatiles were removed under reduced pressure and the remaining solid recrystallised from pentane to give Ph_3SiOH (0.86 g, 62.3%), m.p. 152°C (lit. [35], 153–154°C). (Found: C, 78.4; H, 5.9. $\text{C}_{18}\text{H}_{16}\text{OSi}$ calcd.: C, 78.3; H, 5.8%) ($P^+ m/e$ 276).

Hydrosilylation of trans-crotonaldehyde by triethoxysilane

Crotonaldehyde (2.34 g, 33 mmol), triethoxysilane (1.8 g, 11 mmol), and $[\text{Rh}(\text{acac})_3]$ (20 mg, 0.05 mmol) were heated at 60°C for 15 h with continuous stirring. Volatiles were removed under reduced pressure and vacuum distillation gave compounds XVI and XVII (0.96 g, 47%), b.p. 72°C/5 mmHg. (Found: C,

51.3; H, 9.5. $C_{10}H_{22}O_4Si$ calcd.: C, 51.3; H, 9.4%). GLC-MS showed this to be a mixture of two isomers which were separated by preparative GLC. These were identified from their 1H NMR as *cis*- and *trans*- $CH_3CH_2CH=CHOSi(OEt)_3$.

Hydrosilylation of crotonaldehyde by triethylsilane

Crotonaldehyde (5.7 g, 80 mmol), triethylsilane (3.6 g, 31.5 mmol), and $[Rh(acac)_3]$ (100 mg, 0.25 mmol) were treated as described for the hydrosilylation of crotonaldehyde by triethoxysilane to give a mixture of the isomers *cis*- and *trans*- $CH_3CH_2CH=CHOSiEt_3$ (3.63 g, 62%), b.p. $51^\circ C/2$ mmHg. (Found: C, 64.3; H, 12.0. $C_{10}H_{22}OSi$ calcd.: C, 64.5; H, 11.8%).

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