VIBRATIONAL SPECTRA OF THE TRIHALOSILYL-1- OR -2-BUTENES OBTAINED BY HYDROSILYLATION

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The IR absorption spectra (4000—200 cm^{-1}) of liquid 1-(trihalosilyl)-*cis*-2-butenes ($C_4H_7Cl_3Si$; *I*; $C_4H_7F_3Si$, *II*) and 1-(trihalosilyl)-2-methyl-2-butenes ($C_5H_9Cl_3Si$, *III*; $C_5H_9F_3Si$, *IV*) were measured. For *II* and *IV*, the strongest Raman lines of liquids and the IR spectra of gases and frozen solids were also recorded. Interpretation of the spectra was focused on the characteristic out-of-plane =C—H deformation frequencies (1000—600 cm^{-1}), their relative intensities, and interfering bands. Rules for IR analyses of vinylic, *cis*-, and *trans*-isomer mixtures are presented. The mass spectra (70 eV) of *I*—*IV* were also taken.

In connection with studies of homogeneous catalysis by transition metal complexes[1], we dealt with the hydrosilylation of 1,3-butadiene (and isoprene)[2]. Primarily, the terminal adducts of HSi-.Cl$_3$ to butadiene (1 : 1) were obtained from 1,2- and/or 1,4-addition. Depending on the catalyst used, various mixtures of the isomeric trichlorosilyl butenes resulted[3]. Using the characteristic absorption bands of the out-of-plane =C—H deformation vibrations[4], we found the IR spectroscopy to be the most powerful tool for identification of the components and semiquantitative estimation of their abundances.

However, with larger molecules containing *cis*- CH=HC moiety (750—650 cm^{-1}), complications in the IR spectra arose due to the vibrations of the carbon skeleton and methyl groups (C—C stretching, H$_3$C—C rocking) which may manifest themselves by absorptions in the 1000 to 900 cm^{-1} region[5]. These absorptions nearly coincide with the characteristic bands of isomers containing *trans*-HC=CH (near 965 cm^{-1}) or vinyl grouping (about 910 and 990 cm^{-1}). A pure *cis*-compound may then be erroneously presented as a mixture of isomers[2]. In such cases the relative intensities of bands in the 1000—900 cm^{-1} region are more useful guide than the wavenumbers of band maxima.

The aim of this work was to prepare the pure title compounds, to interpret their IR spectra, and to find rules for semiquantitative analysis of alkenylhalosilanes in mixtures.

EXPERIMENTAL

Preparation of trichlorosilylbutenes. 1-Trichlorosilyl-*cis*-2-butene (*I*) and 1-trichlorosilyl--2-methyl-2-butene (*III*) were prepared by the reported procedure[2]. A mixture of 1-trichlorosilyl-

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-trans-2-butene (*V*) and *I* was prepared by reaction of nickel lactate (10 mg), 50 mg of 1,2-bis-(diphenylphosphine)ethane, 6 ml (72 mmol) of liquid 1,3-butadiene, and 6 ml (60 mmol) of $HSiCl_3$. The reaction mixture in a sealed glass ampoule was heated under argon to 120°C for 3 h ($HSiCl_3$ conversion 95%). The mixture containing 80% (*V*) and 20% (*I*) (by GLC) was obtained by distillation. A mixture of 4-trichlorosilyl-1-butene (*VI*) and *I* was prepared by reacting 1,3-butadiene (7 ml, 8·4 mmol) with $HSiCl_3$ (8·4 ml, 8·4 mmol) in the presence of tetrakis(triphenylphosphine)-platinum[6] (40 mg). The reaction mixture was heated under argon in a sealed ampoule to 95°C for 5 h ($HSiCl_3$ conversion 5%). The mixture of 86% (*VI*) and 14% (*I*) (by GLC) was obtained by distillation.

Preparation of trifluorosilyl- and trimethylsilylbutenes. 1-Trifluorosilyl-*cis*-2-butene (*II*), 1-trifluorosilyl-2-methyl-2-butene (*IV*), and a mixture of 1-trifluorosilyl-*trans*-2-butene (*VII*) and *II* were prepared from appropriate chloro derivatives by exchange reaction with SbF_3. The corresponding derivative (6 ml) was added dropwise to 20 g of SbF_3 and the reaction mixture was slowly heated until the product distilled. A short column (5 TP) was used. Boiling points were 52 (*II*), 69·5 (*IV*), and 49·5°C (*VII* + *II*). Trimethylsilylbutenes were obtained by methylation of the chloro derivatives with methylmagnesium bromide.

The IR absorption spectra were recorded on double-beam spectrometers Beckman IR-7 and Zeiss (Jena) UR-20. Samples were studied as liquids between KBr plates or as solutions in CS_2, CCl_4, or Nujol. Concentration of solutes was gradually decreased and the results of intensity measurements are averages of five measurements. The wavenumber scale was calibrated with a 0·01 mm polystyrene film, the reading accuracy being $\pm 2\,cm^{-1}$. Acetylene was used for calibration[7] of the $4100-4000\ cm^{-1}$ region in which the spectra of liquid isoprene derivatives were taken in a 0·6 cm cell. The spectra of either frozen liquids or frozen solutions in Nujol were recorded in VLT-2 unit (RIIC-Beckman, London) with KRS-5 jackett windows in a 0·01 cm AgCl cell.

The Raman spectra of the liquids at room temperature were excited with He—Ne laser in a sealed cell. Due to a relatively high fluorescence of the samples (presumably because of hydrolytic Si—O—Si impurities), only the strongest lines of trifluorosilyl derivatives were recorded in the $1700-200\ cm^{-1}$ region.

The mass spectra at 70 eV were taken on a LKB-spectrometer, model MS/GC — 9000.

I (m.w. = 188): $m/e = 55$ (100), 29 (11), 27 (9·2), 54 (9·0), 39 (8·5), 135 (7·1), 133 (7·1), 188 (5·6), 190 (5·5), 63 (5·5), 53 (5·5), 56 (4·7), 137 (2·8), 116 (2·4), 65 (2·1);
$m^+ = 88·5 (152^+ \to 116^+ + 36)$.

II (m.w. = 140): $m/e = 55$ (100), 140 (44), 29 (37), 41 (36), 27 (31), 39 (27), 85 (10), 53 (7·5), 105 (6·7), 125 (5·1), 121 (5·0), 93 (4·2), 54 (4·2), 26 (4·0);
$m^+ = 88·2 (125^+ \to 105^+ + 20)$.

III (m.w. = 202): $m/e = 69$ (100), 41 (53), 39 (13·5), 27 (9·3), 133 (8·3), 135 (8·2), 55 (8·2), 202 (6·8), 204 (6·7), 53 (6·5), 63 (6·4), 67 (6·3), 70 (6·2), 68 (5·6), 42 (5·1).

IV (m.w. = 154): $m/e = 41$ (100), 55 (90), 29 (71), 69 (61), 154 (56), 39 (47·5), 139 (45), 27 (39), 42 (26), 53 (20), 85 (17), 125 (15), 105 (13), 28 (13), 126 (11).

The ^1H-NMR data for *I* and *III* were reported earlier[2].

RESULTS

The IR spectra of pure liquids *I*, *II* and *III*, *IV* are presented in Figs 1, 2, respectively, tentative assignments of the bands are summarized in Tables I and II. From Fig. 1*a*, it is clear that with *I* there are three medium to weak bands in the $1000-900\ cm^{-1}$

region, the maxima of which nearly coincide with the characteristic absorptions by vinyl group in *VI* and *trans*-HC=CH moiety in *V* (Table III). These bands of *I* may be mis-interpreted as the bands of isomers *V* and *VI*, in other words, as the bands of impurities in *I*. In this situation a useful guide are the relative intensities of the three bands which are, however, strongly influenced by solvent-effect[8,9].

With 1-alkenes the two bands near 910 and 995 cm^{-1} have been assigned to the wagging and twisting vibrations of =CH$_2$ group, respectively, the 910 cm^{-1} band being always more intense[4]. The same holds for terminal trichlorosilyl-1-alkenes[8], the data for which are summarized in Table IV. It follows from the last column that
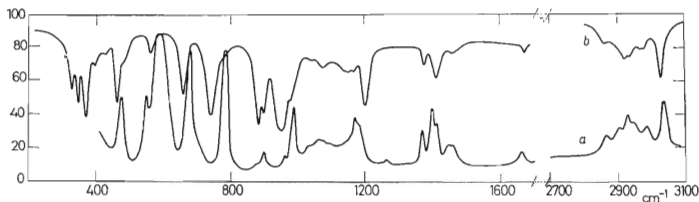

Fig. 1

The IR Spectra of Liquid 1-Trihalosilyl-*cis*-2-butenes

a Trichlorosilyl derivative (*I*), *b* trifluorosilyl derivative (*II*) (700—200 cm^{-1}) in Nujol solution).
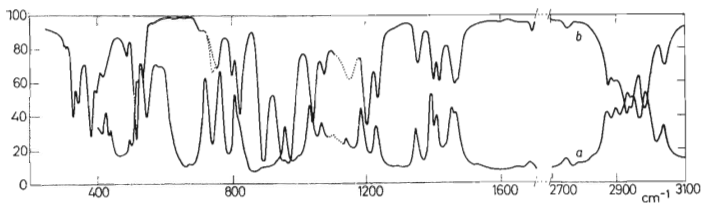

Fig. 2

The IR Spectra of Liquid 1-Trihalosilyl-2-methyl-2-butenes

a Trichlorosilyl derivative (*III*), *b* trifluorosilyl derivative (*IV*) (700—200 cm^{-1} in Nujol solution).

Table I

The Vibrational Assignment (cm^{-1}) for 1-Trichlorosilyl-(*I*) and 1-Trifluorosilyl-*cis*-2-butene (*II*)

I	II		Model compound[b]	Assignment
Solution[a]	Solution[a]	Other bands		
~3 085 sh				} stretching =C—H
3 030	3 027	3 039	A, 3 033 (IR, s)	
2 980	2 975	2 985		} stretching CH$_3$, CH$_2$
2 941	2 938	2 935		
2 923	2 919	~2 915 sh	(IR, g)	
2 900				
2 862	2 858	2 879		
1 653	1 654	1 658 (Ra, l)	A, 1 660 (Ra, s)	stretching C=C
1 450[c] br		1 447 (IR, g)	B, 1 443 (IR, s)	deformation CH$_3$
1 404	1 399	1 404 (IR, g)	A, 1 420 (IR, s)	in-plane bend. =C—H
1 393	1 392 sh		C, 1 390 (IR, s)	scissoring CH$_2$
1 365	1 362	1 369 (IR, g)	B, 1 378 (IR, m)	sym. def. CH$_3$
1 260		1 262 (Ra, l)	A, 1 255 (Ra, m)	in-plane bend. =C—H
1 179	1 187	1 192 (Ra, l)	C, 1 190 (IR, s)	twisting CH$_2$
1 169		1 160 (IR, g)	C, 1 170 (IR, s)	wagging CH$_2$
~1 155 sh	1 155	1 141 (IR, g)		
1 030		1 029 (IR, g)	B, 1 045 (IR, s)	rocking CH$_3$
991	986 sh	~ 990 sh (IR, l)	A, 986 (IR, s)	stretching C—C
961	945 sh		B, 963 (IR, s)	rocking CH$_3$
902	898	900 (Ra, l)	A, 873 (IR, s)	stretching C—C
784	742	744 (Ra, l)	E, 750—710 (Ra, s)	stretching Si—C
~ 775	770 sh	774 sh (IR, g),	D, 788 (IR, w)	rocking CH$_2$
677	659[d]	656 (Ra, l)	A, 673 (IR, s)	o-o-p def. =C—H
542	560[d]	554 (IR, g)	A, 575 (Ra, w)	}
471	477[d] sh	472 (Ra, l)		
	464[d]	458 (IR, g)		} skeletal def.
	426[d]	419 (IR, g)		
	392[d]		A, 396 (Ra, m)	}
	370[d]		F, 360 (IR, s)	
	346[d]			} def. SiF$_3$
	331[d]		F, 325 (IR, m)	
	255[d]			
582 sh	959			stretching SiX$_3$ (E)
575	882			sym. stretch. SiX$_3$
1 070	1 140			impurities

[a] In CS$_2$. The relative intensities are the same as for liquid *I* and *II*, *cf.* Fig. 1. [b] A *cis*-2-butene, ref.[5]; B propen., ref.[5]; C allyltrichlorosilane, ref.[19]; D 1-butene, ref.[5]; E allyltrihalosilanes, ref.[16]; F vinyltrifluorosilane, refs[23,24]. [c] In CCl$_4$. [d] Solution in Nujol.

The Vibrational Assignment (cm^{-1}) for 1-Trichlorosilyl-(*III*) and 1-Trifluorosilyl-2-methyl-2-butene (*IV*)

III	IV		Model	Assignment
Solution^a	solution^a	other bands	compound^b	
4 083 (IR, l)		4 091 (IR, l)	A, broad (IR, m)	?
3 030	3 029	3 041 (IR, g)	B, 3 024 (Ra, m)	stretching =C—H
2 976	2 973	2 985		
2 938	2 932	~2 937 br		
2 921	2 915	~2 910	(IR, g)	stretching CH$_3$, CH$_2$
2 888	~2 890	2 881		
2 863	2 860	~2 860		
2 742	2 740	2 755	A, ~2 750 (IR, w)	2 × 1 380
1 668	1 670	1 676 (Ra, l)	B, 1 680 (Ra, s)	stretching C=C
1 453^c	1 453^c	1 453 (IR, g)	C, 1 450 (Ra, m)	deformation CH$_3$ (gerade)
1 443^c	1 445^c	1 447 (Ra, l)	C, 1 449 (IR, s)	deformation CH$_3$ (ung.)
1 398	1 398	1 400 (Ra, l)	D, 1 390 (IR, m)	scissoring CH$_2$
1 380	1 380	1 389 (IR, g)	C, 1 393 (IR, s)	sym. def. CH$_3$
1 336	1 337	1 342 (Ra, l)	B, 1 338 (Ra, s)	in-plane bend. =C—H
1 221	1 222	1 223 (IR, g)	B, 1 218 (IR, s)	stretching C—C
1 180	1 187	1 194 (IR, g)	D, 1 190 (IR, m)	twisting CH$_2$
1 135	obsc.^{d}	1 141 (IR, g)	D, 1 170 (IR, s)	wagging CH$_2$
1 061	1 063	~1 065 sh (IR, g)	C, 1 057 (IR, m)	rocking CH$_3$
1 026	1 029	1 034 (IR, g)	C, 1 039 (Ra, w)	
954	~ 945 sh	958 (Ra, l)	B, 947 (Ra, w)	stretching C—C
818 sh	828 sh	~ 835 sh (IR, g)	A, (IR, s)	(second isomer)?
807	813	816 (IR, g)	A, (IR, s)	o-o-p def. =C—H
761	793	795 (IR, g)	B, 767 (Ra, s)	stretching C—C
721	750	772 (IR, g)	our II, 770 (IR)	rocking CH$_2$
670 w	693	696 (Ra, l)	E, 750—710 (Ra, s)	stretching Si—C
525	531	527 (Ra, l)	B, 527 (Ra, s)	
511	509	503 (IR, g)		
489	477	476 (IR, g)	B, 443 (Ra, s)	skeletal bend.
442	415 sh	~ 410 sh (IR, g)		
426	395^e sh		B, 387 (Ra, s)	
	377^e		F, 360 (IR, s)	
	344^e			def. SiF$_3$
	328^e		F, 325 (IR, m)	
	306^e sh		B, 292 (Ra, w)	

Table II
(*Continued*)

III	IV		Model compound[b]	Assignment
Solution[a]	solution[a]	other		
581	954	966 (IR, g)		stretching SiX_3 (E)
567 sh	886	891 (IR, g)		sym. stretching SiX_3
1 100	1 140		} impurities	
480	730			

[a] In CS_2. The relative intensities are the same as for liquid III and IV, *cf*. Fig. 2. [b] A trialkylethylene, ref.[21]; B trimethylethylene, ref.[5]; C *trans*-2-butene, ref.[5]; D allyltrichlorosilane, ref.[19]; E allyltrihalosilanes, ref.[16]; F vinyltrifluorosilane, refs[23,24] [c] In CCl_4. [d] Obscured by impurities. [e] Solution in Nujol.

Table III

The Wavenumbers of IR Bands of Liquid 4-(Trichlorosilyl)-butenes in the $1\,000-900$ cm^{-1} Region

4-Trichlorosilyl derivative	Band		
	1	2	3
-*cis*-2-butene (*I*)	902 (stretching C—C)	970 (rocking CH_3)	992 (stretching C—C)
-1-butene (*VI*)	917[a] (wagging =CH_2)	no absorption	994[a] (twisting HC=CH_2)
-*trans*-2-butene (*V* + *I*)	no absorption?	964 (twisting *trans*-HC=CH)	no absorption?
-3-methyl-2-butene (*III*)	no absorption	954 (stretching C—C)	no absorption

[a] Ref.[10]

the peaks 910 and 990 cm^{-1} for *I* have reverse intensities than for the compounds with terminal C=C bond, *i.e.* another vibrations should be responsible for these two absorptions (*cf*. Table III). Band 2 of *I* (near 970 cm^{-1}) is the weakest one of the three mis-interpretable bands 900, 970, 990 cm^{-1}. The intensity ratios are: 900 cm^{-1}/970 cm^{-1} = 1·1 and 990 cm^{-1}/970 cm^{-1} = 3·6.

For the *trans*-isomers *V* and *VII* (in mixture with *I* and *II*, respectively), the strongest bands are listed here, along with the assignments.

V (IR, CS$_2$ solution): 585 (vs, stretching SiCl$_3$), 714 (m, stretching Si—C), 763 (s, rocking CH$_2$), 961 (s, twisting HC=CH), 3030 cm^{-1} (s, stretching =C—H).

VII (IR, CS$_2$ solution): 420 (s, skeletal deformation), 883 and 957 (vs, stretching SiF$_3$), 3025 cm^{-1} (s, stretching =C—H).

VII (Ra, liquid): 527 (vs, skeletal deformation), 696 (vs, stretching Si—C), 1342 (s, in-plane bending =C—H), 1400 (s, scissoring CH$_2$), 1676 cm^{-1} (vs, stretching C=C).

The number of the strongest bands for vinylic isomer *VI* is in agreement with the data of Benkeser[10].

VI (IR, liquid): 461 (s, skeletal bending), 585 (vs, stretching SiCl$_3$), 703 (s, stretching Si—C), 774 (s, rocking CH$_2$), 916 (s, wagging =CH$_2$), 991 (s, twisting HC==CH$_2$), 1642 (m, stretching C=C), 3026 and 3085 cm^{-1} (m, stretching =C—H).

Trichlorosilylated compounds are readily hydrolyzed by moisture and we therefore tried to convert the mixtures to another trisubstituted silyl derivatives. Several possibilities were tested: SiF$_3$, Si(CH$_3$)$_3$, and Si(OC$_2$H$_5$)$_3$. The SiF$_3$-procedure is the simplest one, however, the 1000—900 cm^{-1} region is obscured by the SiF$_3$ stretching E-mode (masking of the *trans-* or vinylic isomer). The Si(CH$_3$)$_3$-derivatives have complicated IR spectra in the 800—600 cm^{-1} region due to the SiC$_4$ stretching vibrations (masking of the *cis*-isomer), trialkoxy derivatives have a huge absorption in the 1100—1000 cm^{-1} region (the Si—O—C out-of-phase stretching), wings of which complicate the intensity measurements between 1000—900 cm^{-1}.

Analyses of the original mixtures of trichlorosilylbutenes proved to be the least time-consuming procedure and the best one follows.

IR Procedure for Analyses of Trichlorosilylbutene Mixtures

The pair of matched 0·01 cm KBr cells is filled with CS$_2$ and the base-line is recorded in the 1100—600 cm^{-1} region. About 8% (wt.) solution of the analyzed mixture in CS$_2$ is placed in the sample cell. The spectrum is recorded five times at gradually decreased concentrations, dilution with CS$_2$ being made directly in the cell. The absorbances of the mixture at maxima around 910, 970, 990 cm^{-1} are evaluated by base-line technique, the intensity ratios 910/990, 910/970, and 990/970 are calculated as the averages of the five measurements. These results are interpreted with the aid of Table V and combined with GLC data.

DISCUSSION

Recently, Zerbi[11] proved only one stable rotamer in *trans*-3-hexene and 1,4-dibromo-*trans*-2-butene, the end groups being in the *skew-trans-skew'* configuration. With our 1-trihalosilylbutenes, it is also possible to assume rotational isomerism around the —(H$_2$)C—C= bond. The IR spectra of solids *II* and *IV* in Nujol matrix

or *in substantiam* gave no remarkable difference in comparison with the liquid samples. Comparing the gases with liquids, the only changes were recognized in the relative intensities of bands between $800-700$ cm^{-1} but not in their number. These facts and the simple overall pattern of our spectra do not exclude the analogous assumption of only one stable rotamer, however, its conformation remains without evidence.

The assignments of spectral bands were made easier by the *isolation* effect of the silicon atom. Parts of the molecules then could be compared with well established models representing these parts without SiX$_3$ grouping. The main difficulty was

TABLE IV

Ratios of Intensities of IR Bands 910 cm^{-1}/995 cm^{-1} in Solutions of Cl$_3$Si(CH$_2$)$_n$HC=CH$_2$ ($n = 0-2$) and I

S^a	$n = 0^b$	$n = 1^b$	$n = 2^c$	I
CCl$_4$	2·89	2·83	1·54	0·25
CS$_2$	2·60	2·54	1·58	0·30

^{a} Solvent; ^{b} ref.[8]; ^{c} our sample (mixture $VI + I$, 6 : 1), *i.e.* inaccurate values.

TABLE V

IR Spectral Evidences for Presence of Isomeric Trichlorosilylbutenes in a Mixture (CS$_2$ Solution)

Isomers present	Intensity criterion: Bands 910, 970, 990 cm^{-1}	Additional evidence for *cis, trans,* vinylic isomers, cm^{-1}
cis + Vinylic	$0·3 < (910/990) < 1·5$ (*cis + vi*)	strong 680 (*cis*) doublet 905, 915 (*cis + vi*) medium to weak 3 085 (*vi*) strong to medium 703 (*vi*)
cis + *trans*	$(910/970) < 1·1$ (*cis + trans*) $(990/970) < 3·6$ (*cis + trans*) $(910/990) = 0·3$ (*cis*)	strong 680 (*cis*) strong to medium 714 (*trans*)
trans + Vinylic	$(910/990) = 1·5$ (*vi*)	strong, broad 710 (*trans + vi*) medium to weak 3 085 (*vi*)

connected with the assignment of deformation modes for the inserted CH_2 group, especially the rocking mode. Despite the profusion of papers dealing with the vibrational spectra of the simplest model, allyltrichlorosilane[12-19], only the three deformation modes were assigned (scissoring ~ 1400 cm^{-1}, twisting ~ 1190 cm^{-1}, wagging ~ 1170 cm^{-1})[14,19]. The rocking mode should be found in the $800-700$ cm^{-1} region[4,5].

With the series of $(CH_2=CH-CH_2)_nSiCl_{4-n}$, (n = 0-4), a complex IR band has been found between $800-750$ cm^{-1}, indicating an overlap of the Si—C stretching and probably the CH_2 rocking mode[12]. With the series $CH_2=CH-CH_2 - SiX_3$ (X = F, Cl, Br) (ref.[16]), the two IR bands occur between $800-700$ cm^{-1}, the lower one being clearly due to the Si—C stretching (Raman line 726 cm^{-1}, intensity 80% for X = F; 749 cm^{-1}, 43%, X = Br). The second band $(800-750$ cm$^{-1})$ does not change its position in the IR spectra of $CH_2=CH-CH_2 - GeX_3$ (X = Cl, Br) (ref.[15]), proving our assignment of it to the CH_2 rocking mode. Summarizing, the CH_2 group inserted between a C=C bond and the silicon atom behaves as the CH_2 groups in short alkyl groups (ethyl, n-propyl) attached to tertiary or quarternary carbon atoms [19,20], i.e. the IR absorption band occurs between $800-750$ cm^{-1}.

The 1,4-addition of $HSiCl_3$ to isoprene can offer two products in which two methyl groups are in cis or trans configuration. The spectral behaviour of such trisubstituted ethylenes in the $4100-4000$ cm^{-1} region has been described by Clark[21]: the cis-di-methyl moiety $H_3C-\overset{|}{C}=CH-CH_3$ has a strong sharp band, whilst the other is characterized by a weaker broad band. From the shapes of the bands we propose for III and IV the structure with the trans configuration of the two methyl groups. This agrees with the reaction mechanism for hydrosilylation of 1,3-butadiene (formation of pure I) using the same catalyst, bis-(benzonitrile) palladium dichloride[2].

Moreover, such mechanism of 1,4-addition requires a conjugated diene to act as a bidentate ligand. According to Mason[22], this requirement is fulfilled in cases when the diene is electronically excited (through a charge-transfer and back-donation bonding with metal). Such an electronically perturbed molecule changes its geometry in the desired manner.

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