

LIGAND EFFECTS IN THE NICKEL CATALYSED ADDITION OF TRICHLOROSILANE TO 1,3-BUTADIENE*

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Hydrosilylation of 1,3-butadiene with trichlorosilane catalysed by nickel(II) complexes of the type $[\text{NiX}_2\text{L}_2]$ ($\text{X} = \text{F}, \text{Cl}, \text{I}, \text{NO}_3, \text{CH}_3\text{C}(\text{=O})=\text{CHC}(\text{=O})\text{CH}_3, \text{CH}_3\text{CH}(\text{OH})\text{COO}$; $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3, \text{P}(\text{n-C}_4\text{H}_9)_3, \text{P}(\text{C}_6\text{H}_{11})_3, \text{P}(\text{OC}_6\text{H}_5)_3, \text{and As}(\text{C}_6\text{H}_5)_3$; $\text{L}_2 = (\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$) was studied. The reaction occurred at elevated temperatures, giving 1-trichlorosilyl-*cis*-2-butene and 1-trichlorosilyl-*trans*-2-butene as main products. The 1,2-addition product, 4-trichlorosilyl-1-butene, and 1,4-bis(trichlorosilyl)-2-butene were also formed in some cases. It was found that selectivity of the reaction is not influenced by anionic group X. The effect of ligand L on the structure of hydrosilylation products is discussed, particularly in regard to the 1,2-adduct. On the basis of these results and of their comparison with the addition catalysed by several nickel(0) complexes $[\text{Ni}(\text{1,5-C}_8\text{H}_{12})_2]$, $[\text{Ni}\{\text{P}(\text{C}_6\text{H}_5)_3\}_4]$, and $[\text{Ni}\{\text{P}(\text{OC}_6\text{H}_5)_3\}_4]$ mechanism of the reaction is proposed.

In our laboratory several addition reactions of organosilicon compounds to 1,3-butadiene catalysed by palladium compounds were studied¹⁻⁴. The well-known ability of nickel to coordinate and activate molecule of 1,3-butadiene⁵ led us to investigate hydrosilylation activity of these less expensive and readily accessible compounds in more detail.

Although addition reactions of organosilicon hydrides to unsaturated hydrocarbons can be catalysed by a variety of noble metal compounds (for review see⁶), nickel complexes have attracted relatively little attention. The earlier reported catalysts such as nickel chloride-pyridine complex^{7,8} or a nickel (powder)-pyridine system⁹ were active only at elevated temperatures (160–180°C) and did not find broader application. Several recent studies have, however, indicated that nickel compounds might be useful hydrosilylation catalysts, particularly for additions to conjugated systems. The addition of trichlorosilane to one of the most easily hydrosilylated substrates, styrene, was catalysed at temperatures around 150°C with several bis(tert-phosphine)nickel dihalides, square planar $[\text{NiCl}_2\{\text{P}(\text{n-C}_4\text{H}_9)_3\}_2]$ being more active than tetragonal $[\text{NiBr}_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$. Additional increase in catalytic activity was achieved by addition of cuprous chloride¹⁰. This reaction can be effected selectively and under very mild conditions with di- μ -carbonyl-di- π -cyclopentadienylnickel¹¹ or nickel tetracarbonyl¹² as catalysts. Nickel phosphine complexes were also effective in hydrosilylations of several other alkenes¹³⁻¹⁶ by alkylchlorosilanes, reactions

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being accompanied in some cases by formation of unusual nonterminal adducts and/or products of disproportionation reactions of silicon hydrides.

Of conjugated dienes, 1,3-butadiene was reacted with trimethylsilane in the presence of several Ni(0) complexes^{17,18}. Apart from the hydrosilylation products, 1-trimethylsilyl-2-butene of not specified isomerism and 1-trimethylsilyl-2,6-octadiene, also cyclodimerisation product, 1,5-cyclo-octadiene, was formed, usually in substantial amounts. Recently, Ziegler catalysts (*e.g.* nickel(II) acetylacetonate and triethylaluminium) have been reported to effect additions of several organo-silicon hydrides to 2-methyl-1,3-butadiene and 1,3-pentadiene. The main product formed was 1,4-adduct, which was accompanied by small amounts of not identified isomers.

In the light of these results it was of interest to investigate the mechanism of and ligand effects in the addition of trichlorosilane to 1,3-butadiene. We have been interested also in the possibility of preparing technically more important, however, less probable 1,2-addition product, 4-trichlorosilyl-1-butene. In the present work we report on the activity of nickel(II) complexes of the type $[\text{NiX}_2\text{L}_2]$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{NO}_3$, acetylacetonate, butyrate; $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3, \text{P}(\text{n-C}_4\text{H}_9)_3, \text{P}(\text{cyclo-C}_6\text{H}_{11})_3$, and $\text{P}(\text{OC}_6\text{H}_5)_3$; $\text{L}_2 = (\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$). These complexes were prepared *in situ* and their catalytic behaviour was compared with that of several nickel(0) complexes.

EXPERIMENTAL

Chemicals

Nickel(II) salts were commercial samples and were purified by crystallisation, except the fluoride, bromide, and iodide which were obtained by reactions of corresponding acids with nickel carbonate. Nickel(0) complexes, tetrakis(triphenylphosphine)nickel¹⁹, tetrakis(triphenyl phosphite)-nickel²⁰, and bis(cyclooctadiene)nickel²¹ were prepared by literature procedures. 1,3-Butadiene (Kaučuk Works, Kralupy n/Vlt.) was condensed, dried over Nalsit 4A and used as a liquid. Trichlorosilane (Synthesia, Kolin) was rectified prior to using and its purity was checked by gas-liquid chromatography. Tricyclohexylphosphine was prepared by reported procedure²². The other tertiary phosphines, phosphites, and triphenylarsine were commercial samples (Fluka A. G., Buchs) and were used without further purification.

Hydrosilylation Products

1-Trichlorosilyl-trans-2-butene (I), 1-trichlorosilyl-cis-2-butene (II), and 4-trichlorosilyl-1-butene (III), *i.e.* the main products of the addition of trichlorosilane to 1,3-butadiene, were identified by IR spectrometric method described earlier²³ and their amounts in reaction mixtures were determined by gas-liquid chromatography.

1,4-Bis(trichlorosilyl)butane, trace amounts of which were detected in several reaction mixtures, was prepared in the following way. A glass tube was successively charged under argon with 20 mg (0.038 mmol) of hexachloroplatinic acid dissolved in 1 ml of tetrahydrofuran, 4 ml (27 mmol) of 1-trichlorosilyl-cis-2-butene, and 3 ml (40 mmol) of trichlorosilane, sealed and heated at 120°C for 3 h. Distillation of the reaction mixture afforded the silylsubstituted butane in 64% yield. For $\text{C}_4\text{H}_8\text{Cl}_6\text{Si}_2$ (325.0) calculated: 14.78% C, 2.48% H, 65.45% Cl; found: 14.59% C, 2.62% H, 65.74% Cl. IR spectrum: $\nu(\text{SiCl}_3)$ 575 and 595 cm^{-1} , bands for $\nu(\text{CH}=\text{C})$ (above 3000 cm^{-1}),

$\nu(\text{C}=\text{C})$ (1550–1700 cm^{-1} region), and $\delta_s(\text{CH}_3)$ absent. $^1\text{H-NMR}$ spectrum: δ 1.0–1.8, multiplet (CH_2).

1,4-Bis(trichlorosilyl)-2-butene (IV) was isolated as side product of the following reaction. A cooled 250 ml stainless steel autoclave was charged under argon with 0.3 g (1.14 mmol) of nickel(II) acetylacetonate, 1.2 g (6 mmol) of tributylphosphine, 100 ml (1.2 mol) of 1,3-butadiene, and 70 ml (0.7 mol) of trichlorosilane, sealed and heated at 125–130°C for 4 h. Distillation of the reaction mixture (which according to gas-liquid chromatography contained 8.5% of 1,4-bis(trichlorosilyl)-2-butene) gave IV in 4.5% yield. For $\text{C}_4\text{H}_6\text{Cl}_6\text{Si}_2$ (323.0) calculated: 14.87% C, 1.87% H, 65.86% Cl; found: 14.66% C, 2.01% H, 66.17% Cl. IR spectrum: $\nu(\text{SiCl}_3)$ 575 and 595 cm^{-1} , $\nu(\text{=CH})$ 3030 cm^{-1} , $\nu(\text{C}=\text{C})$ 1650 cm^{-1} (weak; the band is characteristic of the unconjugated double bond whose carbons are not substituted by silyl groups). $^1\text{H-NMR}$ spectrum: a doublet at δ 2.2 (CH_2 protons), a multiplet around δ 5.3 (=CH protons).

1,4-Bis(trimethylsilyl)-2-butene was obtained in 63% yield by methylation of IV with methylmagnesium bromide. IR spectrum: $\nu(\text{Si-CH}_3)$ 1245 cm^{-1} , a doublet at 840 and 855 cm^{-1} , $\nu(\text{=CH})$ 3010 cm^{-1} ; the band for $\nu(\text{C}=\text{C})$ absent (the molecule has the centre of symmetry and the compound is presumably *trans*-isomer). $^1\text{H-NMR}$ spectrum: a doublet at δ 1.5 (CH_2 protons), a multiplet at δ 5.3 (=CH protons). Mass spectrum showed molecular peak at m/e 200.

1,4-Bis(triethylsilyl)-2-butene was prepared in 67% yield by reaction of IV with ethylmagnesium bromide. IR spectrum: $\nu(\text{=CH})$ 3010 cm^{-1} ; the band for $\nu(\text{C}=\text{C})$ absent (presumably *trans*-isomer). Mass spectrum showed molecular peak at m/e 284.

Procedures

Hydrosilylation was carried out in sealed glass tubes, all manipulations with reactants and catalysts were performed under argon atmosphere. A sealed undercooled glass tube was attached to a vibrator and placed in a thermostated bath. After completion of the reaction, the tube was maintained at -78°C till its content was analysed.

Isomerisation of hydrosilylation products was examined under conditions used in hydrosilylations. In experiments carried out in the presence of both 1,3-butadiene and trichlorosilane, the amounts of the products of separate hydrosilylation experiment (carried out with the same amount of 1,3-butadiene, trichlorosilane and catalyst) were subtracted from the amounts determined for the isomerisation experiment.

Dehydrogenation. A mixture of 5 mg (0.02 mmol) of nickel dichloride, 28 mg (0.1 mmol) of tricyclohexylphosphine, and 1.5 ml (4.6 mmol) of 1,4-bis(trichlorosilyl)butane was heated in a sealed tube under argon at 120°C for 3 h. Gas chromatographic analysis of the reaction mixture showed that 1,4-bis(trichlorosilyl)butane remained intact.

Gas chromatographic analysis was carried out with a chromatograph equipped with a thermal-conductivity detector, using a 4 m \times 0.4 cm column filled with 18% Trifluoropropyl Methyl Silicone FS 1265 (Merck) on Chromaton N (0.2–0.25 mesh) and a nitrogen flow rate of 15 ml/min; trichlorosilylbutenes were analysed at 90°C, IV and 1,4-bis(trichlorosilyl)butane at 220°C. IR spectra were recorded with a double-beam Zeiss, Model UR 20, spectrometer (Jena, GDR), NMR spectra with Tesla, Model BS-447, spectrometer (60 MHz, Tesla, Brno), and mass spectra with MS-GC 9000 spectrometer (LKB, Sweden).

RESULTS AND DISCUSSION

Providing that the trichlorosilyl group is attached to the terminal carbon atom, and we did not find in the present work any example which contradicts this assumption^{1,3}, butadiene could react with trichlorosilane to give three 1:1 adducts (Equations (A) and (B)).

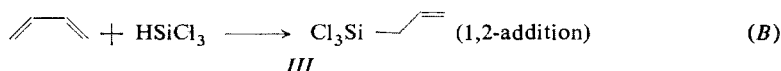
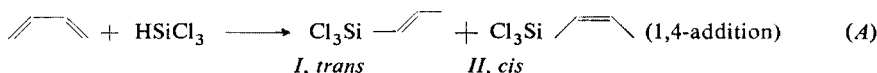


TABLE I

Yields (%) of Silylsubstituted Butenes I–IV in Hydrosilylation of 1,3-Butadiene (32 mmol) with Trichlorosilane (26 mmol) Catalysed by Nickel(II) Salt (0.04 mmol)–Tertiary Phosphine (0.2 mmol) Systems (120°C, 3 h)

Ni(II) compd. ^a	I	II	III	I	II	III	IV
diphos ^b				P(n-Bu) ₃			
NiF ₂	56	13	0	23	43	23	8
NiCl ₂	79	19	0	27	28	18	7
NiBr ₂ ^c	76	17	1	24	28	18	2
NiI ₂	16	4	0	28	31	17	8
Ni(NO ₃) ₂	0	0	0	30	43	13	11
Ni(C ₃ H ₅ O ₃) ₂	74	20	1	22	50	26	0
Ni(acac) ₂ ^d	75	23	0	26	31	18	19
PPh ₃ ^e				P(C ₆ H ₁₁) ₃			
NiF ₂	10	41	8	4	50	32	10
NiCl ₂	10	51	12	4	48	29	12
NiBr ₂ ^c	10	47	8	3	52	30	11
NiI ₂	7	29	5	2	52	24	5
Ni(NO ₃) ₂	11	56	13	16	43	20	14
Ni(C ₃ H ₅ O ₃) ₂	15	64	19	3	55	31	9
Ni(acac) ₂ ^d	3	61	25	3	49	21	25

^a The yields were determined by gas–liquid chromatography and calculated with respect to 26 mmol of 1,3-butadiene. The NiSO₄–L systems were inactive. The tertiary phosphines alone did not catalyse the reaction. ^b 1,2-Bis(diphenylphosphino)ethane (0.1 mmol), IV was not formed. ^c P(OPh)₃ (0.2 mmol): I 12%, II 23%, and III 6%. ^d P(OPh)₃ (0.2 mmol): I 14%, II 46%, III 8%, and IV 13%. ^e IV formed in small amounts (1–2%); Ni(II)–AsPh₃ systems were all inactive.

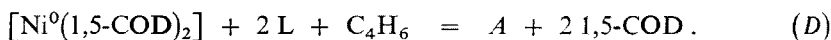
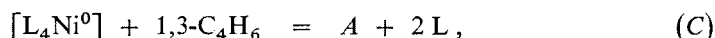
Difficult separation of the above mentioned isomers led us to suggest²³ the IR method for their analysis in mixtures. This method combined with gas chromatographic analysis rendered it possible to study reaction course in dependence on catalyst and conditions in more detail. Table I presents the results obtained with nickel complexes²⁴ of the type $[\text{NiX}_2\text{L}_2]$. These were prepared *in situ*, by the action of L (used in fivefold molar excess) on nickel salt NiX_2 . They were effective catalysts at temperatures comparable to those used for related compounds by Kiso and coworkers¹⁴ and at about 30°C lower than those recorded in a study by Benett¹⁰. Decrease of temperature to 90°C led to their inactivation. Reaction mixtures contained usually three 1 : 1 adducts mentioned above (I–III). With catalytic systems containing more basic phosphines, such as tributylphosphine or tricyclohexylphosphine, also a higher silylsubstituted product was formed which was identified as 1,4-bis(trichlorosilyl)-2-butene (IV), presumably the *trans*-isomer. Its formation was not expected, since the only disilylated product found thus far to arise from the reaction of butadiene with trichlorosilane catalysed by platinum metal compounds was 1,4-bis(trichlorosilyl)butane²⁵.

The results presented in Table I show that for a given phosphine L selectivity of the reaction is not strongly influenced by ligand X (compare *e.g.* $[(\text{C}_6\text{H}_5)_2\text{PCH}_2]_2$ and $\text{P}(\text{C}_6\text{H}_{11})_3$). With several exceptions (the inactivity of the $\text{Ni}(\text{NO}_3)_2 + [(\text{C}_6\text{H}_5)_2\text{PCH}_2]_2$ system and the lower activity of $\text{NiI}_2 + [(\text{C}_6\text{H}_5)_2\text{PCH}_2]_2$ and $\text{NiI}_2 + \text{P}(\text{C}_6\text{H}_5)_3$ systems), also the effectiveness of the catalyst system is comparable (in most cases 70–95% conversion of butadiene was achieved). This fact seems to be surprising, particularly in connection with the results reported by Bennett and Orenski¹⁰. Also Itakani and Bailar in a study on hydrogenation of methyl linoleate showed²⁶ that catalytic effectiveness of the complexes $[\text{Ni}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2\text{X}_2]$ parallels decreasing electronegativity of halide ion ($\text{Cl}^- > \text{Br}^- > \text{I}^-$). The amounts of monoene due to catalysis by iodo-, bromo- and chloronickel compound respectively were found to be 83.5%, 53.0%, and 1.6%. The dependence of reaction rate on halide ligand has also been established²⁷ in the carboxylation of propene catalysed by the above complexes ($[\text{Ni}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2\text{I}_2] > [\text{Ni}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2\text{Br}_2] > [\text{Ni}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2\text{Cl}_2]$). Nonexistence of a relation between results and electronegativity scale for anionic ligands²⁸ indicates that in the initial phase of the reaction the bond of X to nickel atom is cleaved; the anionic ligand then does not affect the electronic structure and stereochemistry of reaction intermediates.

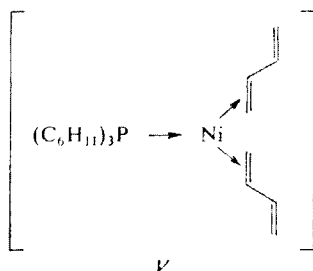
On the other hand, phosphine ligands L exert specific effect on selectivity of the reaction, regardless of the nickel salt used (Table I). With several phosphines, of which two are presented in Table II as an example, we further found that reaction course is not dependent on the L/Ni molar ratio and that conversion of 1,3-butadiene to products does not change even by using tenfold molar excess of L with respect to the metal. These two facts indicate that during formation of catalytically active species at least one ligand L remains coordinated to the central atom and

does not dissociate in the rate and product determining step(s) of the reaction.

The nearly complete absence of effects of anionic ligands X on reaction course has some mechanistic implications. With respect to the well-known reluctance with which nickel forms nickel(IV) complexes, it seems very likely that in the initial stage of the reaction the starting nickel(II) complex is temporarily reduced by the action of silicon hydride to a coordinatively unsaturated low valent nickel species *A* containing π -coordinated 1,3-butadiene molecule (see step 1 in Scheme 1). This intermediate can be expected to arise also from appropriate nickel zerovalent complexes, either by dissociation (Eq. (C)) or by coordination of ligand L (e.g. Eq. (D) where 1,5-COD stands for 1,5-cyclooctadiene).



Several complexes analogous to *A* have already been reported. Thus, for example, Jolly and coworkers²⁹ prepared tricyclohexylphosphine-bis(butadiene)nickel (*V*), also by reaction of 1,3-butadiene with bis(tricyclohexylphosphine)nickel which proceeds³⁰ *via* formation of $[Ni(C_4H_6)\{P(C_6H_{11})_3\}]$. Results presented in Table III further indicate that hydrosilylation catalysed by nickel(II) and nickel(0) complexes proceeds through the same intermediate (presumably of structure *A*, see steps 1 and 2 in Scheme 1). Thus, selectivity of the reaction catalysed by $[Ni(1,5-COD)_2] + L$ system is close to that achieved with $[L_2NiX_2]$. This similarity is most distinct with the chelating ligand, $(C_6H_5)_3PCH_2CH_2P(C_6H_5)_3$. The other nickel(0) complexes presented in the Table were included to show how equilibria in the $L - P(C_6H_5)_3$ or $L - P(OC_6H_5)_3$ exchange influence selectivity of the reaction.



Further reaction step, which is hypothetical in the case of nickel complexes, but generally accepted for homogeneously catalysed hydrosilylation^{9,14,31} (for detailed discussion see review⁶), involves oxidative addition of a silicon hydride (step 3 in

Scheme 1), which results in formation of nickel(II) species *B*. Unfortunately, although we prefer formation of π -bonded butadiene–nickel complex in the step preceding oxidative addition of silicon hydride on the basis of above mentioned facts, our results do not allow us to exclude the possibility that intermediate *B* is formed by the reverse sequence of discussed processes. Notwithstanding, with regard to similarities in the palladium and nickel catalysed hydrosilylations of conjugated dienes pointed out by Takahashi and coworkers¹⁷ and in harmony with the results obtained by us in hydrosilylation of 1,3-butadiene catalysed by palladium(II) complexes^{3,4}, we believe that also in this case decisive steps for formation of *cis*- and *trans*-2-butenes *I* and *II* are formation of corresponding π -allyl complexes *C* and *D* (Scheme 1) and their subsequent conversion to products *via* σ -allyl intermediates. As will be shown later this assumption is supported by negligible role of consecutive isomerisation reactions under hydrosilylation conditions. The effect of ligand *L* on relative amounts of *I* and *II* is illustrative. While in the presence of monodentate tertiary phosphines the reaction led predominantly to the *cis*-isomer, the opposite case was observed with the bidentate, sterically more demanding 1,2-bis(triphenylphosphino)ethane. From Table I it follows further that for monodentate phosphines the relative amount of *III* increases in the order $P(C_6H_5)_3 < P(n-C_4H_9)_3 < P(C_6H_{11})_3$, following apparently increasing donor ability of these phosphines. Since increasing donor ability of the phosphine should stabilise the Ni–H bond, the rearrangement of *B* to *C* and *D* could be retarded, in favour of the 1,2-addition to 1-trichlorosilyl-1-butene (*III*). Whether this addition proceeds *via* a concerted mechanism or through an intermediate con-

TABLE II

Hydrosilylation of 1,3-Butadiene (32 mmol) with Trichlorosilane (26 mmol) Catalysed with Nickel(II) Acetylacetonate (0.04 mmol)–*L* Systems (120°C, 3 h)

L, mmol	Yield, % ^a			L, mmol	Yield, % ^a		
	<i>I</i>	<i>II</i>	<i>III</i>		<i>I</i>	<i>II</i>	<i>III</i>
	PPh ₃ ^b			diphos ^c			
0.4	4	66	24	0.2	69	15	0
0.2	3	61	25	0.1	75	23	0
0.1	3	65	26	0.05	72	26	0
0.05	1	29	12	0.03	70	26	0
0.03	0	6	traces				

^a With respect to the silicon hydride; determined by gas–liquid chromatography. ^b Small amounts of *IV* were also formed (1–2%, by gas–liquid chromatography). ^c 1,2-Bis(diphenylphosphino)ethane.

taining σ -bonded 3-butenyl ligand (this possibility has been mentioned *e.g.* for hydrogenation of 1,3-butadiene catalysed by potassium pentacyanocobaltate³²) is still unclear.

TABLE III

Yields (%) of Silylsubstituted Butenes I–IV in Hydrosilylation of 1,3-Butadiene (32 mmol) with Trichlorosilane (26 mmol) Catalysed by Nickel(0) Complexes (0.04 mmol) in the Presence of L (0.2 mmol) (120°C, 3 h)

L	Ni(COD) ₂ ^a				Ni(PPh ₃) ₄				Ni[P(OPh) ₃] ₄		
	I	II	III	IV	I	II	III	IV	I	II	III ^b
None	3	83	8	6	19	34	8	8	8	67	0
PPh ₃	13	45	11	5	—	—	—	—	17	57	0
P(n-Bu) ₃	29	34	12	10	23	32	24	13	0	0	0
P(C ₆ H ₁₁) ₃	10	38	27	20	10	43	20	26	0	0	0
P(OPh) ₃	10	69	4	1	16	56	10	9	10	61	2
diphos ^c	75	24	1	0	76	24	0	0	73	27	0
AsPh ₃	8	68	11	3	29	41	10	4	10	61	0

^a COD 1,5-cyclooctadiene; ^b IV was not formed; ^c diphos 1,2-bis(triphenylphosphino)ethane (0.1 mmol).

TABLE IV

Hydrosilylation of 1,3-Butadiene (32 mmol) with Trichlorosilane (26 mmol) Catalysed by a NiCl₂ (0.04 mmol)–P(C₆H₁₁)₃ (0.2 mmol) System at 120°C

Product	Relative amount of products (mol. %) at reaction time, h ^a		
	1	3 ^b	6
I	5	4	4
II	52	53	50
III	29	30	33
IV	14	13	13

^a Conversion determined by gas-liquid chromatography and calculated with respect to 26 mmol of 1,3-butadiene was successively 54, 92, and 98%. ^b At 150°C (98% conversion) relative amounts of the compounds were as follows: I 21%, II 35%, III 21%, and IV 23%.

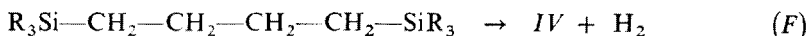
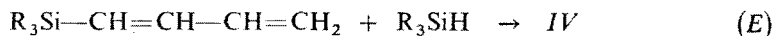
TABLE V

Isomerisation of *II* (32 mmol) to *I* in the Presence of a Nickel(II) Salt (0.04 mmol)–Phosphine (0.2 mmol) System and in the Presence and Absence of Reactants (Trichlorosilane, 26 mmol; Butadiene, 32 mmol) at 120°C (3 h)

L	Yield (%) of <i>I</i> in the presence of reactant ^a		
	none	HSiCl ₃	HSiCl ₃ + 1,3-C ₄ H ₆
		NiCl ₂	
PPh ₃	9	12	2
P(n-Bu) ₃	4	11	9
P(C ₆ H ₁₁) ₃	0	1	8
diphos ^b	3	3	3
		Ni(acac) ₂ ^c	
PPh ₃	8	14	5
P(n-Bu) ₃	3	28	8
P(C ₆ H ₁₁) ₃	0	5	1
diphos ^b	3	7	5

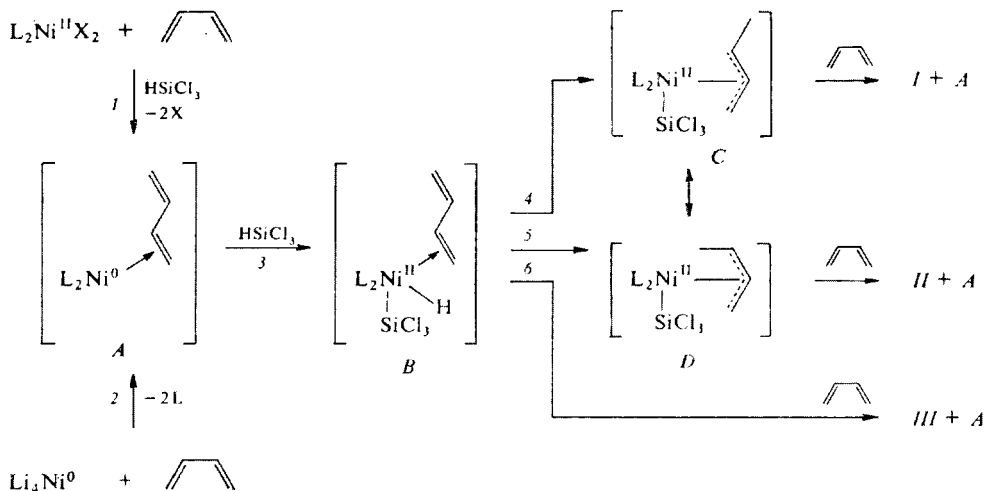
^a The nickel salts or the phosphines alone were inactive. The reaction did not take place also when 1,3-butadiene (32 mmol) was added to the reaction mixture. In none of the experiments *I* and *IV* formation was detected. ^b 1,2-Bis(diphenylphosphino)ethane (0.1 mmol). ^c acac Acetylacetyl.

The higher silylsubstituted substance formed in some cases was 1,4-bis(trichlorosilyl-2)-butene (*IV*), instead of the expected 1,4-bis(trichlorosilyl)butane. A similar situation has recently been observed by us in the palladium catalysed hydrosilylation of 1,3-butadiene^{3,4}. In that case it was confirmed that *IV* was produced by subsequent hydrosilylation of 1-silylsubstituted 1,3-butadiene (Eq. (*E*)). Another route to *IV* could in general be also dehydrogenation of primarily formed 1,4-bis(trichlorosilyl)butane (Eq. (*F*)). As we found, none of these processes occurred in the nickel catalysed hydrosilylation



(see Experimental). From Tables I–III it becomes clear that in those cases in which formation of *III* was suppressed, also *IV* was not formed. Compound *IV* (5–25%)





SCHEME 1

was formed in such cases in which relatively great amounts of *III* (13–32%) were produced. We believe that this trend is not fortuitous; it indicates that *IV* does not arise from π -allyl intermediates *C* and *D* (which lead to *I* and *II*) and that its formation is probably more closely related to intermediates affording *III*. On increasing temperature *I* and *IV* formation is favoured, compared to *II* and *III* formation (Table IV). On the other hand, relative amounts of products *I*–*IV* do not significantly change throughout the reaction, as shown in Table IV. This shows that *IV* is not formed by hydrosilylation of *I*–*III*. A small increase of *III* with increasing conversion, which is accompanied by parallel decrease of *II*, is within experimental errors. We therefore examined isomerisation of *II* in the presence of several combinations of reactants (Table V), since isomerisation could be induced not only by starting nickel salt, but also by some of intermediate catalytically active species which are formed during hydrosilylation. As shown in Table V, neither isomerisation of *II* to *III* nor its hydrosilylation to *IV* occurred in this case. From the table it follows that nickel salts themselves are not isomerisation catalysts. An increase in the amount of the *trans*-isomer observed in the presence of trichlorosilane (compared to nickel-phosphine catalyst alone) is suppressed again when experiment is carried out under conditions close to those used in hydrosilylation reactions (*i.e.* in the presence of both the silicon hydride and 1,3-butadiene). Consecutive *cis*–*trans* isomerisation is not then the process controlling the *I* to *II* ratio, which can be taken as additional support for the mechanism of formation of *I* and *II* proposed in Scheme 1.

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