

PALLADIUM- AND NICKEL-CATALYSED HYDROSILYLATION OF CYCLOPENTADIENE**

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A number of palladium and nickel complexes have been found to be effective catalysts for hydrosilylation of cyclopentadiene with trichlorosilane. The reaction produced a mixture of 3-trichlorosilylcyclopentene, 4-trichlorosilylcyclopentene (1 : 1 adducts) and trichlorosilyl-substituted 4,7-methylene-4,7,8,9-tetrahydroindanes (1 : 2 adducts). In general, palladium complexes directed the reaction predominantly to 1 : 1 adduct formation, while in the presence of nickel complexes substantial amounts of 1 : 2 adducts were also formed, except nickeltetracarbonyl which showed both high activity and selectivity, directing the addition almost exclusively to 3-trichlorosilylcyclopentene. The effect of the ligands on the product distribution is discussed and mechanism of the reaction is suggested.

Until now, only two examples of transition metal-catalysed hydrosilylation of cyclopentadiene have been recorded. Mironov and coworkers¹ were the first to effect the addition of trichlorosilane to cyclopentadiene, using hexachloroplatinic acid as a catalyst. Under drastic conditions (240–250°C, 5 h) the reaction afforded a mixture of trichlorosilylcyclopentenes, with the 3-trichlorosilyl isomer as a predominant product. A similar result was also obtained with a cyclopentadiene dimer, 4,7-methylene-4,7,8,9-tetrahydroindene. In both cases the authors observed formation of a higher boiling product (C₁₀H₁₃Cl₃Si₁) which was assigned the structure of 1-trichlorosilyl-4,7-methylene-4,7,8,9-tetrahydroindane. Recently, Kumada and coworkers² have reported on selective formation of 3-trichlorosilylcyclopentene by reaction of trichlorosilane with cyclopentadiene catalysed by chiral phosphine–palladium complexes prepared *in situ* from bis(benzonitrile)dichloropalladium(II) and menthyl(diphenyl)phosphine or neomenthyl(diphenyl)phosphine (81% and 69% yield, respectively, at 120°C, 58 h).

Our current interest in hydrosilylation of conjugated dienes catalysed by Group VIII transition metal compounds (*cf.*^{3–5} and references to previous works given

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therein) led us to investigate also this addition. The results obtained with a series of palladium and nickel complexes are summarized in the present work.

EXPERIMENTAL

Compounds Used

Cyclopentadiene was freshly prepared by thermal decomposition of dicyclopentadiene (Fluka, AG, Buchs) at 170°C over iron turnings. Trichlorosilane (VCHZ Synthesia, Kolín) was purified before use by distillation and its purity was checked by gas-liquid chromatography. *m*-Xylene (*puriss.*, Fluka AG, Buchs) was stored over a molecular sieve and used without further purification as an internal gas chromatographic standard. The following palladium and nickel complexes were prepared by reported procedures:

$[\text{Pd}\{\text{P}(\text{C}_6\text{H}_5)_3\}_4]$ (ref.⁶), $[\text{PdCl}_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$ (ref.⁷), $[\textit{trans}\text{-PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2]$ (ref.⁸), $[\{\text{PdCl}(\eta\text{-C}_3\text{H}_5)\}_2]$ (ref.⁹), $[\text{PdCl}_2(\text{cyclo-C}_6\text{H}_{11}\text{NC})_2]$ and $[\text{PdCl}_2(\text{cyclo-C}_6\text{H}_{11}\text{NC})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$ (ref.¹⁰), $[\text{Ni}\{\text{P}(\text{C}_6\text{H}_5)_3\}_4]$ (ref.¹¹), $[\text{Ni}(1,5\text{-C}_8\text{H}_{12})_2]$ (ref.¹²), $[\{\text{Ni}(\text{CO})(\eta\text{-C}_5\text{H}_5)\}_2]$ (ref.¹³), $[\text{Ni}(\text{CO})_3\{\text{P}(\text{C}_6\text{H}_5)_3\}]$ (ref.¹⁴) and $[\text{NiCl}_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$ (ref.¹⁵). $[\text{Ni}(\text{CO})_4]$ (Fluka AG, Buchs) and $[\text{Ni}(\text{CO})_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$ (Alfa Inorganics, Beverly, USA) were commercial products.

Procedure and Products

Hydrosilylations were carried out in sealed ampoules to which the substances were introduced in the following order: the catalyst, the alkadiene, *m*-xylene, and trichlorosilane. All operations with the compounds were made in an inert atmosphere (argon) and experiments were carried out under identical conditions: 120°C, 8 h, the trichlorosilane-cyclopentadiene (dicyclopentadiene) molar ratio 2 : 1 (4 : 1), the catalyst to trichlorosilane molar ratio $1 \cdot 10^{-3}$. The resulting reaction mixtures were cooled to a temperature of an dry ice-acetone bath until they were analysed. The product distribution was determined by gas-liquid chromatography, using a chromatograph equipped with a thermal conductivity detector (a 4 m × 0.4 cm column was filled with 18% Fluoropropyl Methyl Silicone FS 1265 on Chromaton 0.2–0.25 mm particle size), the nitrogen flow rate was 20 ml/min and the oven temperature 130°C and 220°C for silyl-substituted cyclopentenes and the adducts of trichlorosilane to dicyclopentadiene, respectively.

An authentic sample of 3-trichlorosilylcyclopentene was obtained by the hydrosilylation catalysed with $[\text{PdCl}_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$: n_D^{20} 1.4821, b.p. 62–64°C/9 Torr; reported¹ n_D^{20} 1.4811, b.p. 40–42°C/6 Torr; IR spectrum (*in substantia*): $\nu(\text{Si}-\text{Cl})$ 580 cm^{-1} , $\nu(\text{C}=\text{C})$ 1606 cm^{-1} , $\nu(\text{C}-\text{H})$ 3050 cm^{-1} ; recorded¹ (for the methyl derivative) $\nu(\text{C}=\text{C})$ 1611 cm^{-1} , $\nu(\text{C}-\text{H})$ 3031 cm^{-1} . The other products were isolated only as the mixtures of isomers. These were used as standards for calibration curves in determining product distribution. The data listed in Tables I and II relate therefore to a sum of the isomers, unless stated otherwise. Based on gas-chromatographic, infrared and mass spectrometric data and elemental analysis of its mixture with 3-trichlorosilylcyclopentene, a compound with relative retention time 1.14 (for 3-trichlorosilylcyclopentene I) was assigned the structure of 4-trichlorosilylcyclopentene. Products of the addition of one molecule of trichlorosilane to two molecules of cyclopentadiene (or to one molecule of dicyclopentadiene), further referred to as 1 : 2 adducts, were obtained by distillation as a fraction boiling at 89.5–90°C/2 Torr. Gas chromatogram of this fraction showed two overlapping peaks with relative retention times 4.26 and 4.29. The IR spectrum ($\nu(\text{Si}-\text{Cl})$ 580 cm^{-1} , $\nu(\text{Si}-\text{H})$ 2210 cm^{-1} and $\nu(\text{C}-\text{H})$ 3055 cm^{-1}) indicated the presence of a product of Si-H/Si-Cl exchange. A rough estimation made on the basis of the elemental analyses of the 1 : 2 adducts

obtained with all the catalysts studied and the IR and gas chromatographic analysis showed that the content of this product did not exceed 10 rel.% in the case of the nickel-catalysed hydrosilylations and this product was absent in the case of the hydrosilylation catalysed with palladium complexes. Attempts to separate individual 1 : 2 adducts by preparative gas chromatography have failed.

RESULTS AND DISCUSSION

The reaction of trichlorosilane with cyclopentadiene catalysed by the palladium and nickel complexes listed in Table I gives in general several products: 3-trichlorosilylcyclopentene (*I*), 4-trichlorosilylcyclopentene (*II*) and a mixture of mono(trichlorosilyl)-4,7-methylene-4,7,8,9-tetrahydroindanes (further referred to as 1 : 2 adducts according to the stoichiometry of the reaction). Even though twofold molar excess of trichlorosilane was used in the experiments, formation of the higher silyl-substituted adducts have not been established. In several cases which will be discussed later, in addition to the trichlorosilyl derivatives also products of an interchange of hydrogen and chlorine on silicon have been found among 1 : 2 adducts in amounts not exceeding 10%. The Si—H/Si—Cl interchange products analogous to trichlorosilylcyclopentenes *I* and *II* were not detected.

In regard to the course of the addition, the catalysts can be classified into three groups: *a*) those yielding *I* and *II* as major products with simultaneous formation of 1 : 2 adducts, *b*) those producing *I* and *II* exclusively, and *c*) those in the presence of which the reaction affords predominantly 1 : 2 adducts. As follows from the results summarized in Table I, the first group comprises all the palladium complexes tested, irrespective of variations in their structure. In contrast to alkenes¹⁶, several alkadienes (butadiene, isoprene, and piperylene¹⁷⁻¹⁹) have been found to undergo hydrosilylation in the presence of palladium complexes not containing stabilizing phosphine ligands. As demonstrated by our results, cyclopentadiene is another substance that adds to this list.

Similar yields of 1 : 1 adducts (*I* + *II*) obtained with palladium-phosphine and nonstabilized palladium complexes result from the experimental conditions used. Except tetrakis(triphenylphosphine)palladium the palladium compounds catalysed the addition also at lower temperatures. Although good yields of *I* (57–68%, 12 h; *II* absent, 6–10% 1 : 2 adducts) were obtained at 80°C, the use of milder reaction conditions is disadvantageous because of substantial formation of dicyclopentadiene which contaminated the product *I*.

The second group of catalysts is represented by nickeltetracarbonyl (Table I) which directs the addition nearly exclusively to *I*. The 1 : 2 adducts and dicyclopentadiene were absent. The exceptional catalytic effectiveness and high selectivity of this complex was preserved also at 80°C (26 h, 92% *I*, 3% *II*, dicyclopentadiene and 1 : 2 adducts absent) and the catalyst exhibited activity even at room temperature (9% of *I* as a sole hydrosilylation product after 17 h at 25°C; the final mixture

contained 37% of dicyclopentadiene). As follows from the data for the other nickel compounds given in Table I, the introduction of cyclopentadiene or triphenylphosphine as a ligand brings about drastic change in the product distribution. These catalysts constitute the third group of the classification mentioned, giving 1 : 2 adducts as major products in yields that are little affected by increasing substitution of the carbonyl groups for triphenylphosphine. They all showed little catalytic activity at lower temperatures (5–10% yields of 1 : 2 adducts were obtained at 80°C after 17 h, about 30% of cyclopentadiene being dimerized). The strongly decreased activity of $[\text{NiCl}_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$ at temperatures below 100°C has been observed by us also in hydrosilylation of 1,3-butadiene by trichlorosilane²⁰.

The results obtained with nickel(carbonyl)phosphine complexes further indicate that the relative amount of 4-trichlorosilyl derivative *II* increases with increasing number of triphenylphosphine ligands in the catalyst, *i.e.* with increasing electron density on the nickel atom. To substantiate this trend, we have examined the effect of several phosphorus-containing ligands with different electron-donating ability on the product distribution. Relevant data obtained with the nickel complexes

TABLE I

Hydrosilylation of Cyclopentadiene with Trichlorosilane Catalysed by Palladium and Nickel Complexes

Reaction conditions: 120°C, 8 h, the HSiCl_3 to cyclopentadiene molar ratio = 2 : 1, the catalyst to HSiCl_3 molar ratio = $1 \cdot 10^{-3}$, *m*-xylene to HSiCl_3 molar ratio = 1 : 2.

No	Complex	Conversion ^a , %		
		<i>I</i>	<i>II</i>	1 : 2 adducts
1	$[\{\text{PdCl}(\eta\text{-C}_3\text{H}_5)\}_2]$	60	0	8
2	$[\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2]$	74	4	10
3	$[\text{PdCl}_2(\text{cyclo-C}_6\text{H}_{11}\text{NC})_2]$	78	4	16
4	$[\text{PdCl}_2(\text{cyclo-C}_6\text{H}_{11}\text{NC})\{\text{P}(\text{C}_6\text{H}_5)_3\}]$	86	0	12
5	$[\text{PdCl}_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$	67	0	12
6	$[\text{Pd}\{\text{P}(\text{C}_6\text{H}_5)_3\}_4]$	74	4	8
7	$[\text{Ni}(\text{CO})_4]$	90	5	0
8	$[\text{Ni}(\text{CO})_3\{\text{P}(\text{C}_6\text{H}_5)_3\}]$	7	3	72
9	$[\text{Ni}(\text{CO})_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$	0	2	65
10	$[\text{NiCl}_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$	0	5	67
11	$[\text{Ni}\{\text{P}(\text{C}_6\text{H}_5)_3\}_4]$	0	5	61
12	$[\{\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{CO})\}_2]$	7	0	63
13	$[\text{Ni}(1,5\text{-C}_8\text{H}_{12})_2]$	9	0	57

^a Determined by gas-liquid chromatography.

prepared *in situ* from $[\text{Ni}(\text{CO})_4]$ and ligand are presented in Table II. Although in this case the structure of the species formed by interaction of ligand with $[\text{Ni}(\text{CO})_4]$ may not correspond to the ligand: Ni ratio used (*e.g.* it is known that triphenylphosphine when used in excess substitutes only two carbonyl groups, while triphenylphosphite all four²¹), several tendencies seem undoubtful. The activity of catalyst systems (measured by total yield) decreases with increasing ligand: Ni ratio, this decrease being most pronounced with the less basic triphenylphosphite. The *II* : *I* ratio increases with increasing electron-donating ability of the ligand ($\text{P}(\text{OC}_6\text{H}_5)_3 < < \text{P}(\text{C}_6\text{H}_5)_3 < \text{P}(\text{n-C}_4\text{H}_9)_3$). Substantial changes in relative amounts of *I* and *II* take place on increasing the P : Ni ratio up to 2 : 1. The amounts of 1 : 1 adducts formed decrease with increasing P : Ni ratio but vary irregularly with the ligand (both triphenyl phosphite and tributylphosphine direct the reaction to 1 : 1 adduct formation, in contrast to triphenylphosphine). A similar irregularity reflects also in the 1 : 2 adduct formation. The reason for these irregularities is at present unclear.

Analogous effects of the ligands on the structure of 1 : 1 adducts as described in the present work have also been established in the nickel-catalysed hydrosilylation of 1,3-butadiene by the same silicon hydride²¹. It was found that formation of 4-trichlorosilyl-1-butene (the 1,2-addition product analogous to *II*) with respect to that of 1-trichlorosilyl-2-butene (the 1,4-addition product analogous to *I*) increases

TABLE II

The Effect of Phosphine Ligands L on the Product Distribution in Hydrosilylation of Cyclopentadiene by Trichlorosilane Catalysed by $[\text{Ni}(\text{CO})_4] + \text{L}$ Systems

For experimental conditions see Table I.

L	L : Ni	Conversion ^a , %		
		<i>I</i>	<i>II</i>	1 : 2 adducts
None	0	90	5	0
$\text{P}(\text{OC}_6\text{H}_5)_3$	1 : 1	55	4	10
	4 : 1	0	b	0
$\text{P}(\text{C}_6\text{H}_5)_3$	1 : 1	19	4	50
	2 : 1	0	7	55
	4 : 1	0	5	40
$\text{P}(\text{n-C}_4\text{H}_9)_3$	1 : 1	23	44	2
	2 : 1	4	34	29
	4 : 1	2	6	37

^a See note^a in Table I.

in dependence on the ligand in the order $P(C_6H_5)_3 < P(n-C_4H_9)_3 < P(\text{cyclo-}C_6H_{11})_3$, following apparently increasing σ -donor ability of the ligand. This dependence has been attributed to the increased stabilization toward rearrangement to η -allyl intermediate (leading to 1,4-adducts) of the transient nickel(silyl)hydride species (in the case of bulky tricyclohexylphosphine also steric effects seem to contribute largely to this stabilization^{22,23}). The results obtained with cyclopentadiene do not contradict this assumption.

Formation of 1 : 2 adducts deserves comment. Mironov and coworkers¹ reported that in the presence of chloroplatinic acid both cyclopentadiene and dicyclopentadiene is hydrosilylated at 250°C to give besides the expected hydrosilylation product, 3-trichlorosilylcyclopentene, also 1-trichlorosilyl-4,7-methylene-4,7,8,9-tetrahydroindane(III). The authors found that the latter compound is formed by Diels-Alder type condensation of cyclopentadiene with the 1 : 1 adduct (equation (A)). As found



by separate experiments, the reaction (A) does not proceed under the conditions used in this work. Dimerization of cyclopentadiene to dicyclopentadiene and its subsequent hydrosilylation accounts for formation of 1 : 2 adducts in our case. The effectiveness of palladium and nickel complexes in hydrosilylation of dicyclopentadiene is exemplified by the following data (for numbering of the catalysts and experimental conditions see Table I):

Catalyst	3	6	7	8	9	11
1 : 2 Adducts, %	35	67	0	60	63	65

The data obtained so far indicate that 1 : 2 adducts formed in the nickel- and palladium-catalysed hydrosilylation of cyclopentadiene are a mixture of isomers. The position of the trichlorosilyl group in these adducts has not been identified.

The occurrence of 1 : 2 adducts in the reactions catalysed by palladium complexes not containing stabilizing phosphine ligands (catalysts 1-3, Table I) is worthy of note. Although these complexes are effective for hydrosilylation of conjugated dienes or simple dienes with isolated C=C bonds, they were found by us to be inactive for the additions to monoenes. This finding has been recently utilized by us to hydrosilylate selectively the 1,3-butadiene present in pyrolytic C₄-hydrocarbon fraction²⁴. The inactivity of the above complexes in the case of monoenes results from their facile reduction by the present silicon hydride to metallic palladium and

can be ascribed to the low ability of monoenes to stabilize transient Pd(0) species formed in the first step of reduction of Pd(II) complexes. Formation of low valent transition metal species is generally thought to be necessary condition for effecting hydrosilylation^{25,26}. In the light of these facts the possibility to hydrosilylate dicyclopentadiene (*i.e.* the diene with isolated C=C bonds in the 1,5-position) with the use of such complexes can be accounted for by the increased coordination ability of this diene which can act as a bidentate ligand. One example of such 1,5-coordination of dicyclopentadiene to palladium was recorded in the literature²⁷.

In the presence of nickel catalysts the 1 : 2 adducts consisted also a substance containing Si—H bond. The IR spectrum of the 1 : 2 adducts showed one band in the region of $\nu(\text{Si—H})$ at 2210 cm^{-1} . The wavenumber of the $\nu(\text{Si—H})$ band shows that the substance is substituted by the SiHCl₂ group: $\nu(\text{Si—H})$ in HSiCl₃ 2258 cm^{-1} (ref.²⁸), C₈H₁₇SiCl₂H 2200 cm^{-1} (ref.²⁹), C₈H₁₇(CH₃)SiClH 2150 cm^{-1} (ref.²⁹). Such an assignment is made possible by the fact that in alkyl chlorohydrosilanes the $\nu(\text{Si—H})$ vibration is controlled by the number of chlorine atoms and is essentially unaffected by the structure of the alkyl group. As already mentioned, analogous 1 : 1 adducts, chlorohydrosilylcyclopentenes were not formed. This difference in the composition of 1 : 1 and 1 : 2 adducts compares well with the results obtained by Kiso and coworkers²⁹ for hydrosilylation of olefins catalysed by nickel-phosphine complexes. The authors classified the olefins into two categories: those for which the hydrosilylation is accompanied by the H/Cl interchange process and those which gave only the expected (normal) product. The former consisted, of alkenes and 1,5-cyclooctadiene, among others and the latter mainly conjugated dienes (isoprene, 1,3-cyclooctadiene). The appartenance of cyclopentadiene and dicyclopentadiene to different classes is evident. The Japanese authors also found that the amount of the H/Cl exchange product increases with increasing electron-donating ability of the phosphine ligands. Likely because of the generally small extent of the H/Cl replacement reaction (the HCl₂Si-substituted 1 : 2 adducts did not exceed 10%), we were not able to confirm this trend in our case.

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