

Catalysis of hydrosilylation

Part XXV. Effect of nickel(O) and nickel(II) complex catalysts on dehydrogenative silylation, hydrosilylation and dimerization of vinyltriethoxysilane

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Received 17 March 1994

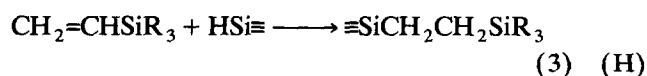
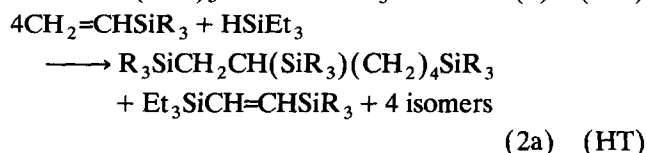
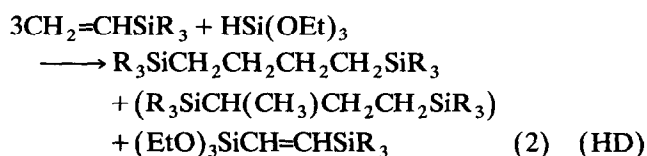
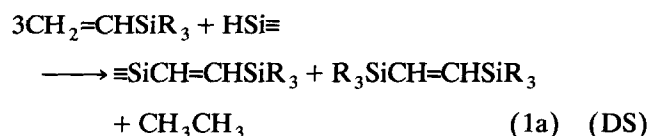
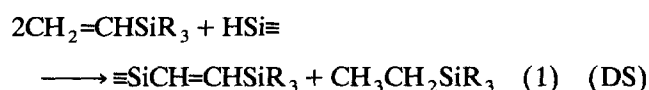
Abstract

General catalysis by Ni(O) and Ni(II) phosphine and non-phosphine complexes of the competitive-consecutive reaction of vinyltriethoxysilane with triethoxysilane has been observed to give mainly products of dehydrogenative silylation and hydrogenative dimerization accompanied by products of regular hydrosilylation, disproportionation of substrates and secondary reactions of the product—bis(silyl)ethene. In an excess of vinylsilane, side reactions can be practically eliminated. Tertiary phosphine and phosphite ligands of nickel acetylacetonate ($\text{Ni}(\text{acac})_2 \cdot 2\text{PR}_3$) stop the consecutive reactions of bis(silyl)ethene but in the presence of σ -basic and bulky tricyclohexylphosphine the system catalyzes selectively the regular hydrosilylation of bis(silyl)ethene.

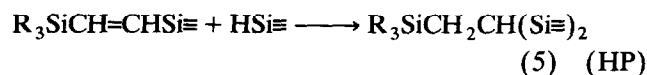
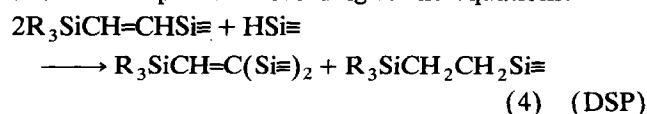
Keywords: Nickel; Silicon; Hydrosilylation; Silane; Catalysis

1. Introduction

In previous studies we have shown that nickel acetylacetonate catalyses a competitive-consecutive reaction of trisubstituted silanes ($(\text{EtO})_3\text{SiH}$ and Et_3SiH) with a variety of vinyltrisubstituted silanes. Main products of the following reactions are obtained: dehydrogenative silylation (DS), hydrogenative oligomerization (HD) and (HT) and regular hydrosilylation (H); these occur according to the following equations [2,3]

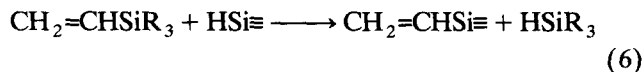


The main processes are accompanied by the following consecutive and side reactions: dehydrogenative silylation (DSP) and regular hydrosilylation (HP) of the unsaturated product according to the equations:



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as well as by disproportionation of substrates (if different substituents are present at the silicon of both substrates) given by the equation



followed by some of the main reactions [1].

The conversion yield and selectivities of the reaction have been found to be influenced by many factors such as electronic and steric effects of the substituents at silicon of both substrates, and by the ratio of vinylsilane/hydrosilane catalysts, the temperature and the presence of dioxygen.

In view of many recently reported examples of dehydrogenative silylation competing with hydrosilylation of olefins, occurring in the presence of ruthenium, iron, rhodium, osmium, iridium and some platinum catalysts [4,5] the above reaction is the first dehydrogenative silylation observed for nickel catalyst. And although the latter complexes are well-known catalysts for dimerization of vinylsilanes (usually using a Ziegler catalytic system e.g. $\text{Ni}(\text{acac})_2 \cdot \text{AlEt}_n \text{Cl}_{3-n} + \text{PPh}_3$) giving (without hydrosilanes) bis(silyl)butenes [6,7], hydrodehydrogenative dimerization (HD) seems also to be a novel pathway observed in the system examined.

The aim of this work is to extend our knowledge of the types of nickel complex which can influence (as a catalyst precursor) the stoichiometry and the course of this competitive-consecutive reaction.

2. Experimental section

2.1. Materials

Triethoxysilane was obtained by alcoholysis of SiHCl_3 according to the standard procedure. Bis(2,4-pentanedionate)nickel(II) [8] [*o*-tol-O] $_3\text{P}$ $_2\text{Ni}(\text{C}_2\text{H}_4)$

[9], [(thym-O) $_3\text{P}$] $_2\text{Ni}(\text{C}_2\text{H}_4)$ [10] and (cod) $_2\text{Ni}$ [11] were prepared as described in the literature. Other chemicals were obtained as follows: vinyltriethoxysilane, triethylaluminum, triphenylphosphine, tetrakis(triphenylphosphino)nickel(O) and nickelocene from Fluka; nickel trifluoroacetylacetonate from Strem Chemicals, triphenylphosphite and other phosphines from Aldrich. All were used without further purification.

2.2. Equipment and analytical measurements

Most products were identified by gas chromatography (GC)–mass spectrometry (MS) analysis (Varian 3300 gas chromatograph equipped with a DB-1 30m capillary column and a Finnigan Mat 800 ion trap detector) by comparing spectra and the retention times of the peaks with those of previously described standards [3].

2.3. Hydrosilylation reaction (general procedure)

The catalyst $\text{Ni}(\text{acac})_2$ + tertiary phosphine or phosphite or other nickel complex precursors were placed in a glass ampoule (or in a flask equipped with a condenser) and filled with a mixture of vinyltriethoxysilane and triethoxysilane. All manipulations were carried out using standard Schlenk and high vacuum-line techniques.

Sealed ampoules (or flasks) were heated at a given temperature (120°C) or under reflux (flasks). The distribution of substrates and products, conversions of substrates and the yield of the reaction products were detected and calculated by GC–MS and GLC analysis.

2.4. Isolation and characterization of the product of dehydrogenative silylation and regular hydrosilylation of bis(triethoxysilyl)ethene

Products of the reaction were isolated by distillation and then identified by GLC using standard samples

Table 1

Effect of tertiary phosphines (and phosphites) in the catalytic system $\text{Ni}(\text{acac})_2 \cdot 2\text{PR}_3$ on the yield and selectivity of the reaction of vinyltriethoxysilane with triethoxysilane 120°C, glass ampoules, Ar; $[\text{SiH}]:[\text{CH}_2=\text{CHSi}\equiv]:[\text{Ni}]:[\text{PR}_3] = 1:1:5 \cdot 10^{-3}:10^{-2}$

Phosphine/phosphite Time, h	None		PPh $_3$		PPh $_3$ ^a		P(OPh) $_3$	P(Cy) $_3$		P(C $_6\text{H}_4(\text{OMe})_2$) $_3$	
	24	40	24	40	24	40	40	24	40	24	40
Conversion [%]											
HSi(OEt) $_3$	70	89	22	57	40	55	13	57	85	30	34
CH $_2$ =CHSi(OEt) $_3$	100	100	38	95	73	82	21	95	100	58	62
Yield [%]											
CH $_3\text{CH}_2\text{Si}\equiv$	14	14	9	18	15	16	4	14	14	15	17
Si(OEt) $_4$	6	8	7	12	7	8	7	6	9	6	7
$\equiv\text{SiCH}=\text{CHSi}\equiv$	13	4	14	40	31	38	1	42	2	24	25
$\equiv\text{SiCH}_2\text{CH}_2\text{Si}\equiv$	14	19	trace	7	2	3	trace	2	13	trace	trace
$\equiv\text{SiCH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{Si}\equiv$	8	7	1	2	3	4	1	6	6	2	3
$\equiv\text{Si}(\text{CH}_2)_4\text{Si}\equiv$	24	24	5	9	13	13	3	21	20	8	8
$(\equiv\text{Si})_2\text{C}=\text{CHSi}\equiv$	21	–	–	–	–	–	–	1	trace	–	–
$(\equiv\text{Si})_2\text{CHCH}_2\text{Si}\equiv$	trace	trace	–	–	–	–	–	–	35	–	–

^a $[\text{Ni}]:[\text{PR}_3] = 1:1$; in the presence of PBu_3 and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ slight conversion of substrates was noted yielding predominantly products of silane redistribution.

and on the basis of their spectra (^1H and ^{13}C NMR, IR, MS).

2.4.1. Tris(triethoxysilyl)ethene $[(\text{EtO})_3\text{Si}]_2\text{C}=\text{CHSi}(\text{OEt})_3$

^1H -NMR (C_6D_6 , δ ppm) 1.19 (dt, $-\text{CH}_3$); 3.93 (dq, $-\text{CH}_2\text{O}$); 7.97 (s, $=\text{CH}-$); ^{13}C -NMR (C_6D_6 , δ ppm) 19.16 (CH_3-); 59.32 ($-\text{CH}_2\text{O}$); 158.07 ($=\text{CH}-$); 164.31 ($=\text{C} < >$); IR (film) 1618 cm^{-1} ($> \text{C}=\text{C} <$).

2.4.2. Tris(triethoxysilyl)ethane $[(\text{EtO})_3\text{Si}]_2\text{CHCH}_2\text{Si}(\text{OEt})_3$

^1H -NMR (C_6D_6 , δ ppm) 1.36 (dt, $-\text{CH}_3$); 4.01 (dq, $-\text{CH}_2\text{O}$); 1.70 (m, $-\text{CH}_2-$); 0.81 (t, $-\text{CH}_3$); ^{13}C -NMR (C_6D_6 , δ ppm) 19.16 (CH_3-); 59.18 ($-\text{CH}_2\text{O}$); 11.37 ($-\text{CH}_2\text{Si}$); 27.32 ($-\text{CHSi}-$).

3. Results and discussion

The previously studied reaction of triethoxysilane and vinyltriethoxysilane was selected as a test to check the effects of various nickel catalysts and tertiary phosphine ligands in the system with nickel acetylacetonate. If this reaction catalyzed by $\text{Ni}(\text{acac})_2$ occurs at a vinylsilane: hydrosilane ratio 1:1 (at 120°C) then (after 2h) the products of dehydrogenative silylation (DH), hydrogenative dimerization (HD) and regular hydrosilylation (H) [3] predominate. However, when the process has been extended, dehydrogenative silylation of the preliminary product (bis(silyl)ethene (DSP), according to Eq. (4)) is seen (see Table 1). Similar final effects have been noticed already after 2 h of the reaction occurring under reflux, i.e. at a temperature of about 160°C (see Table 2).

Under such conditions the reduction of nickel acetylacetonate to nickel precipitate is observed within 0.5 h, i.e. when the first stage of the reaction is almost

completed. Further study of the intermediates formed in the system $\text{Ni}(\text{acac})_2 + \text{HSi}\equiv + \text{CH}_2=\text{CHSi}\equiv$ is being continued.

Synthetic work allowed us to isolate and characterize for the first time a final product—tris(triethoxysilyl)ethene (see Experimental section). Previously, only trialkyl- [12] and tri(methyl, chloro)-derivatives [13] were synthesized via the regular hydrosilylation of ethyne derivatives in the presence of platinum catalysts. Thus, all products of this competitive consecutive reaction are isolated and identified.

In order to stabilize the catalyst precursor, nickel acetylacetonate, various tertiary phosphines and phosphites of different σ -donor and π -acceptor properties as well as of different cone angle θ were added to the reaction mixture. Catalytic results are compiled in Tables 1 and 2.

The conditions of the above mentioned reaction i.e. $[\text{HSi}\equiv]:[\text{CH}_2=\text{CHSi}\equiv] = 1:1$ and 120°C ampoules (Table 1) or reflux (Table 2) were chosen to enable us to follow the effect of phosphines on the yield and selectivity of this complex process.

The presence of triphenylphosphine ($\theta = 145^\circ$; $\text{pK}_a = 2.73$) [12,13] ($[\text{Ni}]:[\text{phosphine}] = 1:2$) apparently stabilizes the nickel complex, decreasing its catalytic activity in such a way that after 72 h at 120°C the reaction yield and selectivity reach levels that are characteristic for the $\text{Ni}(\text{acac})_2$ catalyzed reaction after 2 h [3]. When $[\text{Ni}(\text{acac})_2]:[\text{PPh}_3] = 1:1$ the nickel complex remains in solution without precipitation of nickel but the yield is much lower than in the absence of phosphine. Yet no products of secondary dehydrogenative silylation (DSP) or hydrosilylation (HP) are observed. A drastic decrease in the catalytic activity of nickel acetylacetonate in the presence of triphenylphosphine is noted when the process takes place under reflux. Phosphites which are weak bases (e.g. triphenylphosphite, $\text{pK}_a = -2.00$, $\theta = 128^\circ$ [14,15]) practically stop the catalytic reaction.

However, when tricyclohexylphosphine ($\theta = 170^\circ$ and $\text{pK}_a = 9.70$ [13,14]) acts as a ligand of nickel acetylacetonate there is almost the same activity as when the precursor is alone. But steric hindrance at the nickel complex caused by the phosphine ligand directs the consecutive reaction via regular hydrosilylation of the product (Eq. (5)) instead of dehydrogenative silylation (Eq. (4)) observed in the case of $\text{Ni}(\text{acac})_2$ catalyst. Dehydrogenative silylation requires a coordination of the second molecule of bis(silyl)ethene to the nickel complex which is not possible where such a bulky (but basic) phosphine is coordinated.

If a more bulky (though sufficiently basic) phosphine is used e.g. $\text{P}[(2,6\text{-MeO})_3\text{C}_6\text{H}_3]_3$, $\theta = 184^\circ$, $\text{pK}_a = 9.33$ [14,15] then we again observe marked inhibition of all the reactions, yet formation of products of dehydrogenative silylation has priority. However, when we used

Table 2
Effect of tertiary phosphines in the catalytic system $\text{Ni}(\text{acac})_2 + 2\text{PR}_3$ on the yield and selectivity of the reaction of vinyltriethoxysilane with triethoxysilane occurring under reflux (2 h, Ar)

Phosphine	None	PPh_3	$\text{P}(\text{Cy})_3$	$\text{P}[\text{C}_6\text{H}_3(\text{OMe})_2]_3$
Conversion, %				
$\text{HSi}(\text{OEt})_3$	97	25	76	13
$\text{CH}_2=\text{CHSi}(\text{OEt})_3$	100	25	100	25
Yield, %				
$\text{CH}_3\text{CH}_2\text{Si}\equiv$	15	4	13	7
$\text{Si}(\text{OEt})_4$	5	5	5	4
$\equiv\text{SiCH}=\text{CHSi}\equiv$	3	11	10	8
$\text{SiCH}_2\text{CH}_2\text{Si}\equiv$	28	traces	16	—
$\text{SiCH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{Si}\equiv$	5	1	7	1
$\equiv\text{Si}(\text{CH}_2)_4\text{Si}\equiv$	22	2	19	3
$(\equiv\text{Si})_2\text{C}=\text{CHSi}\equiv$	20	—	—	—
$(\equiv\text{Si})_2\text{CHCH}_2\text{Si}\equiv$	traces	—	29	—

$[\text{HSi}\equiv]:[\text{CH}_2=\text{CHSi}\equiv]:[\text{Ni}]:[\text{PR}_3] = 1:1:5 \cdot 10^{-3}:10^{-2}$.

process in a similar way but as a result of redistribution of triethoxysilane much more tetraethoxysilane is yielded and, in two cases, traces of consecutive reactions of bis(silyl)ethene have also been observed.

Table 4 shows how the catalysts under consideration when in two-fold excess of vinylsilane compared to hydrosilane, practically eliminate most of the side reactions and always give predominantly products of dehydrogenative silylation of vinylsilane i.e. bis(silyl)ethene (40–50%) and ethylsilane (10–20%) and of hydrogenative dimerization, yielding two isomers of bis(silyl)butanes (20–30%).

4. Conclusions

1. The consecutive-competitive reaction of vinylsilanes with triethoxysilane gives products of dehydrogenative silylation (DS) (Eq. (1)) and hydrogenative dimerization (HD) (Eq. (2)) with by-products of regular hydrosilylation and of other processes occurring in the presence not only of nickel acetylacetonate but also of many nickel(O) and nickel(II) complexes with phosphorous and non-phosphorous ligands. Catalysis by nickel complex is a general feature of this process.

2. When there is a two-fold excess of vinylsilane over hydrosilane their reaction, catalyzed by various Ni(O) and Ni(II) complexes, yields practically only products of dehydrogenative silylation (DS) and hydrogenative dimerization (HD) and most side reactions are excluded.

3. While most tertiary phosphine and phosphite ligands of nickel complexes, regardless of their σ -donor and π -acceptor properties and value of cone angle θ , stop both consecutive reactions of bis(silyl)ethene (the precursor Ni(acac)₂ alone enables its dehydrogenative silylation) a σ -basic but relatively bulky ligand (tricyclohexylphosphine) catalyzes selectively the regular hydrosilylation of bis(silyl)ethene. Both products have been isolated and for the first time fully characterized.

4. Although in the presence of phosphine and phosphite complexes of nickel(O) the redistribution of triethoxysilane is much increased and, in general, tertiary phosphine lowers the catalytic activity (and selectivity) of the system Ni(acac)₂ + 2 PR₃, there seems to be no difference between the mechanisms of catalysis by all Ni(O) and Ni(II) complexes used in the reaction examined. This will be considered in a forthcoming paper.

Acknowledgement

This work was supported by funds from the Committee of Scientific Research, Research Project 2 0681 91 01.

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