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NICKEL COMPLEXES WITH VINYLSILANES

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Summary

Three methods for preparing the following nickel complexes of vinylsilanes are described: $(CH_2{=}CHSiR_3)Ni(PPh_3)_2$ (R = Me, OMe), $[(CH_2{=}CH)_2SiMe_2]Ni(PPh_3)_2$, $[(CH_2{=}CH)_4Si][Ni(PPh_3)_2]_2$, $[(CH_2{=}CH)_2SiMe_2]Ni(PPh_3)$, $[(CH_2{=}CH)_4Si]Ni(PPh_3)$ and $[(CH_2{=}CH)_4Si][Ni(PPh_3)]_2$. The structure of these complexes is discussed on the basis of ^1H NMR spectra.

Introduction

The chemistry of transition metal olefin complexes containing vinylsilanes as ligands has been investigated quite recently. At present such complexes are available for Cu^I, Pt^{II} and Pt^0, Fe, Cr, Mo and W [1–6]. The interest attached to these complexes is fully justified. This is connected with the investigation of the nature of the bond between vinylsilanes and transition metals and, on the other hand, some representatives of this group of compounds have been found to be active catalysts in hydrosilylation and telomerization of vinylsilanes [7,8].

The synthesis of nickel(0) monovinylsilane complexes by the replacement of ethylene in π-ethylenebis(triphenylphosphine)nickel by vinyltrimethyl- or vinyltrimethoxy-silane was described recently in our brief report [9]. The present paper is concerned with the investigation of the interaction of various nickel compounds with monovinyl-, divinyl- and tetravinyl-silanes. The complexes isolated were characterized from ^1H NMR spectra.

Results and discussion

The following reactions were performed to synthesize nickel(0) complexes with vinylsilane ligands:

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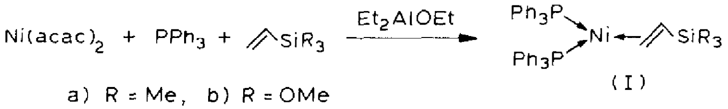
(1) The interaction of nickel salts with diethylaluminium ethoxide in the presence of vinylsilanes and triphenylphosphine.

(2) The substitution of coordinated ethylene in π-ethylenebis(triphenylphosphine)nickel by mono-, di- and tetravinyl-silanes.

(3) The substitution of the π-cyclooctadiene ligand in bis(cycloocta-1,5-diene)nickel by vinylsilanes in the presence of triphenylphosphine.

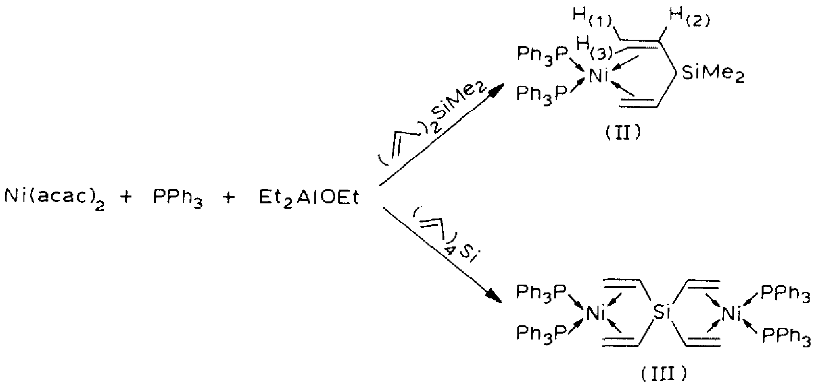
The first method is traditional and is often used for the synthesis of nickel olefin complexes [10,11]. It has been found that the reaction of nickel acetylacetonate with diethylaluminium ethoxide in the presence of vinyltrimethyl- and vinyltrimethoxy-silanes and triphenylphosphine in ether solution at room temperature produces three-coordinate nickel vinylsilane complexes stabilized by two triphenylphosphine ligands (Ia, b):



(1)

The ^{1}H NMR spectra of complexes Ia and Ib contain multiplets (with the centres at δ 2.81 and 2.50 ppm) which belong to the protons of the coordinated vinyl groups of the silane. The proton NMR spectra of complexes Ia and Ib show a characteristic upfield shift which the signals of the olefin protons undergo upon coordination of the double C=C bond with nickel. The values of the chemical shifts of the vinyl protons are in good agreement with the chemical shift (δ 2.55 ppm) of the protons of the coordinated ethylene [12]. The phenyl protons of triphenylphosphine ligands in complexes Ia and Ib appear in the ^{1}H NMR spectra as two multiplets with the centres at δ 7.06 (*m*-, *p*-Ph) and 7.59 (*o*-Ph) ppm and at 7.07 and 7.66 ppm, respectively, with the ratio of integrated intensities being 3:2. In addition, the spectrum of compound Ia contains a singlet from the methyl protons at δ 0.15 ppm, while the spectrum of compound Ib contains the singlet from the protons of the three CH_3O groups at δ 3.51 ppm. The ratio of integrated intensities in spectra Ia and Ib corresponds to the proposed structure.

The method considered here may be suitable for the synthesis of nickel divinyl- and tetravinyl-silane complexes. The interaction of nickel acetylacetonate and diethylaluminium ethoxide in the presence of divinyldimethylsilane and triphenylphosphine results in the formation of the divinylsilane complex II:



(2)

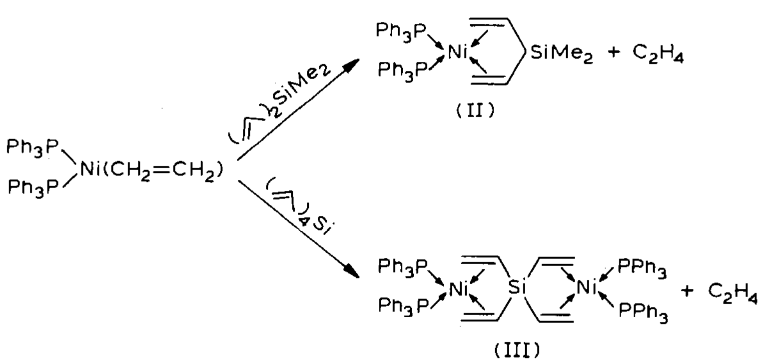
(3)

The ^1H NMR spectrum of complex II contains a singlet signal from the methyl protons of the Me_2Si group at δ 0.33 ppm and two poorly resolved multiplets with centres at δ 7.06 and 7.44 ppm belonging to the phenyl ring protons of the PPh_3 ligand. In the range characteristic of the protons of the vinyl groups π-bonded to the nickel atom a set of multiplets is observed which is typical of three spin systems: δ 3.46(H(1)), 3.92(H(2)), 3.98(H(3)) ppm; $J_{1,2} = 13$, $J_{1,3} = 15$, $J_{2,3} \leqslant 4$ Hz. Inspection of the spectrum of complex II shows that this compound contains as an admixture about 20% of a three-coordinate nickel divinylsilane complex with one PPh_3 ligand. The synthesis of the latter complex was performed by replacing the π-cyclooctadiene ligand in bis(cycloocta-1,5-diene)nickel with divinyldimethylsilane and is described below.

The binuclear nickel tetravinylsilane complex III was prepared for the first time by treatment of nickel acetylacetonate with diethylaluminium ethoxide in the presence of tetravinylsilane and triphenylphospine. According to the elemental analysis and the ^1H NMR spectrum, complex III contains one molecule of solvent ether. Vinylic protons in the ^1H NMR spectrum of this complex are revealed as three multiplets in the range characteristic of coordinated vinyl groups with the centres at δ 3.13(H(1)), 3.46(H(2)), 4.31(H(3)) ppm; $J_{1,2} = 9$, $J_{1,3} = 15$, $J_{2,3} \leqslant 6$ Hz. The signals from phenyl protons of the PPh_3 ligands are observed in the spectrum as two multiplets at δ 7.08 (*m*-, *p*-Ph) and 7.48 (*o*-Ph) ppm. The absence of the signals of free vinyl groups as well as the integrated intensities ratio of the phenyl and vinyl protons being equal to 5:1 prove unambiguously the structure of complex III.

It should be noted that in reactions 1–3 described above a negligible amount of the σ-ethyl compound $EtNi(PPh_3)(acac)$ is formed along with the nickel vinylsilane complexes.

As the second method of preparing nickel vinylsilane complexes, the substitution of the ethylene ligand in π-ethylenebis(triphenylphosphine)nickel by the corresponding vinylsilane has been studied. The reaction of π-ethylenebis(triphenylphosphine)nickel with divinyldimethylsilane in benzene solution at room temperature proceeds with evolution of ethylene and leads to (π-divinyldimethylsilane)bis(triphenylphosphine)nickel (II), the yield being 78%.



(II)

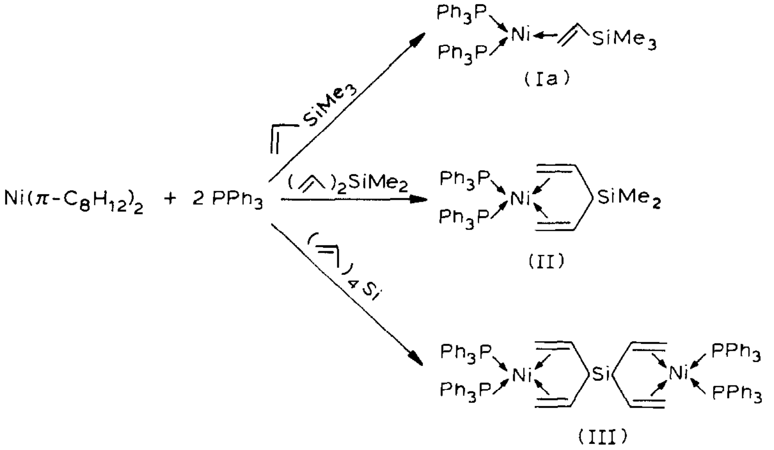
(4)

(III)

(5)

Similarly, (π-tetravinylsilane)tetrakis(triphenylphosphine)dinickel is formed by interaction of nickel ethylene complex with tetravinylsilane.

Complexes Ia, II and III can also be prepared by replacement of the cycloocta-1,5-diene ligand in bis(cycloocta-1,5-diene)nickel with vinyltrimethyl-, divinyldimethyl- and tetravinyl-silanes in the presence of two equivalents of triphenylphosphine:



(6)

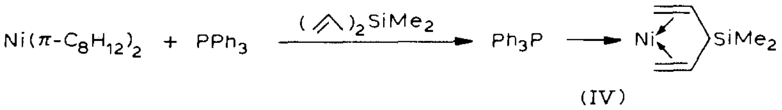
(7)

(8)

The reaction proceeds under mild conditions (22°C), the vinylsilane complexes being formed in high yield. However, in the case of monovinylsilane a competing reaction is observed resulting in the formation of tris(triphenylphosphine)nickel.

The comparison of the ^{1}H NMR spectra of samples of complex Ia prepared by three different methods indicates the identity of their structure independently of the method of preparation. The same holds for complexes II and III.

The third method also allowed synthesis of the previously unknown nickel monophosphine complexes with vinylsilane ligands. Thus, if the reaction of bis(cycloocta-1,5-diene)nickel with divinyldimethylsilane is carried out in the presence of a one equivalent of triphenylphosphine, the three-coordinate nickel complex (π-divinyldimethylsilane)triphenylphosphinenickel (IV) is formed:

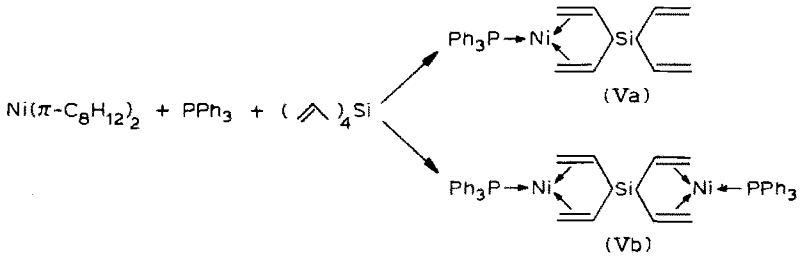


(9)

The ^{1}H NMR spectrum of complex IV contains a multiplet of coordinated vinyl group protons in the range 2.7–3.6 ppm, its analysis giving the following parameters: δ 3.28(H(1)), 3.54(H(2) or H(3)) or 2.78 (H(2) or H(3)) ppm; $J_{1,2} = J_{1,3} = 15$, $J_{2,3} \simeq 5$ Hz. The multiplet from the vinyl proton at δ 3.54 ppm is also split by the phosphorus nucleus with $J \simeq 15$ Hz, which is indicative of a non-equivalent arrangement of the protons in the terminal CH_2 group with respect to the phosphorus atom. The multiplet centres of the phenyl ring protons of the PPh_3 ligand are at δ 7.14 (*m*-, *p*-Ph) and 7.62 (*o*-Ph) ppm. In addition, a singlet signal from the methyl group protons is observed in the spectrum at δ 0.26 ppm.

For the analogous platinum complex (tert-$Bu_2MeP)Pt[(CH_2{=}CH)_2SiMe_2]$, a conformation of the C=C groups with respect to each other as well as to the metal atom similar to that in (*trans,trans,trans*-cyclododeca-1,5,9-triene)nickel was proved on the basis of the ^{1}H NMR spectrum [3b]. We suggest that the double bonds in complex IV are arranged in a similar manner. Such an assumption is in good agreement with the equivalence of the methyl groups in this complex.

The nickel monophosphine derivatives with the tetravinylsilane ligand were prepared likewise by the action of tetravinylsilane on bis(cycloocta-1,5-diene)nickel in the presence of a single equivalent of triphenylphosphine:



(10)

On examining the ^1H NMR spectrum of the reaction product, the latter was found to be a mixture of two substances. The spectrum shows a complex multiplet centered at δ 6.15 ppm and another multiplet of the same intensity at δ 3.42 ppm, which are assigned to the protons of uncoordinated and coordinated vinyl groups of mononuclear complex Va, respectively. The spectrum also contains a multiplet at δ 2.79 ppm which we consider to belong to the protons of the vinyl groups of the binuclear complex Vb. The ratio of the integrated intensities of the vinyl protons of compounds Va and Vb indicate that the mixture contains 66% Va and 34% Vb. The phenyl proton signals of the PPh_3 ligands appear as multiplets at δ 7.12 (*m*-, *p*-Ph) and 7.62 (*o*-Ph) ppm.

Comparison of the integrated intensities of the phenyl group protons with the intensities of the uncoordinated and coordinated vinyl group protons is in good agreement with the percentages of complexes Va and Vb above.

The vinylsilane complexes I–V thus obtained are solid crystalline substances of yellow colour sensitive to atmospheric oxygen and decomposing upon heating at temperatures above 100°C. Monophosphine complexes IV and V are more soluble in aromatic hydrocarbons and ether than are complexes I and II which, in their turn, are more soluble than complex III.

Experimental

The ^1H NMR spectra were recorded on a Bruker WP-200 Sy spectrometer at 22°C. Deuterobenzene was used as a solvent for all the samples. The chemical shifts are given with respect to residual benzene (7.24 ppm). π-Ethylenebis(triphenylphosphine)nickel [13] and bis(cycloocta-1,5-diene)nickel [11] were prepared according to reported methods. The preparation and isolation of the nickel vinylsilane complexes were carried out under argon using absolute solvents distilled under argon prior to use.

Method I

(π-Vinyltrimethylsilane)bis(triphenylphosphine)nickel(Ia). A solution of $Et_2Al(OEt)$ (15 mmol) in ether was carefully added to an ether solution of $Ni(acac)_2$ (5 mmol), PPh_3 (10 mmol) and vinyltrimethylsilane (28 mmol) cooled to −20°C. The reaction mixture was stirred at 22°C for 4 hours, evaporated to the minimum volume and then treated with pentane; the yellow crystalline residue was filtered off and washed with pentane to remove $EtNi(PPh_3)(acac)$. The yield of

$(CH_2{=}CHSiMe_3)Ni(PPh_3)_2$ was 1.78 g (52%), m.p. 125–130°C (dec.) (benzene–ether). Found: C, 71.92; H, 6.03; $C_{41}H_{42}NiP_2Si$ calcd.: C, 72.04; H, 6.19%.

(π-Vinyltrimethoxysilane)bis(triphenylphosphine)nickel (Ib). The yield of $[CH_2{=}CHSi(OMe)_3]Ni(PPh_3)_2$ was 1.56 g (43%), m.p. 95–98°C (dec.) (ether-pentane). Found: C, 66.74; H, 5.68. $C_{41}H_{42}NiO_3P_2Si$ calcd.: C, 67.32; H, 5.79%.

(π-Divinyldimethylsilane)bis(triphenylphosphine)nickel(II). The yield of $[(CH_2{=}CH)_2SiMe_2]Ni(PPh_3)_2$ was 1.96 g (56%), m.p. 102–105°C (dec.) (ether). According to the ^1H NMR spectrum, the substance contains about 20% of complex IV.

(π-Tetravinylsilane)tetrakis(triphenylphosphine)dinickel(III). The yield of $[(CH_2{=}CH)_4Si][Ni(PPh_3)_2]_2 \cdot Et_2O$ was 2.03 g (59%), m.p. 138–143°C (dec.)(benzene–ether). Found: C, 73.30; H, 5.70. $C_{84}H_{82}Ni_2OP_4Si$ calcd.: C, 73.27; H, 6.00%.

Method II

(π-Divinyldimethylsilane)bis(triphenylphosphine)nickel (II). A solution of divinyldimethylsilane (43 mmol) was added to a benzene solution of $(\pi\text{-}C_2H_4)Ni(PPh_3)_2$ (4 mmol) at 22°C. The reaction was accompanied by evolution of ethylene (GLC). After 2 hours the reaction mixture was evaporated almost to dryness; the residue was dissolved in a minimum amount of ether and treated with pentane; the yellow precipitate formed was washed with pentane and dried in vacuum. 2.10 g (76%) of $[(CH_2{=}CH)_2SiMe_2]Ni(PPh_3)_2$ was obtained, m.p. 102–105°C(dec.) (ether). Found: C, 72.42; H, 5.81. $C_{42}H_{42}NiP_2Si$ calcd.: C, 72.53; H, 6.09%.

(π-Tetravinylsilane)tetrakis(triphenylphosphine)dinickel(III). The yield of $[(CH_2{=}CH)_4Si][Ni(PPh_3)_2]_2 \cdot Et_2O$ was 1.60 g (58%), m.p. 140–144°C (dec.) (benzene–ether). Found: C, 73.68; H, 5.90. $C_{84}H_{82}Ni_2OP_4Si$ calcd.: C, 73.27; H, 6.00%.

Method III

(π-Divinyldimethylsilane)bis(triphenylphosphine)nickel(II). A benzene solution of triphenylphosphine (18 mmol) was added to a mixture of $(\pi\text{-}C_8H_{12})_2Ni$ (9 mmol) and divinyldimethylsilane (43 mmol) in 20 ml of benzene at 22°C. The reaction mixture was stirred for 18 hours. It was then evaporated to dryness; the residue was dissolved in a minimum amount of ether and treated with pentane. The yellow precipitate formed was filtered off, washed with pentane and dried in vacuum. 3.97 g (65%) of $[(CH_2{=}CH)_2SiMe_2]Ni(PPh_3)_2$ was obtained, m.p. 102–105°C (dec.)(ether). Found: C, 71.42; H, 6.03. $C_{42}H_{42}NiP_2Si$ calcd.: C, 72.53; H, 6.09%.

(π-Divinyldimethylsilane)triphenylphosphinenickel(IV). The yield of $[(CH_2{=}CH)_2SiMe_2]Ni(PPh_3)$ was 2.43 g (66%), m.p. 123–125°C (dec.) (benzene–ether). Found: C, 66.82; H, 6.38. $C_{24}H_{27}NiPSi$ calcd.: C, 66.53; H, 6.29%.

(π-Tetravinylsilane)tetrakis(triphenylphosphine)dinickel(III). The yield of $[CH_2{=}CH)_4Si][Ni(PPh_3)_2]_2 \cdot Et_2O$ was 4.00 g (68%), m.p. 140–143°C (dec.) (benzene–ether). Found: C, 71.83; H, 6.05. $C_{84}H_{82}Ni_2OP_4Si$ calcd.: C, 73.27, H, 6.00%.

(π-Tetravinylsilane)triphenylphosphinenickel)(Va) and (π-tetravinylsilane)bis(triphenylphosphine)dinickel(Vb). 2.40 g of a mixture of complexes Va and Vb in the ratio 2:1 was obtained, m.p. 130–133°C (dec.) (benzene–ether).

(π-Vinyltrimethylsilane)bis(triphenylphosphine)nickel (Ia). The yield of $(CH_2{=}CHSiMe_3)Ni(PPh_3)_2$ was 2.06 g (35%), m.p. 128–132°C (dec.). Found: C, 71.94; H, 6.18. $C_{41}H_{42}NiP_2Si$ calcd.: C, 72.04; H, 6.19%. A yellow-brown product (2.02 g) consisting of a mixture of Ia and $Ni(PPh_3)_3$ was isolated from the mother liquor

after separation of complex Ia. The ^{31}P-{^{1}H} NMR spectrum of this mixture recorded in toluene at -70°C contained two singlets at δ 39.53 and 22.11 ppm. According to the literature data [14], the ^{31}P-{^{1}H} NMR spectrum of $Ni(PPh_3)_3$ recorded in deuterotoluene at -80°C shows a singlet at δ 21.8 ppm.

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