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REVERSIBLE INSERTION OF NORBORNENE INTO A NICKEL—METHALLYL BOND

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Summary

Norbornene reacts at room temperature with π-methallyl nickel chloride giving a red-brown complex in which norbornene is presumably π-bonded to nickel. This complex gives, on reaction with $KOOCCH_3$, an acetato-bridged compound, $(C_{11}H_{17}NiOCOCH_3)_2$, in which norbornene is inserted into the nickel—methallyl bond. X-ray structural analysis of the acetato complex indicates an *exo-cis* insertion of norbornene. The insertion reaction was found to be reversible, depending on the anionic ligand, as shown by the fact that reaction of the acetato compound with HCl, LiBr or KI gives again π-methallyl halide and norbornene.

Introduction

In recent years insertion reactions into transition metal—carbon bonds have been intensively investigated, because of their importance in the field of catalysis [1-5].

We report in this paper on the insertion reaction of norbornene into a nickel—methallyl bond*. From the reaction of norbornene and π-methallyl—NiCl we have isolated a crystalline compound, some derivatives of which contain one molecule of norbornene inserted into the nickel—carbon bond. Single crystal X-ray structural analysis of these compounds has shown that the insertion is of the *exo-cis* type. It has also been found that norbornene insertion is reversible, depending on the anionic ligand bonded to nickel.

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* A preliminary account on this work has already been published [6].

Insertion reactions of norbornene into a palladium—allyl bond have been investigated by Hughes and Powell using NMR methods and have been reported while this work was in course [4,5].

Results and discussion

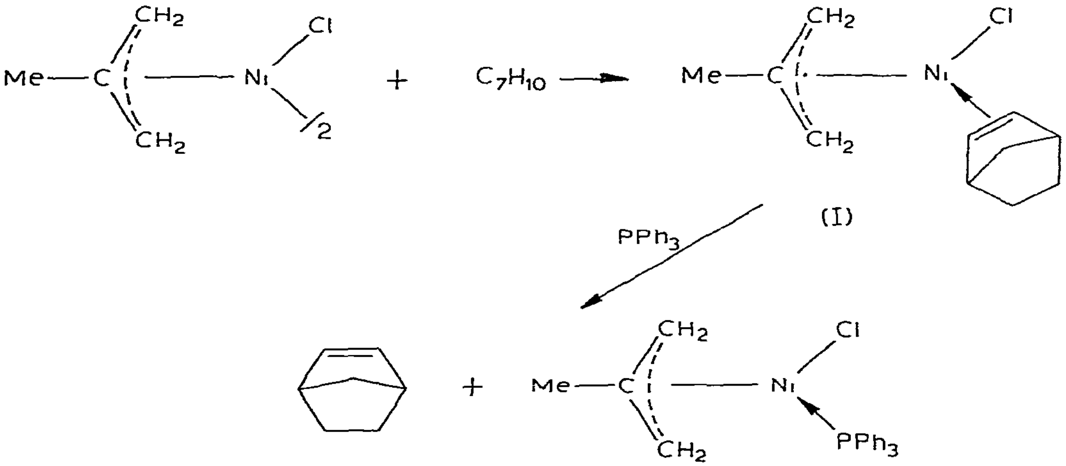
The reaction of norbornene with π-methallyl nickel chloride in benzene solution, at room temperature, yields a crystalline red precipitate of formula $C_{11}H_{17}NiCl$ (I). The analogous reaction of norbornene with π-allyl nickel chloride does not yield a crystalline precipitate, but proceeds further after the insertion of one norbornene molecule, with formation of oligomers and polymers. The different behaviour between the allyl and the methallyl derivative is presumably due to the influence of the methyl group in stabilizing the π-allyl bond.

Complex I is stable at room temperature under N_2, but rapidly decomposes in the air. It is diamagnetic, insoluble in ethanol but slightly soluble in benzene and chlorinated solvents.

Reaction of I with PPh_3 at a P/Ni ratio of about 0.5 yields $(\pi\text{-}C_4H_7)NiCl \cdot PPh_3$, whereas at higher P/Ni ratios $(PPh_3)_3NiCl$ is obtained. When I is heated in a sublimation apparatus at 80°C in high vacuum, π-methallyl nickel chloride and norbornene are obtained in a yield of about 80%.

All the above findings suggest that in complex I norbornene is coordinated to nickel and that the reactions reported above occur according to Scheme 1.

SCHEME 1



This scheme is consistent with the ^1H NMR spectrum of complex I. The singlets at τ 7.65, 8.07 and 8.23, with relative intensities 2/2/3, are assigned to the methallyl ligand on the basis of the data reported in the literature [7].

The signal at τ 6.27 (relative intensity 2) is attributed to protons H(2) and H(3) of the double bond of norbornene π-bonded to metal; the signal at τ 7.21 is attributed to protons H(1) and H(4). All the other signals due to the saturated hydrogens of norbornene lie between τ 8.23 and 9.43.

Various reactions of I lead to the formation of products that derive from

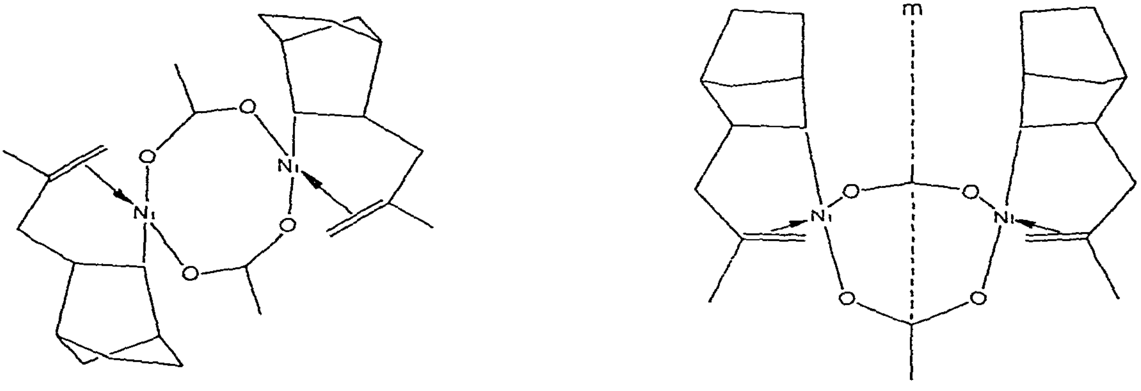


Fig. 1. (Va) (Vb)

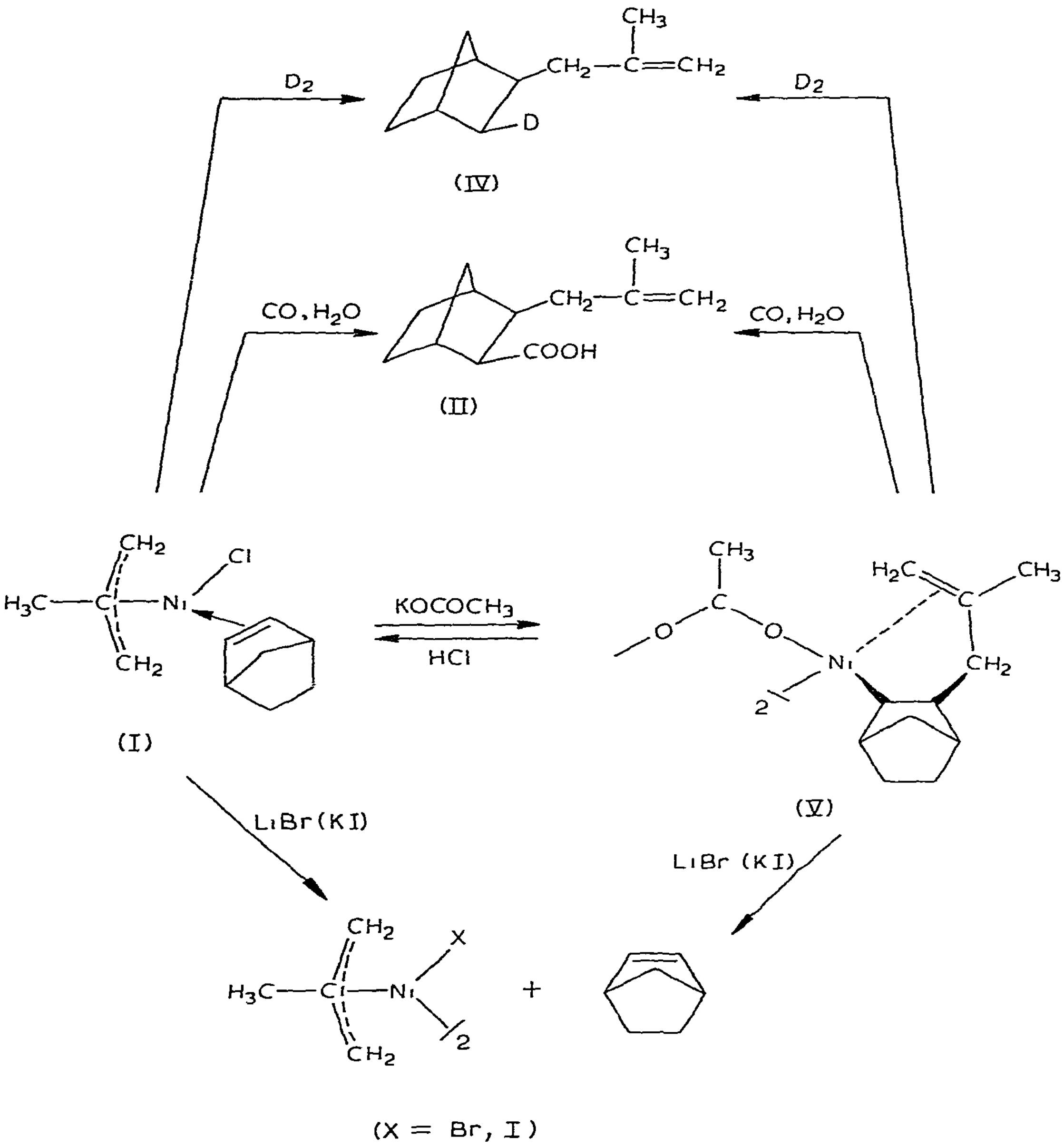
the insertion of norbornene into the nickel—allyl bond. (*1*) Reaction of I with carbon monoxide in toluene at about −40°C, followed by hydrolysis, gives 3-*exo*-methallyl-2-*exo*-norbornylic acid (II) with minor amounts (~5%) of the 2-*endo* isomer. The *exo* structure of II has been determined by single crystal X-ray examination [8]. (*2*) Reaction of complex I with H_2 in methanol suspension gives 2-*exo*-methallylnorbornane (III), along with metallic nickel and nickel chloride. The analogous reaction with D_2 in CD_3OD gives 2-*exo*-d-3-*exo*methallylnorbornane (IV). The *exo* configuration of IV has been assigned on the basis of the ^1H NMR spectrum, which shows two *exo* protons (τ 8.4 ÷ 8.6) and four *endo* protons (τ 8.8 ÷ 9.1), and has also been confirmed by the fact that compound IV can also be obtained from the reaction of complex V (see below) with D_2. (*3*) Treatment of complex I with $KOCOCH_3$ in petroleum ether leads to the formation of a red crystalline solid, soluble in hydrocarbon solvents, of stoichiometry $C_{11}H_{17}NiOOCCH_3$ (V). In different crystallizations we isolated crystals of two different shapes but of the same stoichiometry. The structure of both of them was determined by X-ray analysis, which showed them to be the acetato-bridged configurational isomers (Va and Vb) represented in Fig. 1 [9]. Treatment of complex I with $KOCOCF_3$ gives a red crystalline complex, whose structure, determined by X-ray analysis, was found to be similar to that of complex Vb, but with one of the trifluoroacetato bridges much more distant from the nickel atom [10].

Treatment of V with PPh_3 in benzene gives a red-brown complex, $C_{11}H_{17}NiOCOCH_3 \cdot PPh_3$, soluble in aromatic and chlorinated solvents, sparingly soluble in polar solvents. Complex V gives the acid II on reaction with CO and compound III on reaction with H_2.

The geometry of complexes V, in which the norbornene moiety is *exo* bonded to both the nickel atom and the methallyl group, indicates that insertion of norbornene occurs through a *cis* addition of the nickel—carbon bond to the coordinated norbornene. Also, the products of the reaction of I with D_2 and CO are consistent with an *exo-cis* insertion of the norbornene.

It is known that various transition metal catalysts are capable of polymerizing norbornene to polymers constituted of monomeric units of 2,3-linked norbornane. The insertion reactions described above represent an individual

SCHEME 2

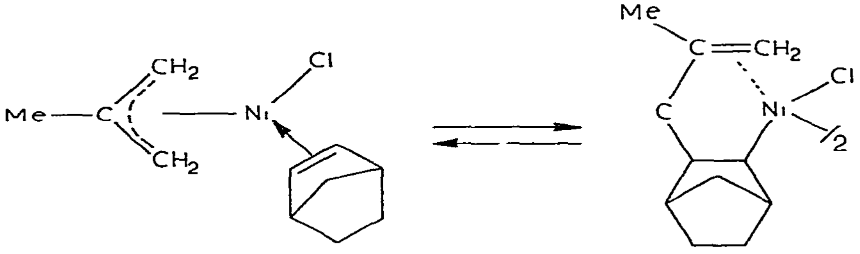


step of the polymerization and constitute direct evidence for the *cis* insertion of the monomer. The same conclusion, with regard to the mode of monomer insertion in polymerizations by transition metal catalysts, has been reached by various authors on the basis of the structure of olefin polymers derived from partially deuterated monomers [11-14].

Replacement of the acetato group in complex V by Cl, Br or I was found to cause the disinsertion of norbornene. Thus, complex V reacts with HCl in diethyl ether to give again complex I, and with LiBr of KI in acetone to yield

π-methallyl—Ni-Br or -I and free norbornene (Scheme 2). Reversible insertions of this type have been observed with carbon monoxide [15], but are rather unusual with olefinic compounds.

At least two factors seem to contribute to the driving force for the reverse reaction: (*a*) the different *trans* effect of the anionic ligand bonded to nickel; (*b*) the tension of the substituted norbornane ring. It is also possible that I exists, in solution, in equilibrium with a very small amount of the species I′ with the norbornene inserted:



(I)

(I′)

The presence of such an equilibrium could easily explain the reactions of I with CO, H_2 and $KOCOCH_3$, and also the reactions of V with HCl or LiBr.

Experimental

All operations were carried out in an atmosphere of dry nitrogen. All solvents were dried and deoxygenated before use. NMR spectra were recorded on a Brucker 90 MHz spectrometer; all the chemical shifts were measured with respect to internal C_6H_6 or $CHCl_3$ and subsequently transformed in τ units. Infrared spectra were determined on a Perkin—Elmer 475 recording spectrometer. Mass spectra were obtained on a RMV 6D SN spectrometer.

Reaction of π-methallyl nickel chloride with norbornene

(π-C_4H_7)NiCl (1 g, 6.7 mmol) and norbornene (1 g, 10.6 mmol) were dissolved in benzene (15 ml) and the solution was allowed to stand for 24 h at room temperature. The red-brown solid formed (I) was isolated by filtration, washed thoroughly with ethanol, then with n-pentane, and finally dried in vacuo. Complex I is stable under N_2 at room temperature, but is rapidly decomposed in air. Yield ca. 90%. (Anal. Found: C, 54.02; H, 7.17; Cl, 14.6; Ni, 24. $C_{11}H_{17}ClNi$ calcd.: C, 54.27; H, 7.03; Cl, 14.56; Ni, 24.11%.)

Reaction of complex I with PPh₃

Triphenyl phosphine (35 mg, 0.13 mmol) was added to a solution of complex I (45 mg, 0.3 mmol) in benzene (15 ml). After about 10 min the red-brown solution was evaporated and the solid residue was recrystallized from benzene/n-pentane (1/1) at 0°C to give dark red crystals (50 mg) identified as (π-C_4H_7)-NiCl · PPh_3. (IR and NMR spectra identical with those of an authentic sample.) (Anal. Found: C, 65.5; H, 5.41; Cl, 8.40. (C_4H_7)NiCl · P(C_6H_5) calcd.: C, 64.2; H, 5.38; Cl, 8.61%.)

Reaction of complex I with H_2

Hydrogen was bubbled at room temperature through a stirred suspension of $(C_{11}H_{17})NiCl$ (0.5 g, 2 mmol) in MeOH (10 ml). After about 2 h the suspension was filtered and the filtrate distilled in vacuo. From the distillate a liquid product was isolated (0.25 g, b.p. 80°C/18 Torr) via preparative vapor phase chromatography. The product was found to be identical (NMR, IR) with an authentic sample of *exo*-methallylnorbornane (III). Yield ca. 83%. Anal. Found: C, 87.5; H, 12.0. $C_{11}H_{18}$ calcd.: C, 87.92; H, 12.07%.)

The reaction between D_2 and I was carried out under the same conditions in CD_3OD. The product was identified as 2-*exo*-*d*-3-*exo*-methallylnorbornane (IV) on the basis of ^1H NMR (see results and discussion).

Reaction of complex I with carbon monoxide

A solution of complex I (1 g, 4 mmol) in toluene (100 ml) was cooled to —40°C, and connected, with stirring, to a carbon monoxide container. When carbon monoxide absorption was completed (about 2 h), 2 ml of water were added, while stirring was continued.

The solution was allowed to reach room temperature, then was repeatedly washed with water in a separatory funnel, and finally dried over $MgSO_4$. The filtered solution was evaporated under reduced pressure to give as residue white crystals identified as 3-*exo*-methallyl-2-*exo*-norbornylic acid (II) (0.67 g, yield ca. 86%) m.p. 105°C; *m/e* 194. (Anal. Found: C, 74.02; H, 9.17. $C_{12}H_{18}O_2$ calcd.: C, 74.19; H, 9.33%.)

Reaction of complex I with CH_3COOK

A suspension of potassium acetate (5 g) and complex I (0.5 g, 2.05 mmol) in n-pentane (20 ml) was shaken for about 2 h, during which time complex I slowly dissolved. The resultant red-brown mixture was filtered to separate NaCl and the filtrate was evaporated under reduced pressure to give red crystals (0.49 g) soluble in the common organic solvents. (Anal. Found: C, 58; H, 7.6; Ni, 23. $C_{13}H_{20}NiO_2$ calcd.: C, 58.47; H, 7.54; Ni, 21.98%.) The compound was identified as di-μ-acetato-bis(*exo*-3-methallyl-norborn-2-yl-*exo*-nickel) (V) on the basis of X-ray structural analysis on single crystals [9].

The reaction between complex I and $KOCOCF_3$ was carried out in a similar way and gave red crystals of a complex identified, by elemental analysis and X-ray structure determination [10], as the trifluoroacetato corresponding to complex Vb. (Anal. Found: C, 48.5; H, 5.40; F, 16.00; Ni, 18.00. $NiC_{13}H_{17}F_3O_2$ calcd.: C, 48.64; H, 5.30; F, 15.89; Ni, 18.30%.)

Reaction of complex V with H_2

Hydrogen was bubbled through a solution of the acetato complex V (0.5 g, 1.87 mmol) in CCl_4 (10 ml) until decoloration occurred. The solution was filtered, CCl_4 was removed under vacuum at room temperature, leaving a liquid residue, which was analyzed by GLC, IR and NMR analysis. By comparison with an authentic sample it was found to consist of 2-*exo*-methallylnorbornane (0.24 g), with minor amounts (~4%) of the *endo* isomer, and traces of 2-*exo*-iso-propylnorbornane.

Reaction of complex V with carbon monoxide

A slow stream of carbon monoxide was bubbled through a solution of V (0.5 g, 1.87 mmol) in n-pentane (20 ml) for about 2 h. The resultant solution was evaporated under reduced pressure giving a residue of composition $C_{14}H_{20}O_3$, whose IR spectrum shows two bands (1805 and 1740 cm^{-1}) typical of the C=O group of anhydrides.

Treatment of $C_{14}H_{20}O_3$ with hot 10% KOH followed by acidification with dilute H_2SO_4 gave acid II, and CH_3COOH, which indicates compound $C_{14}H_{20}O_3$ to be the mixed anhydride of II and CH_3COOH.

Reaction of complex V with PPh_3

Triphenylphosphine (53 mg, 0.2 mmol) was added to a solution of complex V (54 mg, 0.2 mmol) in benzene (15 ml). After about 30 min the solution was evaporated to 4 ml under reduced pressure, n-pentane (5 ml) was added, and the solution left at room temperature. Red crystals of formula $C_{11}H_{17}NiOCOCH_3$ PPh_3 (60 mg) separated in a few hours. (Anal. Found: C, 70.1; H, 6.5; P, 6.2; Ni, 11.5. $C_{31}H_{35}NiO_2P$ calcd.: C, 70.34; H, 6.66; Ni, 11.09; P, 5.05%.)

Reaction of complex V with KI and LiBr

Potassium iodide in slight excess was added to a solution of $(C_{11}H_{17})NiOAc$ (0.5 g, 1.87 mmol) in acetone (15 ml). The mixture was stirred for about 30 min, filtered, and the filtrate evaporated under reduced pressure. The residual solid was crystallized from n-pentane at —80°C to give red crystals (0.43 g, 1.8 mmol) identified as π-methallyl nickel iodide by comparison with an authentic sample. (Anal. Found: C, 19.61; H, 2.78; I, 53.3; Ni, 24.4. C_4H_7NiI calcd.: C, 19.95; H, 2.94; I, 52.7; Ni, 24.38%.)

Lithium bromide in slight excess was added to a solution of complex V (0.5 g) in acetone (10 ml) and the solution treated as in the reaction with KI. Red crystals were obtained, identified as π-methallyl nickel bromide by comparison with an authentic sample. (Anal. Found: C, 25.1; H, 3.8; Br, 40.9; Ni, 29.9. C_4H_7BrNi calcd.: C, 24.80; H, 3.64; Br, 41.24; Ni, 30.30%.)

A diethyl ether solution of HCl (1.87 mmol) was added to an ethereal solution of complex V (0.5 g, 1.87 mmol, in 20 ml). A red-brown precipitate immediately formed (0.45 g), which was identified as complex I on the basis of elemental analysis, IR, X-ray powder spectrum and chemical behaviour (reaction with PPh_3 and $KOCOCH_3$).

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