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π-ALLYLNICKEL COMPLEXES FROM CONJUGATED DIOLEFINS AND NICKEL HALIDES

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Summary

Some π-allylnickel derivatives were prepared in good yield and under mild conditions from the reaction of conjugated dienes and nickel halides in the presence of metallic zinc.

Introduction

In a previous paper we reported the preparation of *anti*-π-2-butenylbutadiene(triphenylphosphine)cobalt, (π-C_4H_7)(C_4H_6)$CoPPh_3$, by the reaction of butadiene with cobalt(II) chloride, zinc and triphenylphosphine [1]. This preparation was of special interest, because π-butenyl complexes of *anti* configuration are difficult to prepare owing to their much lower thermodynamic stability with respect to *syn* isomers. We have now extended the reaction to nickel halides, in order to see whether butenyl complexes of *anti* configuration could also be obtained in this case. More generally the reaction with nickel halides also appeared of interest as a new preparative method for π-allyl derivatives of nickel, which are important in the field of homogeneous catalysis [2]. We describe below the reactions of butadiene, isoprene and 2,3-dimethylbutadiene with nickel chloride and metallic zinc.

Results and discussion

Conjugated diolefins react rapidly with nickel chloride in the presence of zinc to give π-allyl products of the type I-III. The course of the reactions is summarized in Table 1. Complexes I were prepared by treating butadiene, isoprene or 2,3-dimethylbutadiene with nickel chloride, metallic zinc, ethanol, and

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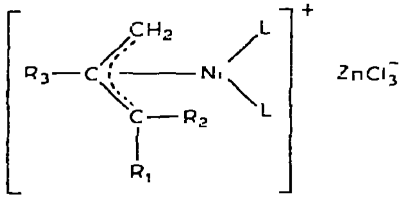
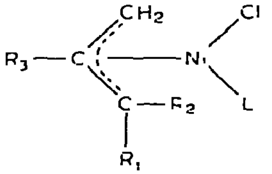
TABLE 1

π-ALLYL COMPLEXES PREPARED FROM DIENES

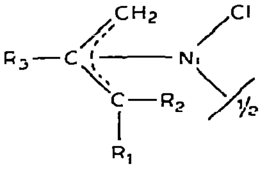
Diolefin	Solvent(ligand)	Temp. (°C)	Time (h)	π-Allyl products	Yield (%)
1,3-Butadiene	C_6H_6/EtOH(PPh$_3$)	18	2	$[(\pi\text{-}C_4H_7)Ni(PPh_3)_2]^+ZnCl_3^-$ (Ia)	25
1,3-Butadiene	CH_3CN	0	12–48	$(\pi\text{-}C_4H_7)_nNiCl$ $(1 < n < 4)$	25
Isoprene	EtOH(PPh$_3$)	70	0.2	$[(\pi\text{-}C_5H_9)Ni(PPh_3)_2]^+ZnCl_3^-$ (Ib + Ic) $(\pi\text{-}C_5H_9)Ni(PPh_3)Cl$ (IIb)	30 15
Isoprene	CH_3CN	0	48	$[(\pi\text{-}C_5H_9)NiCl]_2$ (IIIb)	25
2,3-Dimethyl-1,3-butadiene	EtOH(PPh$_3$)	80	0.2	$[(\pi\text{-}C_6H_{11})Ni(PPh_3)_2]^+ZnCl_3^-$ (Id) $(\pi\text{-}C_6H_{11})Ni(PPh_3)Cl$ (IId)	35 20



(Ia-d)



(IIa-d)



(IIIb)

(a) $R_1 = Me$, $R_2 = H$, $R_3 = H$,
(b) $R_1 = Me$, $R_2 = Me$, $R_3 = H$,
(c) $R_1 = H$, $R_2 = Me$, $R_3 = Me$;
(d) $R_1 = Me$, $R_2 = Me$, $R_3 = Me$;

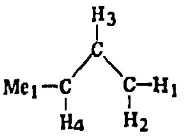
$L = PPh_3$

triphenylphosphine. Formation of large amounts of metallic nickel was observed in the absence of triphenylphosphine. The complexes are red-orange, diamagnetic, crystalline solids and are unstable in air. They are almost insoluble in hydrocarbon solvents, sparingly soluble in polar solvents (methanol, ethanol), and soluble in chloroform and pyridine. The solutions in alcohols, chloroform or pyridine are unstable, and give complexes II almost quantitatively. The complexes were identified from their elemental analyses and chemical properties (reaction with pyridine, ethanol, chloroform); the identity of complex Id was confirmed by X-ray analysis [3].

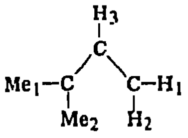
Complexes II can be conveniently prepared from complexes I by reaction with small amounts of pyridine (Py/Ni 2/1) in benzene solution. With isoprene and 2,3-dimethylbutadiene, complexes II were always formed along with com-

TABLE 2

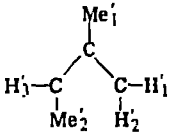
NMR DATA[a] FOR THE COMPLEXES II AND III



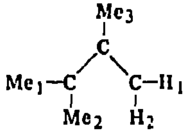
(a)



(b)



(c)



(d)

Complex	H_1	H_2	H_3	H_4	Me_1	Me_2	Me_3	H'_1	H'_2	H'_3	Me'_1	Me'_2
$(\pi\text{-}C_4H_7)Ni(PPh\ )Cl$ (IIa)	5.23 dd; J_2 2.5 Hz, J_3 7.5 Hz	5.79 dd; J_3 13 Hz	2.34 dt; J_4 13 Hz	3.39 dq[b] $J(Me_1)$ 6 Hz	5.73 d							
$(\pi\text{-}C_5H_9)Ni(PPh_3)Cl$ (IIb)	5.22 dd; J_2 3 Hz, J_3 7.5 Hz	5.63 dd; J_3 13 Hz	2.34 dd		5.64 s	6.01 s						
$(\pi\text{-}C_5H_9)Ni(PPh_3)Cl$ (IIb + IIc)	5.23 dd; J_2 3 Hz, J_3 7.5 Hz	5.66 dd; J_3 13 Hz	2.33 dd		5.65 s	6.01 s		5.34 s	6.03 s	3.45 q; $J(Me'_2)$ 6.5 Hz	5.5 s	5.79 d
$(\pi\text{-}C_6H_{11})Ni(PPh_3)Cl$ (IId)	5.33[c]	5.33[c]			5.71 d; $J(P)$ 5 Hz	5.9 d; $J(P)$ 3.5 Hz	5.33 s					
$[(\pi\text{-}C_5H_9)NiCl]_2$ (IIIb)	4.41 dd; J_2 1 Hz, J_3 7 Hz	5.29 dd; J_3 13 Hz	2.52 dd		6.56 s	6.6 s						

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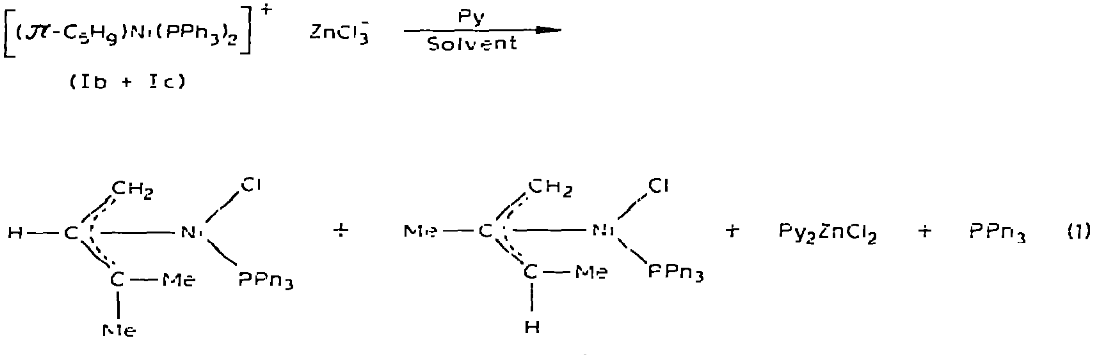
[a] Measured in C_6D_6. The chemical shifts are in ppm relative to internal benzene; s, singlet; d, doublet; q, quartet; dd, doublet of doublets; dt, doublet of triplets; dq, doublet of quartets. [b] Overlapping quartets appeared as six lines. [c] Observed only by integration.

plexes I (Table 1) and were separated from the latter by extraction with benzene. The complexes II were identified from their elemental analyses and NMR spectra, which are summarized in Table 2.

The complex $[(\pi\text{-}C_5H_9)Ni(PPh_3)_2]^+ZnCl_3^-$, prepared using isoprene as the diolefin, gives after treatment with chloroform or pyridine in benzene (eqn. 1), 1,1-dimethyl- and *anti*-1,2-dimethyl-π-allylnickel(triphenylphosphine) chloride in the ratio 1.5/1 (by NMR analysis). The ratio of the two isomers in the NMR spectra does not change with time or temperature.

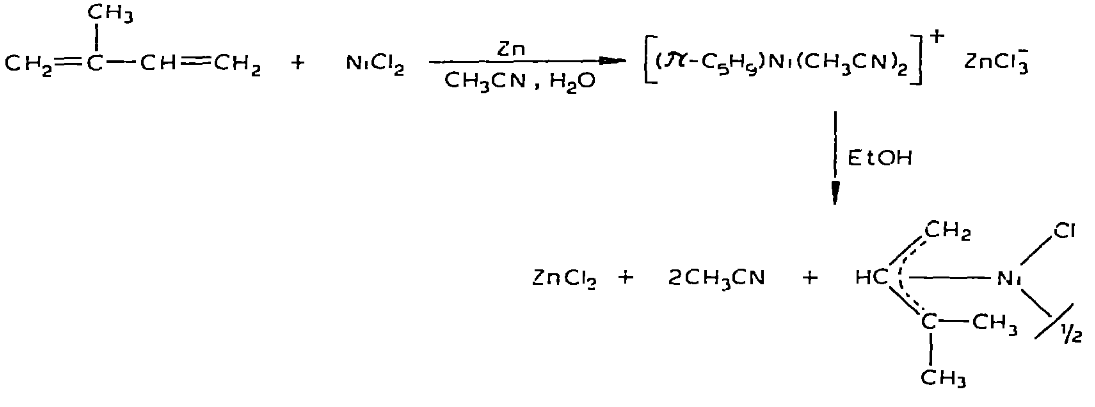


(IIb) 60%   (IIc) 40%

An interesting first example of isomerization of a 1,1-dimethyl-π-allyl compound to the corresponding 1,2-dimethyl-π-allyl compound has been recently reported for complexes of cobalt and rhodium [4]. In view of the very mild conditions of reaction 1, a similar isomerization seems to be ruled out in our case. It is reasonable to believe that the starting complex $[(\pi\text{-}C_5H_9)Ni(PPh_3)_2]^+ZnCl_3^-$ is a mixture of the two isomers Ib and Ic.

It can be seen from Table 2 that the *syn* isomer was obtained from butadiene and the *anti*-1,2-dimethyl isomer from isoprene. A possible interpretation of this unexpected result is that the *anti* isomer is initially formed in both cases, as observed for the analogous reaction of cobalt [1], and that subsequently an *anti*—*syn* isomerization occurs by action of triphenylphosphine. The transformation into the more stable *syn* isomer could be much slower for the compound with isoprene because of steric effects.

The (1,1-dimethyl-π-allyl)nickel chloride (IIIb), which is an important



(IIIb)

starting material in terpenoid synthesis [5], can be obtained easily by reaction at 0° of nickel chloride and isoprene with metallic zinc in acetonitrile in the presence of water; formation of metallic nickel is not observed under these conditions. A red oily product of approximate composition $[(\pi\text{-}C_5H_9)Ni(CH_3CN)_2]^+$-$ZnCl_3^-$ is obtained from the solution, and after treatment with ethanol this gives (1,1-dimethyl-π-allyl)nickel chloride, identified by its elemental analysis and NMR spectrum (Table 2).

The same reaction with butadiene gave oily compounds of composition $(\pi\text{-}C_4H_7)_nNiCl$ $(1 < n < 4)$. 2,3-Dimethylbutadiene reacts under these conditions but to give very low yields of products. The mechanism of formation of complexes I-III has not been completely clarified, but the following observations can be made.

(1) Small amounts of water are essential in the formation of the complexes; this suggests that water may be the hydrogen source for the formation of a Ni—H bond. The π-allyl group could probably form by reaction of the Ni—H bond with a coordinated diene.

(2) We were unable to prepare complexes I by reaction of the corresponding complexes II with triphenylphosphine and zinc chloride. The insertion of the diolefin probably occurs by reaction with intermediates which already contain zinc.

(3) The reaction in benzene of nickel chloride and triphenylphosphine with ethanol and zinc in the absence of diolefins rapidly gives a mixture of $(PPh_3)_2NiZnCl_2$ and $(PPh_3)_nNi$ $(n = 3,4)$ in a ratio depending on the amount of triphenylphosphine [6]. If small amounts of water are added. the yellow complex $(PPh_3)_3NiCl$ is also formed, with evolution of hydrogen. Hydrolysis of $ZnCl_2$ to form HCl and subsequent oxidative addition to Ni^0 species could occur: the resultant unstable species L_nNiHCl could rapidly decompose to give Ni^I complexes and hydrogen, but in the presence of a diolefin could give a π-allyl complex.

Experimental

All reactions and manipulations were carried out under pure dry nitrogen. Solvents were used after drying and distillation. NMR spectra were obtained on a BRUKER 90 MHz spectrometer.

Preparation of $[(\pi\text{-}C_4H_7)Ni(PPh_3)_2]^+ZnCl_3^-$ (Ia)

Butadiene (20 ml), ethanol (10 ml), benzene (20 ml), triphenylphosphine (3.44 g, 1.31 mmoles), nickel chloride (1.7 g, 1.31 mmoles) and zinc powder (7 g) were successively introduced into a glass vessel. The suspension was kept at room temperature for ca. 2 h, with occasional shaking. The colour rapidly changed to red. The suspension was filtered at ca. —10° with rigorous exclusion of air; the filtrate was concentrated under reduced pressure to 30 ml and n-pentane (5 ml) was added. The solution was set aside, and after a few days gave red-orange crystals of Ia (2.7 g, yield 25%). (Found: C, 59.2; H, 4.7; Cl, 13.22; Ni, 7.41; Zn, 7.89. $C_{40}H_{37}Cl_3NiP_2Zn$ calcd.: C, 59.3; H, 4.6; Cl, 13.12; Ni, 7.24; Zn, 8.06%.)

From the mother liquor after concentration to small volume was obtained the known complex $(PPh_3)_3NiCl$ [7] (1.6 g, yield 15%). (Found: C, 79.12; H, 5.5; Cl, 4.4; Ni, 7.31. $C_{54}H_{45}ClNiP$ calcd.: C, 79.2; H, 5.54; Cl, 4.33; Ni, 7.17%.)

Preparation of $[(\pi\text{-}C_5H_9)Ni(PPh_3)_2]^+ZnCl_3^-$ (Ib,c)

A mixture of 2.5 g (19.3 mmoles) of nickel chloride, 5.06 g (19.3 mmoles) of triphenylphosphine, 10 g (150 mmoles) of zinc dust, 50 ml of isoprene and 15 ml of ethanol was boiled under reflux with magnetic stirring for 15 min. The resulting red solution was filtered and concentrated to 35 ml and n-pentane (5 ml) was added. The product Ib,c precipitated as yellow-red crystals (4.78 g, yield 30%). (Found: C, 59.84; H, 4.68; Cl, 12.87; Ni, 7.25; Zn, 7.8. $C_{41}H_{39}Cl_3NiP_2Zn$ calcd.: C, 59.8; H, 4.77; Cl, 12.9; Ni, 7.12; Zn, 7.93%.)

The mother liquor was concentrated to small volume (5 ml) and n-pentane (5 ml) was added. By cooling to −20° a red solid was obtained. Recrystallization from benzene/n-pentane afforded red-brown crystals of IIb (1.24 g, yield 15%). (Found: C, 64.81; H, 5.72; Cl, 8.28; Ni, 13.7. $C_{23}H_{24}ClNiP$ calcd.: C, 64.9; H, 5.66; Cl, 8.33; Ni, 13.8%.)

Preparation of $[(\pi\text{-}C_6H_{11})Ni(PPh_3)_2]^+ZnCl_3^-$ (Id)

A mixture of 2.5 g (19.3 mmoles) of nickel chloride, 5.06 g (19.3 mmoles) of triphenylphosphine, 10 g of zinc dust, 50 ml of 2,3-dimethylbutadiene and 15 ml of ethanol was boiled under reflux with magnetic stirring for 15 min. The resulting red solution was filtered and concentrated to 35 ml, and n-pentane (5 ml) was added. A mixture of red-orange (Id) and red-brown (IId) crystals gradually formed. Extraction with benzene removed complex IId, and the residual Id was dried under vacuum (5.66 g, yield 35%). (Found: C, 60.14; H, 5.01; Cl, 12.73; Ni, 7.11; Zn, 7.66. $C_{42}H_{41}Cl_3NiP_2Zn$ calcd.: C, 60.2; H, 4.95; Cl, 12.68; Ni, 7.0; Zn, 7.79%.) Compound IId was obtained from the benzene extract, after removal of the solvent under reduced pressure (1.7 g, yield 20%). (Found: C, 65.65; H, 5.91; Cl, 8.0; Ni, 13.49. $C_{24}H_{26}ClNiP$ calcd.: C, 65.6; H, 5.96; Cl, 8.07; Ni, 13.35%.)

Preparation of (1,1-dimethyl-π-allyl)nickel chloride (IIIb)

Zinc powder (1.2 g, 18.4 mmoles) was added to a suspension of acetonitrile (20 ml), isoprene (10 ml), water (0.36 ml, 17 mmoles) and nickel chloride (1.1 g, 8.5 mmoles) at −5°. The mixture was set aside for two days at 0° with occasional shaking, during which time the colour changed gradually from pale yellow to orange, then to red. The solution was filtered and the solvent evaporated under reduced pressure. The red oily product obtained was dissolved in ethanol and the solution evaporated at 0° and 0.5 mmHg pressure. Recrystallization of the residue from n-pentane at −78° gave IIIb (0.35 g, yield 25%). (Found: C, 36.79; H, 5.61; Cl, 21.7; Ni, 35.85. C_5H_9ClNi calcd.: C, 36.75; H, 5.56; Cl, 21.74; Ni, 35.95%.)

Preparation of complexes II from I by reaction with pyridine

Only the preparation of compound IId is described in detail, the experimental procedure being substantially the same for all other compounds of the same type.

To a suspension of 1.5 g (1.79 mmoles) of the complex $[(\pi\text{-}C_6H_{11})Ni$-

$(PPh_3)_2]^+ZnCl_3^-$ (Id) in benzene (20 ml), 0.3 ml (3.6 mmoles) of pyridine were added and the mixture was shaken for ca. 2 h. After this time the solution was concentrated to a small volume (3 ml) and n-pentane (5 ml) was added. The product was precipitated by cooling to 0° and was recrystallized from benzene/n-pentane (1/1 by v/v) to give red-brown crystals of IId (0.70 g, yield 90%). (Found: C, 65.54; H, 5.9; Cl, 8.13; Ni, 13.29. $C_{24}H_{26}ClNiP$ calcd.: C, 65.6; H, 5.96; Cl, 8.07; Ni, 13.35%.)

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