PENTACOORDINATED NICKEL COMPLEXES AS INTERMEDIATES IN CARBONYLATION REACTIONS OF ALLYL COMPOUNDS

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SUMMARY

Preparation and properties of a new class of halo(carbonyl)(phosphine)-(π-allyl)nickel complexes are discussed. All the possible equilibria appear to exist in solution. Evidence is given that pentacoordinated intermediates are involved in carbonylation reactions.

INTRODUCTION

We recently reported[1] the formation of halo(carbonyl)(phosphine)(π-allyl)-nickel complexes, (I). These complexes appear able to undergo carbonylation and
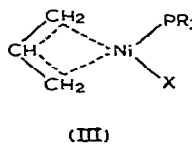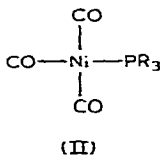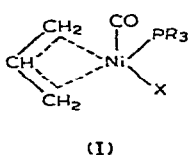
other insertion reactions. We have therefore carried out a study of the preparation, properties and reactivity of this class of complexes in order to clarify the part played by pentacoordinated structures in insertion reactions, and the dependence of the ease of such reactions on the mobility of the ligands.

RESULTS

The new class of pentacoordinated complexes can be prepared in two distinct ways, starting from phosphine carbonyls such as (II), or allyl complexes such as (I) or (III)[2,3]. PR_3 is a phosphine (R = alkyl or aryl) and X is Br, I. Other allylic ligands may replace the allyl group in (III) and (I).

An important feature of the pentacoordinated complexes is that they are in equilibrium with the tetracoordinated complexes (III). In order to effect their separation a solvent in which they are only slightly soluble must be chosen. Thus allyl halides slowly react with (II)(R = C_6H_5) in benzene/methanol (9/1 in volume) at room temperature with formation of the corresponding complex (I). Starting from (III) in the same medium, the uptake of 1 mole of carbon monoxide results in the separation of the same complex (I). In all cases well-crystallized solids separate from the mixture. They are generally fairly pure, but they can also be easily crystallised out of contact with air.

PROPERTIES

The solids thus obtained are intensely coloured (orange to red) and air sensitive. They are diamagnetic. They conduct in solution more than the corresponding tetracoordinated complexes (III), thus indicating a dissociation.

The k values (determined at 25° in a 0.072 M solution of the complexes in a 9/1 mixture of benzene/methanol) are $7 \cdot 10^{-7} \, \Omega^{-1} \cdot cm^{-1}$ for (III) (R$=C_6H_5$, X$=$I), and $9 \cdot 10^{-6}$ for the corresponding (I). In the same conditions tetrabutylammonium iodide gives $7.9 \cdot 10^{-5}$.

In the solid state complexes (I) turn out to be pentacoordinated, as revealed by X-ray measurements on (I) (R$=C_6H_5$, X$=$I) (limited to two dimensional analysis, owing to gemination of crystals[4]), which indicate a Ni–P distance of about 2.35 Å, a Ni–I distance of about 2.55 Å and an angle of 97° for the plane I–Ni–P*.

IR spectra are typical of π-allylic complexes, showing no absorption for a free allyl group. The CO absorption is in the region of 2020–2060 cm^{-1}.

NMR spectra are also typical of coordinated π-allyl groups. A study has been made on (I) (R$=C_6H_5$, X$=$I) and on the corresponding π-methallyl complex (Ia). The observed signals are collected in Table 1. It is easily shown that the reported values are not absolute for the reason that the solution of both complexes contains the two species (I) and (III) in equilibrium:

$$(I) \rightleftarrows (III) + CO$$
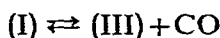
This is demonstrated by lowering the temperature, which results in the shift of the absorptions, as shown in Table 1. Furthermore, if increasing amounts of (III) are added to the solution of (I) [or if the corresponding π-methallyl complex (IIIa) is added to (Ia)] the τ values resulting from the above equilibrium shift continuously from those observed for (I) (or Ia) towards those observed for (III) (or IIIa).

It is well known that the NMR absorptions of pentacoordinated allyl nickel complexes containing two moles of triethylphosphine reveal a fast equilibrium between

TABLE 1

NUCLEAR MAGNETIC RESONANCE DATA FOR THE ALLYLIC LIGAND IN COMPLEXES OF TYPE (I)
R$=C_6H_5$, X$=$I; measurement at 100 MHz, tetramethylsilane as internal reference.

Solvent	Allylic ligand	Temp. (°C)	τ_1	τ_2	τ_3	τ_4
CDCl$_3$	Allyl	+20	5.03	6.07[a]	6.72[b]	
		+5	5.11	6.02	6.51	
		−10	5.12	5.99	6.47	
C$_6$H$_5$Cl	2-Methyl-allyl	+30		6.55	7.30	8.52
		+10		6.55	7.24	8.57
		−10		6.55	7.21	8.64
		−20		6.54	7.18	8.64

[a] $J_{1,2}=7$ Hz. [b] $J_{1,3}=13$ Hz.

* The structure of the pentacoordinated complex bromo[bis-1,2-(diphenylphosphino)ethane] (π-methallyl)nickel has been published recently[7].

π and σ forms[5]. NMR measurements on (I) reveal only the π-allyl form. However, the ability to undergo the insertion reactions, that will be described later, suggests that also a small amount of the σ-form is present in a slow equilibrium with the π-form.

The presence of another equilibrium, involving (I) and the ionic complex is indicated by the k values reported above.

It seems likely that an equilibrium with the phosphine also exists, as suggested by the absence of H–P coupling.

We are thus led to argue that all the ligands present in the complex participate in the equilibria shown in Scheme 1.

SCHEME 1

MOBILITY OF LIGANDS IN COMPLEXES (I)
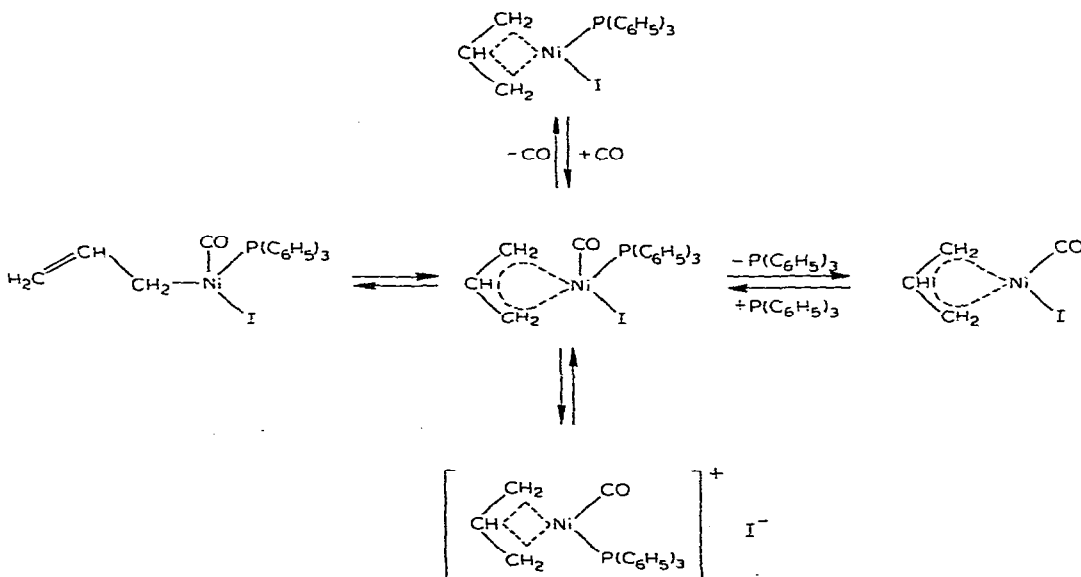
REACTIONS

When (I) (R=C$_6$H$_5$, X=I) is treated in benzene with triphenylphosphine in the presence of carbon monoxide, the allyltriphenylphosphonium iodide is formed:

$$(I) + P(C_6H_5)_3 + 2\ CO \rightarrow [CH_2{=}CHCH_2P(C_6H_5)_3]^+I^- + (CO)_3Ni{-}P(C_6H_5)_3$$

In the absence of carbon monoxide, tricarbonyl(triphenylphosphine)nickel forms at the expenses of complex (I), which is converted to (III). The latter is in equilibrium with complex (IV), already obtained by Wilke[5]:
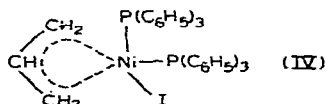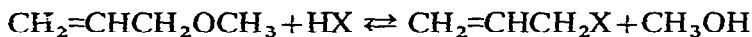

If complex (I) is treated with carbon monoxide in methanol the formation of allyl methyl ether and methyl 3-butenoate takes place.

More than one reaction occurs according to the following scheme:

$$(I) + 2\ CO + CH_3OH \rightarrow CH_2{=}CHCH_2OCH_3 + Ni(CO)_3PR_3 + HX$$

$$(I) + 3\ CO + CH_3OH \rightarrow CH_2{=}CHCH_2COOCH_3 + Ni(CO)_3PR_3 + HX$$

If the HX is not neutralized, the formation of 1,5-hexadiene also occurs through the following reactions:

$$CH_2{=}CHCH_2OCH_3 + HX \rightleftarrows CH_2{=}CHCH_2X + CH_3OH$$

$$(I) + CH_2{=}CHCH_2X \rightarrow CH_2{=}CHCH_2CH_2CH{=}CH_2 + NiX_2 + PR_3 + CO$$

which have been proved experimentally.

Reaction of allyl bromide with (I) in methanol in the presence of carbon monoxide and MgO gives both hexadiene and methyl butenoate.

Complex (I) $(R = C_6H_5, X = I)$, treated with acetylene and carbon monoxide in methanol, gives methyl cis-2,5-hexa-dienoate in a 47% yield:

$$(I) + CH{\equiv}CH + CO + CH_3OH \rightarrow CH_2{=}CHCH_2CH{=}CHCOOCH_3 +$$
$$+ Ni(PR_3)(CO)_3 + HX$$
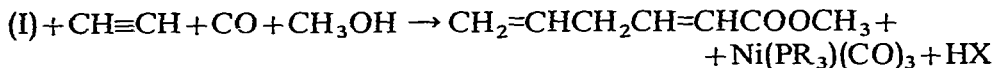
Other products, resulting from the addition of more molecules of carbon monoxide and acetylene, also form. This type of reaction in the absence of phosphines has been already described[6].

DISCUSSION

Two main observations can be drawn from the above experiments. The first refers to the behavior in solution of the pentacoordinated complexes. It can be said that all the possible equilibria are present in solution. Some equilibria can affect the $\pi{-}\sigma$ interconversion of the allyl group, whilst others can leave unaltered the allyl group and affect the other ligands. The other observation refers to the reactivity of the allylnickel complexes. They always seem to react via the pentacoordinated complex, since only the latter possesses the required reactivity. Suitable ligands, able to promote an efficient $\pi{-}\sigma$ conversion, must however be present in the complex. Thus the addition of one molecule of triphenylphosphine to a tetracoordinated complex of type (III) $(R = C_6H_5)$ results in the formation of the pentacoordinated complex (IV), which however, is not very reactive towards another molecule of triphenylphosphine. On the contrary, by addition to (III) $(R = C_2H_5, X = Br)$ of two new molecules of a suitable phosphine, such as triethylphosphine, a reaction takes place with formation of the allyltriethylphosphonium salt. The same salt can be obtained in the case of (I).

It is reasonable to apply these observations to the case of carbonylation reactions where carbon monoxide is present in place of phosphine. In the light of the above results the occurrence of pentacoordinated intermediates appears a necessary stage in carbonylation reactions. It is likely that insertions of other molecules take place in the same way.

In the reaction of complex (I) with allyl bromide methyl 3-butenoate and 1,5-hexadiene are formed together. This is consistent with the coordination of the entering molecule of allyl bromide, which favors both the coupling as well as the carbonylation reactions of the allylic ligand.

The formation of allyl methyl ether in the reaction of the complex (I) with carbon monoxide can also be explained as an insertion reaction.

The ambident allyl group thus displays an important function in the organic syntheses, allowing the insertion of certain molecules in a specific position. This could also be the reason for the stereospecificity of the acetylene insertion, as shown in Scheme 2.

SCHEME 2

PENTACOORDINATED NICKEL COMPLEXES AS INTERMEDIATES IN THE FORMATION OF METHYL cis-2,5-HEXA DIENOATE FROM ALLYL HALIDES, ACETYLENE AND CARBON MONOXIDE IN METHANOL
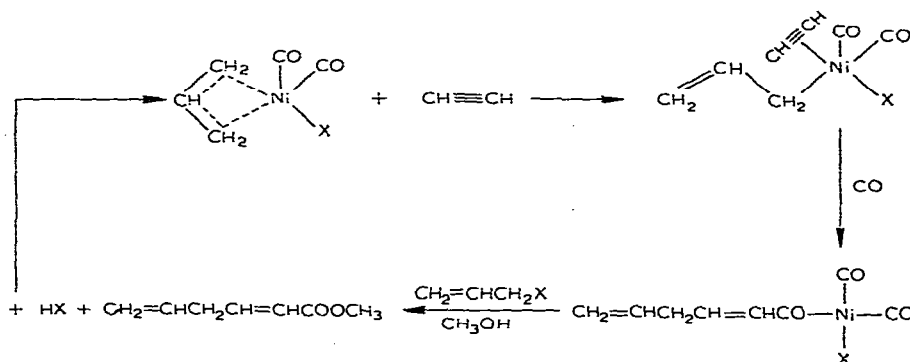
EXPERIMENTAL

Bromo(carbonyl)(triphenylphosphine)(π-allyl)nickel

Tricarbonyl(triphenylphosphine)nickel (12.15 g, 0.03 mole) and 4 ml (0.047 mole) of allyl bromide are caused to react under stirring at room temperature in 25 ml of benzene and 3 ml of methanol. In 3 hours about 90% of the theoretical amount of CO has been evolved. Orange-red crystals begin to separate during the CO evolution. The separation is completed by adding 10 ml of n-hexane. After filtration under nitrogen the crystals are first washed with a 10/10/5 mixture of benzene/hexane/ethanol, then with ethanol and with hexane. After drying under argon the product weighs 10 g (0.0213 mole). (Found: C, 55.91; H, 4.37; Br, 16.8; Ni, 12.4. $C_{22}H_{20}BrNiOP$ calcd.: 56.2; H, 4.26; Br, 17.0; Ni, 12.5%.) The IR spectrum* in nujol shows a strong CO absorption at 2057 cm^{-1}. The complex is stable at room temperature under inert atmosphere. It can be stored for long time at $-15°$. Recrystallization of this complex, as well as of its homologs can be easily carried out from chlorobenzene/ethanol and toluene/ethanol at $-30°$.

Iodo(carbonyl)(triphenylphosphine)(π-allyl)nickel

The complex is prepared as above. After 3 h 0.059 mole of CO have been evolved. The product (9.6 g, 0.0186 mole) has a red-orange colour. (Found C, 51.4; H, 4.10; I, 24.3; Ni, 11.2. $C_{22}H_{20}INiOP$ calcd.: C, 51.1; H, 3.9; I, 24.55; Ni, 11.35%.) The IR spectrum shows a strong CO absorption at 2043 cm^{-1}. The complex is more stable than the corresponding bromo derivative and can be stored for a long time at room temperature under inert atmosphere.

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* The IR spectra of this complex and of the following ones are being contributed to the DMS index.

Bromo(carbonyl)(triphenylphosphine)(π-methallyl)nickel

The complex is prepared as above. After 4 h 0.0435 mole of CO have been evolved. The product (4.8 g, 0.010 mole) has an orange colour. (Found: C, 57.19; H, 4.57; Br, 16.3; Ni, 12.2. $C_{23}H_{22}BrNiOP$ calcd.: C, 57.06; H, 4.58; Br, 16.15; Ni, 12.13%.) The IR spectrum shows a strong CO absorption at 2027 cm^{-1}. This complex is stable at room temperature under inert atmosphere.

Iodo(carbonyl)(triphenylphosphine)(π-methallyl)nickel

(III) (R=phenyl, X=I)[*] (3.805 g, 0.0076 mole) is treated with CO in 8 ml of benzene and 1 ml of methanol at room temperature under stirring. The CO uptake, which is initially rapid, gradually decreases and stops after 20 min (0.0076 mole). The orange, microcrystalline precipitate is filtered under argon, washed with ethanol and hexane and dried under argon (2.8 g, 0.00526 mole). The yield is 69.4%. (Found C, 51.93; H, 4.27; I, 24.0; Ni, 11.0. $C_{23}H_{22}INiOP$ calcd.: C, 52.20; H, 4.17; I, 23.91; Ni, 11.05%.) The IR spectrum shows the CO absorption at 2029 cm^{-1}.

By the same procedure it is possible to prepare also the first three complexes described above.

(Iodo)(carbonyl)(tributylphosphine)(π-allyl)nickel

Di-μ-iododi-π-allyldinickel (1.387 g, 0.0061 mole) and 1.236 g (0.0061 mole) of tri-n-butylphosphine are stirred under argon at room temperature in 50 ml of n-hexane. As soon as the nickel complex completely dissolves the apparatus is evacuated from argon and carbon monoxide is fed into. After few minutes orange crystals separate. After 20 min the total carbon monoxide taken up is 0.0062 mole. The crystals are filtered, washed with n-hexane and dried under carbon monoxide in order to avoid loss of carbon monoxide from the complex with formation of a complex of type (III). The IR absorption of CO is observed at 2040 cm^{-1}.

Reaction of complex (I) with triphenylphosphine

(I) (R=C_6H_5, X=I) (1.65 g, 0.0032 mole) and 0.84 g (0.0032 mole) of triphenylphosphine are stirred under CO in 20 ml of benzene at room temperature. After 1 h about 0.0065 mole of carbon monoxide have been taken up. A white crystalline precipitate of allylphosphonium iodide is filtered, washed with a small amount of benzene and dried (1.3 g). The remaining solution is evaporated to dryness under vacuum. A few ml of methanol are added to the residue. The solution is filtered and dried (1.1 g). The IR spectrum shows that it is constituted by tricarbonyl(triphenylphosphine)-nickel (90%) and by dicarbonylbis(triphenylphosphine)nickel (10%). Very small amounts of $Ni(CO)_4$ and NiI_2 are also present in the reaction mixture.

Reaction of complex (I) with carbon monoxide

(I) (R=C_6H_5, X=Br) (2 g, 0.00425 mole) and 0.16 g (0.004 mole) of MgO are stirred under carbon monoxide in 20 ml of methanol and 5 ml of benzene at room temperature. The uptake of CO proceeds slowly (after 14 h 0.010 mole of CO) and the

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[*] Easily prepared as crystalline precipitate from di-μ-iododi-π-methallyldinickel in ether and the stoichiometric amount of $P(C_6H_5)_3$. Homologous complexes with Cl, Br and I are also prepared by the same procedure.

colour of the solution passes from orange-red to yellow. The mixture is distilled at room temperature under 0.01 mm Hg and the light products are collected in a liquid nitrogen trap. 0.0007 mole of $Ni(CO)_4$, 0.004 mole of methyl allyl ether, 0.0003 mole of methyl 3-butenoate are contained in the distillate. Water and acetic acid are added to the residue. The solution is filtered and dried to give crystalline tricarbonyl(triphenylphosphine)nickel (1.4 g, 0.00346 mole).

Reaction of (I) with acetylene and carbon monoxide

In a 250 ml flask 0.517 g (0.001 mole) of (I) $(R = C_6H_5, X = I)$ is dissolved under nitrogen in 16 ml of toluene and 4 ml of methanol. The solution is cooled at $0°$, the flask is evacuated from nitrogen and a gaseous mixture containing 70% of CO and 30% of C_2H_2 is fed into. The reaction proceeds rapidly, the solution turning to dark red and reverting to orange in about 30 min. The light products are distilled at 0.01 mm Hg in a liquid nitrogen trap. The distillate is chromatographed. It contains 0.00047 mole of methyl cis-2,5-hexadienoate, identified by comparison with an authentical sample. The residue contains heavier products which have been already described[6].

Reaction of (I) with allyl bromide

(I)$(R = C_6H_5, X = Br)$ (2 g, 0.00425 mole) is treated for 24 h at $20°$ under nitrogen with 0.5 ml (0.0058 mole) of allyl bromide and 0.16 g of MgO in 20 ml of methanol and 5 ml of benzene. The mixture is evaporated at room temperature under 0.01 mm Hg and the distillate is collected in a liquid nitrogen trap. The gas-chromatographic analysis reveals the presence of 0.18 g (0.0023 mole) of 1,5-hexadiene, 0.17 g (0.0017 mole) of 3-butenoate and little amounts of allyl methyl ether.

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