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REACTIONS OF DIOXYGEN WITH BENZYLNICKEL COMPLEXES

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Summary

The benzyl complexes $Ni(X)(CH_2C_6H_5)(PCy_3)$ (X = Cl, CN; Cy = cyclohexyl) react with molecular oxygen to give benzaldehyde and benzyl alcohol as main oxidation products. The ratio of the two products is strongly dependent on the nature of X and is also influenced by the solvent and the temperature. Isotopic labelling and mass spectra show that the hydrogen atoms necessary for the formation of the benzyl alcohol are supplied by the phosphine ligands. Isolation and characterization of the chloride complex by conventional spectroscopic techniques (IR, ^1H ^{31}P NMR, visible spectra) provide evidence in favour of a η^3-π-benzyl structure for the compound.

Introduction

Although much research has been conducted into π-allyl complexes of nickel, the analogous π-benzyl derivatives are still rare. It has been shown that a solution of the species $(Ph_3P)_2Ni(\sigma\text{-}CH_2Ph)Cl$ (Ph = phenyl) in benzene gives rise to the equilibrium

$$(Ph_3P)_2Ni(\sigma\text{-}CH_2Ph)Cl \rightleftarrows (Ph_3P)Ni(\pi\text{-}CH_2Ph)Cl + PPh_3$$

The evidence in favour of a π-benzyl structure for the complex was based on ^1H NMR spectra (signals at τ 8.4 and near 9.0 ppm) and on the intense violet colour (band at 18100 cm^{-1}) which is not expected for the σ-species $(Ph_3P)_2Ni(CH_2C_6H_5)Cl$ [1]. Species with composition $Ni(X)(CH_2C_6H_5)(PCy_3)$ (Cy = cyclohexyl; X = Cl, Br, I) which are believed to be π-benzyl complexes are mentioned in the literature, but experimental evidence of their existence is yet to be presented [1–3]. The π-benzyl nature of such species is assigned on the basis of unpublished work (^1H NMR spectra), and experimental detail of their characteriza-

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tion is not available. Thus the existence of complexes of the type mentioned above must be regarded as uncertain in the lack of more definite information.

We recently described the complex $Ni(CN)(CH_2C_6H_5)(PCy_3)$ [4]. As far as we know this is the only formally tri-coordinate benzylnickel complex isolated in the solid state. Although little is known in detail about the type of bonding of the benzyl group in the complex, the well-known reactivity of allylic hydrogens and the expectation of an easy abstraction of hydrogen from the saturated benzyl carbon suggested a study of the reaction of the complex with molecular oxygen. The work described here stems from our interest in both autoxidation reactions and the chemistry of organo-nickel compounds. As an obvious extension of the study on the cyanide complex we also isolated the corresponding chloride derivative $Ni(Cl)(CH_2C_6H_5)(PCy_3)$. We here report on the characterization of this chloride complex and on the reactions with O_2 of both the cyanide and chloride derivatives.

Results and discussion

(i) The complex $Ni(Cl)(\eta^3\text{-}CH_2C_6H_5)(PCy_3)$

The complex was isolated as blue-violet crystals from toluene solutions of $Ni(PCy_3)_2$ in the presence of $ClCH_2C_6H_5$. It reacts very rapidly with oxygen, is fairly stable under argon at temperatures below −20°C, but slowly decomposes at room temperature to give bibenzyl and small amounts of toluene. We assign the complex an η^3-allylic structure on the basis of the following considerations.

The infrared spectra of the compound in Nujol mulls show the absorptions characteristic of the PCy_3 group in the range 1400–400 cm^{-1} and bands characteristic of the C–H stretch of the aromatic ring at 3010 and 3050 cm^{-1}. An intense absorption at 682 cm^{-1}, which is not present in the spectra of the complex $Ni(Cl)_2(PCy_3)_2$, is assigned to the coordinated benzyl group. A band of medium intensity occurring at 318 cm^{-1} is assigned to the Ni–Cl stretching of the coordinated chloride.

The visible spectra of the intensely violet solutions of the complex in benzene show an intense band centered at 555 nm (18000 cm^{-1}). A violet colour, arising from an intense absorption at 18100 cm^{-1}, has previously been interpreted as characteristic of an η^3-benzyl structure in the complex $Ni(Cl)(\pi\text{-}CH_2C_6H_5)(PPh_3)$ [1].

The ^1H NMR spectra of the compound in $C_6H_5CD_3$ in the temperature range +20–60°C exhibit the resonance characteristic of the cyclohexyl hydrogens in the range δ 0.5–2.0 ppm. A doublet at δ 4.2 ppm, with a coupling constant of 6 Hz, and a very broad signal in the same zone are assigned to the protons of an allylic system. The signals from the phenyl protons of the coordinated benzyl appear at δ 6.8 ppm. Lowering the temperature does not cause changes indicative of a *syn* → *anti* conversion of allylic protons. The ^{31}P NMR spectra in the same solvent show a singlet at 41.1 ppm which is attributed to the resonance of coordinated phosphorus atoms in a complex in which there is no interaction of the cyclohexyl carbons with the metal (cyclometallation). The well-resolved spectra rule out the presence of paramagnetic atoms and show that we are dealing with a diamagnetic nickel(II) complex. Bubbling of O_2 through the solution of the NMR sample caused an immediate change of colour from violet to green, accompanied by the disappearance of the peak at δ 4.2 and the appearance of a new one at 9.3 ppm; the latter can be attributed to the resonance of protons present in CHO or CH_2OH groups. The reaction with O_2 is also accompanied by a simplification in the multiplet at δ 6.8 ppm assigned to the phenyl protons of the benzyl group.

In conclusion, the evidence presented here strongly suggests that the compound can be formulated as the π-complex $Ni(Cl)(\eta^3\text{-}CH_2C_6H_5)(PCy_3)$. It is also noteworthy that a formulation as a σ-complex $Ni(Cl)(\eta^1\text{-}CH_2C_6H_5)(PCy_3)$ would imply three-coordination, and this is unlikely for a diamagnetic nickel(II) complex of the type discussed.

(ii) Thermolysis of the $Ni(X)(CH_2C_6H_5)(PCy_3)$ complexes and their reactions with dioxygen

The mass spectra derived from solid samples of $Ni(Cl)(CH_2C_6H_5)(PCy_3)$ showed that bibenzyl, the phosphine PCy_3, and small amounts of toluene are the main products of the thermal decomposition of the complex in the ion source. When the solid complex was heated with oxygen (1 atm) in small capillary tubes at 50°C, the mass spectra of the samples after reaction revealed that benzaldehyde and benzyl alcohol were the main decomposition products, along with smaller amounts of bibenzyl and toluene. Heating at 100°C produced an increase in the (bibenzyl + toluene)/(aldehyde + alcohol) ratio, showing that high temperatures favour thermal decompositions more than oxidation processes.

GLC of freshly prepared benzene solutions of $Ni(Cl)(CH_2C_6H_5)(PCy_3)$ under argon revealed the presence of substantial amounts of bibenzyl and toluene (in a 3/1 ratio), and we attribute this to rapid thermolysis in the hot parts (220°C in the injector) of the apparatus. GLC analysis of the same solutions after oxidation in the air (complete reaction with O_2 required about 5 min) gave the results summarized in Table 1.

As Table 1 column I shows, the total amount of the organic products originating from the coordinated benzyl group corresponds to 100% based on the formulation $Ni(Cl)(CH_2C_6H_5)P(C_6H_{11})_3$.

The reactions of dioxygen with the complex in the solid state were also studied at room temperature (see Experimental section). The results of the GLC analysis carried out in benzene solutions of the oxidized complex are summarized in Table 1 column II. Comparison with the data of column I shows that the reaction in case of

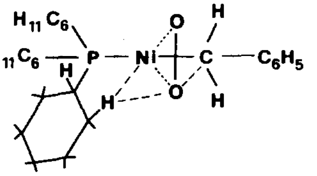
TABLE 1

PRODUCTS OF THE REACTION OF $Ni(Cl)(CH_2C_6H_5)(PCy_3)$ WITH DIOXYGEN (I: reaction of air oxygen with benzene solution of the complex at 22°C; II: reaction of O_2 with the solid complex at 22°C; III: reaction in benzene solutions under various pressures of O_2)

Compound	I [a]	II [a]	III [b]	
			O_2/Ar [c] = 0.01	O_2 [c]
toluene	6	–	–	–
benzaldehyde	31.8	9.7	4.1	4.2
benzyl chloride	–	1.1	–	–
benzyl alcohol	58.2	66.6	82.7	90.7
bibenzyl × 2	3.5	3.0	13.2	5.1
	Tot 99.5	Tot 80.4		

[a] Yields (mol%) based on starting complex. [b] Relative percentages. [c] Total pressure 1 atm.

the solid favours the formation of $C_6H_5CH_2OH$. This suggests that the supply of hydrogen necessary for the formation of the alcohol molecule can occur even without the presence of solvent. The stoicheiometry of the reaction with O_2, in which alcohol is produced in amounts larger than aldehyde, requires an extra hydrogen atom in addition to the CH_2 hydrogens of the benzyl group. Mass spectroscopy of solutions of the complex in C_6D_6 after reaction with O_2 showed that no deuterium atom was contained in the oxidation products (alcohol and aldehyde). The result confirmed that the extra hydrogen needed for the reaction came from the cyclohexyl groups of the phosphines. This implies activation of hydrogen atoms of the ligands in addition to coordination and activation of O_2. If the transfer of oxygen to the benzylic carbon occurs at the same time as the abstraction of hydrogen from the C_6H_{11} groups, then an activated state of the type depicted below is involved in the reaction.



The fate of the nickel and the influence of the experimental conditions (temperature, solvent, pressure of O_2) on the reaction products were not investigated in detail. We did observe that the aldehyde/alcohol ratio depends on the nature of the solvent used and hardly depends at all on the partial pressure of O_2 if other factors are kept constant (Table 1, column III).

The complex $Ni(CN)(CH_2C_6H_5)(PCy_3)$ was found to react with O_2 much more slowly than the chloride derivative. Some days are necessary before the reaction of the solid with air produces appreciable amounts of benzaldehyde. The mass spectra of solid samples of $Ni(CN)(CH_2C_6H_5)(PCy_3)$ (spectra of the thermolysis products formed in the ion source) show that bibenzyl and $C_6H_5CH_2CN$ are the main decomposition products. The chloro-derivative does not produce $C_6H_5CH_2Cl$ under identical conditions. Moreover, only trace amounts of $C_6H_5CH_3$ are detectable in the mass spectra of the cyanide. After reaction with O_2 (10^{-2}–10^{-4} torr, 150°C) the spectra of $Ni(CN)(CH_2C_6H_5)(PCy_3)$ show that C_6H_5CHO is the main product, accompanied by small amounts of bibenzyl and benzyl cyanide. In contrast to that of the chloride derivative, the reaction of the solid complex does not give benzyl alcohol.

Table 2 summarizes the results of GLC analysis of toluene solutions of the cyanide complex (10^{-1} *M*) after shaking with O_2 (1 atm) at 40°C (identification of the products was confirmed by MS analysis). Comparison of Table 1 and Table 2 clearly shows that on going from the chloride to the cyanide complex benzaldehyde and not benzyl alcohol becomes the preferred oxidation product from the benzyl group.

The reactions of the cyanide complex with O_2 were also investigated in benzene, n-hexane and benzyl cyanide. For reaction in benzene, the MS results showed that the formation of toluene is still less important than in the case of $Ni(Cl)(CH_2C_6H_5)$ (PCy_3). The yields of aldehyde and alcohol were similar to those in toluene. In n-hexane the value found for the aldehyde/alcohol ratio was ca. 8 (instead of 3–4 as

TABLE 2

PRODUCTS OF THE REACTION OF $Ni(CN)(CH_2C_6H_5)(PCy_3)$ WITH DIOXYGEN (1 atm) AT 40 °C IN TOLUENE

Component	Yield [a] (mol%)
Benzyl nitrile	9
Benzaldehyde	51
Benzyl alcohol	17
Bibenzyl × 2	1

[a] Yield based on starting complex.

found in toluene). In benzyl cyanide the value of the yield ratio dropped markedly to about 0.1.

Replacement of chloride by cyanide in the $Ni(X)(CH_2C_6H_5)(PCy_3)$ complex leads to reduction in the reactivity of the coordinated benzyl moiety toward oxygen, a higher propensity to follow reductive elimination routes (formation of benzyl cyanide) and a smaller propensity to afford compounds requiring the supply of hydrogen atoms (alcohol, toluene). If we assume, by analogy with the results for the chloro-derivative, that the necessary hydrogens are supplied by cyclohexyl groups, the effect of the CN ligand is apparently to inhibit the abstraction of hydrogen from the ligands. It is not easy to account for these observations. We know from DSC experiments that thermal decomposition of the chloride complex under argon from 50° to 280 °C and reaction with O_2 under similar conditions are both exothermic. Thermodynamically, the driving force for both decomposition and oxidation involves a favourable thermal contribution which is easily understood in terms of the large heats of formation of C–C (bibenzyl) C–CN (benzyl cyanide) or C–O bonds (aldehyde, alcohol). In conclusion, we believe that the observed differences in reactivity toward dioxygen are to be ascribed to kinetic factors. However, without a detailed knowledge of the reaction mechanism any interpretation of the observed behaviour would be speculative. Insight into the mechanism of the oxygen transfer is expected from kinetic studies which are currently under way.

Experimental

Instruments

Infrared and visible spectra were recorded with the Perkin–Elmer 599B and 576 instruments respectively. The Differential Scanning Calorimeter used was a Perkin–Elmer DSC-4. ^1H and ^{31}P NMR spectra were recorded on a JEOL FX 90Q spectrometer at 89.55 MHz. Gas chromatographic analyses were performed with a Perkin–Elmer Sigma 3 instrument equipped with an SGE Unijector (split ratio 1/20) and fitted with an SGE capillary column (vitreous silica with bonded phase BP10, equivalent to OV 1701, i.d. 0.33 mm, length 25 m). The mass spectra of products were recorded with a VG M16 spectrometer operating at 70 eV, interfaced with a gas chromatograph fitted with a capillary column (identical to that used in the Sigma 3 instrument). Solid samples were analysed by means of the direct inlet system (DIS) or using an all-glass heated inlet system (AGHIS).

Materials

The solvents used were anhydrous and oxygen-free. The benzyl chloride and the benzyl cyanide were from Aldrich and were treated with anhydrous sodium sulphate before use. The complexes $Ni(CN)(CH_2C_6H_5)(PCy_3)$ and $Ni(PCy_3)_2$ were prepared as previously described [5]. Biphenyl (Aldrich) was used as an internal standard for the GLC analyses.

Preparation of $Ni(Cl)(CH_2C_6H_5)(PCy_3)$

Equimolar amounts of $Ni(PCy_3)_2$ and benzyl chloride were brought into reaction in toluene solutions (ca. 0.1 *M*) at −20°C. Addition of n-hexane caused precipitation of a blue diamagnetic solid in good yield. This is stable in an inert atmosphere but decomposes when exposed on the air giving, inter alia, benzaldehyde and a black residue.

Analytical

Nickel and phosphorus were determined by standard spectrophotometric analyses. For nickel, samples were dissolved by refluxing them with concentrated nitric and perchloric acid. For phosphorus, samples were refluxed with 72% perchloric acid and ammonium vanadate. Chlorine was determined by Schöniger's method. Found: Cl, 7.3; P, 6.5; Ni, 12.3. $C_{25}H_{40}ClNiP$ calcd.: Cl, 7.6; P, 6.6; Ni, 12.6%.

Thermal decomposition and reactions of the $Ni(X)(CH_2C_6H_5)(PCy_3)$ complexes (X = Cl, CN) with dioxygen

Small aliquots of the solid chloride complex were rapidly introduced through a DIS into the ion source of the mass spectrometer and the temperature was rapidly increased (ca. 7 min) from ambient to 300°C. The main species observed under these conditions were tricyclohexylphosphine and bibenzyl, accompanied by small amounts of toluene and trace amounts of benzaldehyde and benzyl alcohol. The presence of oxygen-bearing compounds must be ascribed to the unavoidable (even if very short) exposure of the samples to the air just before the injection. Ions containing the metal were undetectable (probably because of a combination of their poor stability and low volatility).

The reactions of oxygen with the chloride complex in the solid state at 50 and 100°C were performed in sealed capillary tubes. After reaction these were cooled to −50°C, broken, and the samples then introduced into the spectrometer through the AGHIS operating at 220°C.

The reactions of the chloride complex in benzene solution were investigated by GLC analyses in the presence of biphenyl as an internal standard. At ambient temperature under argon the main products, bibenzyl and toluene in a 3/1 ratio, were accompanied by trace amounts of alcohol and aldehyde. The complex reacts rapidly in the air, with complete fading of the blue color. The final composition of the solutions is reported in Table 1. The residual but substantial presence of bibenzyl and toluene is attributed to the decomposition of the starting complex before the reaction with oxygen and the GLC analysis. It is noteworthy that under the conditions used for the GLC analyses the phosphine and its oxide were undetectable owing to their high retention times.

Table 1 also summarizes the results of the reaction of oxygen with the chloride complex in the solid state at room temperature. Samples of the compound in closed vessels were allowed to react for 2 d with pure oxygen at 22°C. The samples were extracted with benzene and the solution was analyzed by GLC in the presence of the internal standard.

The experiments with the cyanide complex involved the procedures described above for the chloride derivative. Treatment of solid $Ni(CN)(CH_2C_6H_5)(PCy_3)$ at 150°C under an inert blanket followed by introduction of the product via DIS into the mass spectrometer revealed the presence of tricyclohexylphosphine, bibenzyl, benzyl cyanide, and trace amounts of benzonitrile. At the same temperature keeping the solid compound under oxygen (ca. 10^{-2}–10^{-4} atm) for high reaction times (hours) produced tricyclohexylphosphine and its oxide, benzaldehyde, benzyl cyanide, and bibenzyl. In benzene or toluene solutions at ambient temperature the cyanide complex reacts slowly with oxygen to give the products listed in Table 2. When the reaction is carried out in n-hexane, in which the complex is sparingly soluble, the product of the very slow reaction is mainly the aldehyde, accompanied by traces of the nitrile, while bibenzyl and the alcohol are barely detectable. Conversely, when the reaction is carried out in benzyl nitrile the principal product is benzyl alcohol.

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