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THE BEHAVIOUR OF NICKEL(0) DIPHOSPHINE COMPLEXES TOWARDS UNSATURATED ORGANIC COMPOUNDS

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SUMMARY

The reactions of Ni(Dpb)$_2$ [Dpb = 1,4-bis(diphenylphosphino)butane], and Ni(Dpp)$_2$ [Dpp = 1,3-bis(diphenylphosphino)propane] with a variety of unsaturated organic compounds have been investigated. It was found that Ni(Dpb)$_2$ is more reactive than Ni(Dpp)$_2$ and that cyano-alkenes and alkynes are more reactive than alkenes under comparable experimental conditions. The reaction products have been identified and the new complex, Ni(Dpb) (tetracyanoethylene) has been isolated and characterised. Catalytic properties of the Ni^0 complexes are described.

INTRODUCTION

Phosphino complexes of Pt^0 and Pd^0 of the type M(PPh$_3$)$_n$ where $n = 2$, 3 or 4 have been shown to react with alkenes and alkynes to give products of the type M(PPh$_3$)$_2$(Uns) where Uns represents the unsaturated organic compound[1,2]. However, although analogous complexes of nickel are known, none has been prepared by the direct interaction of NiP$_4$ (where P is a phosphorous atom of tertiary phosphine) and the organic compound. The well known complex Ni(PPh$_3$)$_2$(CH$_2$=CH$_2$)[3] was obtained by reduction of nickel bis(acetylacetonate) with Al(C$_2$H$_5$)$_2$OC$_2$H$_5$ in the presence of PPh$_3$, and has been used as a convenient starting material to prepare some complexes of the type Ni(PPh$_3$)$_2$(Uns)[3,4]. Recently it has been reported[5] that the complexes tetrakis(triethylphosphine)nickel, tetrakis(methyldiphenylphosphine)-nickel and [1,2-bis(diphenylphosphino)ethane]bis(tri-n-butylphosphine)nickel react with C$_2$F$_4$ to give the corresponding octafluoronickelcyclopentane complexes.

We report here the results of our investigation on the reactivity of bis[1,4-bis(diphenylphosphino)butane]nickel Ni(Dpb)$_2$ and bis[1,3-bis(diphenylphosphino)-propane]nickel, Ni(Dpp)$_2$ towards a series of unsaturated organic compounds. The aim of this study was to gain a better understanding of the established catalytic properties of the Ni^0 complexes[6] as well as to investigate the chemistry of nickel–phosphine complexes with respect to organic ligands[7].

EXPERIMENTAL

The reactions were conducted in an inert atmosphere as the products are particularly air sensitive. A standard gas volumetric apparatus, thermostatted to 0.1° was employed for gas uptake experiments. IR spectra were recorded on a Perkin–Elmer 357 instrument.

TCNE was recrystallised from chlorobenzene and fumaronitrile (Fluka) was used without further purification. Acetylene was purified by removing the acetone, while ethylene (polymerisation grade) was used as received. Dpb and Dpp were prepared as described elsewhere[8,9] and all other organic materials were redistilled before use. Nickel bis(acetyl acetonate) was a Schuchardt reagent.

Preparation of $Ni(Dpb)_2$ and $Ni(Dpp)_2$

Nickel bis(acetylacetonate) (13 mmoles) and the diphosphine (26 mmoles) were added to approximately 70 ml benzene which had been saturated with argon. $i\text{-}Bu_3Al$ (8.7 g) dissolved in 250 ml anhydrous ether saturated with argon, was added dropwise while stirring vigorously at room temperature. The green solution gradually turned red after about 1 h and stirring was stopped when the complex started to precipitate. The mixture was allowed to stand for 48 h and then the orange red crystalline product filtered off under argon and washed with anhydrous ether saturated with argon. Yield approx. 80%.

$Ni[P(C_6H_5)_2(CH_2)_4P(C_6H_5)_2]_2$. M.p. 200–201° (decompn. in evacuated tube). (Found: C, 73.63; H, 6.42; Ni, 6.48; P, 13.15. $C_{56}H_{56}NiP_4$ calcd.: C, 73.76; H, 6.20; Ni, 6.43; P, 13.58%.)

$Ni[P(C_6H_5)_2(CH_2)_3P(C_6H_5)_2]_2$. M.p. 281–283° (decompn. in evacuated tube). (Found: C, 73.40; H, 5.88. $C_{54}H_{52}NiP_4$ calcd.: C, 73.40; H, 5.93%.)

$Ni(Dpp)_2$ may also be prepared by the reaction of Cp_2Ni with Dpp[9].

Reaction of $Ni(Dpb)_2$ and $Ni(Dpp)_2$ with organic reagents

The general method for the reactions between $Ni(Dpp)_2$ or $Ni(Dpb)_2$ and various organic reagents made use of a device enabling addition of reagents to be made under an atmosphere of argon. A suspension of the Ni^0 complex (0.3 mmole) in benzene saturated with argon (10–20 ml) was prepared and liquid organic reagents were added by means of microsyringes under vigourous stirring. Solid reagents such as TCNE (tetracyanoethylene) were dissolved in benzene before the addition of the Ni^0 complex. Ni(Dpb) (TCNE) precipitated as a microcrystalline yellow powder after about 10 min, and was washed with 50 ml of benzene and a little ether.

$Ni[P(C_6H_5)_2(CH_2)_4P(C_6H_5)_2]C_6N_4$. M.p. 210–212° (decompn. in evacuated tube). (Found: C, 66.25; H, 4.49; N, 9.16. $C_{34}H_{28}N_4NiP_2$ calcd.: C, 66.59; H, 4.60; N, 9.13%.)

RESULTS AND DISCUSSION

The unsaturated compounds investigated were alkenes, cyanoalkenes and alkynes. For solid and liquid materials, approximately equimolar quantities of the organic material and Ni^0 complex were dispersed in benzene and the reaction observed at room temperature. Reactions with enthylene, butadiene and acetylene were conducted by saturating 10 ml portions of benzene with the gas at 25° and 1 atm. and addition of 0.3 mmole of the Ni^0 complex. The results, subdivided into homologous series, are described below.

Alkenes and dienes

Ethylene, 1-pentene, 1-hexene, styrene, cyclohexene, butadiene and 2-methyl-1,3-butadiene all fail to react with $Ni(Dpb)_2$ as shown by the absence of any change in the position and intensity of the C=C IR stretching frequency, the absence of any colour change, and, in the case of the ethylene and butadiene, by the absence of any measurable gas absorption over several hours.

Cyanoalkenes

$Ni(Dpp)_2$ and $Ni(Dpb)_2$ both react with tetracyanoethylene (TCNE) and with fumaronitrile, while only $Ni(Dpb)_2$ reacts readily with acrylonitrile. The products are microcrystalline, sparingly soluble in benzene, and air sensitive; the fumaronitrile and acrylonitrile products are occasionally pyrophoric. A medium to strong band between 2250 and 2100 cm^{-1} is found in the IR spectrum of nujol mulls which is attributed to the C≡N stretching frequency in the coordinated alkene. This was usually found to be ca. 40 cm^{-1} below the equivalent vibration in the free ligand and is in accordance with data for other complexes of Ni^0 (ref. 6), Pd^0 (ref. 10) and Pt^0 (ref. 11) in which coordination has taken place through the double bond of the alkene. The product of the reaction with acrylonitrile has neither a C=C stretching frequency nor a vinylic absorption in the 900–1000 cm^{-1} range[6].

The product of $Ni(Dpb)_2$ and TCNE is diamagnetic, moderately air stable, and has an elemental analysis in agreement with the composition Ni(Dpb) (TCNE). Its IR spectrum contains a composite band centered at 2220 cm^{-1} when taken in a nujol mull, but the peak is nearly symmetrical when the complex is dissolved in methylene chloride. The behaviour of these Ni^0 complexes is similar to that of $Pd(PPh_3)_4$ which readily reacts with TCNE in benzene to give $Pd(PPh_3)_2TCNE$, but differs from $Pt(PPh_3)_4$ which gives a mixture of $Pt(PPh_3)_2(CN)_2$[11] and $Pt(PPh_3)_2TCNE$[2].

An orange-red suspension of $Ni(Dpb)_2$ in benzene changes to a yellow solution upon addition of either 1-phenyl-2-cyanoethylene or 1-cyano-1-propene. In addition to the ν(CN) peak for the free species at 2220 cm^{-1}, the solutions show strong absorbances (at 2190 cm^{-1} for 1-phenyl-2-cyanoethylene and 2185 cm^{-1} for 1-cyano-1-propene) which can be assigned to the C≡N stretching frequencies for the coordinated ligands. $Ni(Dpp)_2$ does not react under these conditions.

The IR spectra, in particular the decrease in ν(CN) on complex formation, suggests that the reaction between the Ni^0 complexes and cyanoalkenes leads to compounds in which coordination has occurred through the double bond[6,11]. Similar compound, *i.e.* $Ni(n\text{-}Bu_3P)_2$ (Uns) (Uns = 1,1-dicyanoethylene, phenyltricyanoethylene), have been prepared by Schrauzer through a $Ni(CO)_4$ preparative route[6].

Alkynes

$Ni(Dpb)_2$, but not $Ni(Dpp)_2$, reacts rapidly with 1-hexyne, phenylacetylene, and 2-propyn-1-ol in benzene. The IR spectra of the yellow solutions obtained show the formation of strong bands in the region 1700–1750 cm^{-1} (for 1-hexyne, 1750; phenylacetylene, 1720; 2-propyn-1-ol 1730) and the disappearance of the C≡C stretch at about 2150 cm^{-1}.

The decrease of ca. 400 cm^{-1} in ν(C≡C) observed in these complexes is very similar to that found for a series of compound $M(PPh_3)_2$(fluoroalkyne)[4] where

M=Ni, Pd, Pt, in which the decrease was 400 to 500 cm^{-1} and was attributed to coordination of the alkynes through the triple bond. We therefore propose that our products exhibit the same type of coordination. Attempts to isolate the products from solution have so far been unsuccessful.

Both $Ni(Dpb)_2$ and $Ni(Dpp)_2$ readily absorb one molecular equivalent of acetylene giving respectively red and brown precipitates which are unstable and decompose upon washing with deoxygenated benzene.

It is interesting to note that, after the first rapid absorption of acetylene by $Ni(Dpb)_2$, the uptake of gas continues slowly, suggesting a catalytic process of polymerisation. At 25° the molar ratio acetylene/$Ni(Dpb)_2$ is approximately 3 after two hours, whereas after three hours at 39°, the ratio is about 8. Similar behaviour was observed when $Ni(Dpb)_2$ and phenylacetylene (molar ratio Ni/Uns 1/100) were refluxed in benzene. After 3 h the alkyne had been converted nearly quantitatively into a tacky red-orange substance which is soluble in benzene and petroleum ether and was probably a mixture of oligomers. The polymerisation of the phenylacetylene and of acetylene proceeds very likely via the initial formation of a species Ni(Dpb)-(alkyne). A similar intermediate has been postulated in the same type of reactions promoted by $Ni(CO)_2(PPh_3)_2$[12]. Free diphosphine does not cause polymerisation under these conditions.

The enhanced reactivity of alkynes over alkenes is most probably a consequence of the superior strength of the organometallic bond in the alkyne complexes, in common with current views on Pt^0 complexes[1]. Moreover similar reasoning can explain the greater reactivity of cyanoalkenes over alkenes, as the presence of a CN group bound to a carbon of the alkene double bond facilitates the back donation from the metal to the olefins[2,11].

Finally the remarkably different reactivity of $Ni(Dpb)_2$ and $Ni(Dpp)_2$ towards both cyanoalkenes and alkynes seems noteworthy and it must largely be due to the different lengths of the alkyl chain in the diphosphines.

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