

Interaction of Nickel σ -Ethyl Derivatives with Diethylaluminium Halides. Influence of Steric Factors

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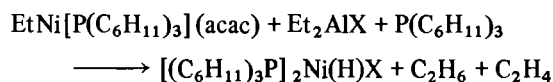
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Recently we reported the isolation of the new nickel hydride complex, $(\text{Ph}_3\text{P})_3\text{Ni}(\text{H})\text{Br}$, from the reaction between diethylaluminium bromide and ethyl(acetylacetonato)(triphenylphosphine)nickel or nickel acetylacetonate in the presence of triphenylphosphine [1].

Later Tolman and co-workers have synthesized similar penta-coordinate nickel hydrides by the action of HCN on zero-valent nickel complexes of the type NiL_4 where L is a tertiary phosphine [2].

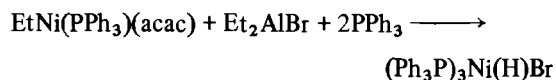
In this work we describe the effects of steric factors on the composition and structure of the complexes formed in the reactions of nickel σ -ethyl derivatives with organoaluminium compounds in the presence of various tertiary phosphines.

Treatment of ethyl(acetylacetonato)(tricyclohexylphosphine)nickel with diethylaluminium chloride or bromide in the presence of excess tricyclohexylphosphine has been found to produce high yields of nickel hydrides, $[(\text{C}_6\text{H}_{11})_3\text{P}]_2\text{Ni}(\text{H})\text{X}$ (X is Cl, Br), containing two molecules of tricyclohexylphosphine:



where X is Cl, Br; acac stands for acetylacetonate anion. The ^1H NMR and IR spectra of the products are consistent with those reported in the literature [3].

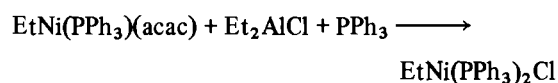
As mentioned above, the analogous reaction between $\text{EtNi}(\text{PPh}_3)(\text{acac})$ and Et_2AlBr yields a nickel hydride stabilized by three triphenylphosphine molecules:



Nickel hydride compounds may thus contain two or three tertiary phosphine molecules depending on the steric characteristics of the latter. Bulky ligands like tricyclohexylphosphine give tetra-coordinate nickel hydrides, $[(\text{C}_6\text{H}_{11})_3\text{P}]_2\text{Ni}(\text{H})\text{X}$ (X is Cl, Br). Steric

filling in the coordination sphere of these complexes is discussed by the authors [4] who describe unsuccessful attempts at introducing one more ligand (R_3P , Et_3N , or NH_3) into the compounds. With less bulky triphenylphosphine [5], penta-coordinate nickel hydrides are formed by the addition of the third tertiary phosphine molecule. Thus reactions of σ -ethylnickel derivatives described provide a convenient route to nickel hydride complexes otherwise accessible only with difficulty.

The reaction of ethyl(acetylacetonato)(triphenylphosphine)nickel with diethylaluminium chloride [6] proceeds in a different manner to yield another nickel complex, *viz.* $\text{EtNi}(\text{PPh}_3)_2\text{Cl}$, containing two triphenylphosphine molecules:



The product, ethylbis(triphenylphosphine)nickel chloride, is extremely unstable in solution and cannot be recrystallized. Dissolution of the product in benzene leads to its decomposition to ethane and ethylene (1:1) and the paramagnetic univalent nickel complex, $(\text{Ph}_3\text{P})_2\text{NiCl}$ [7]. Acidic hydrolysis of the product proceeds likewise. According to GLC the reaction of ethylbis(triphenylphosphine)nickel chloride with glacial acetic acid gives ethane and ethylene in a ratio of 1:1 and small amounts of hydrogen (5%) along with $(\text{Ph}_3\text{P})_2\text{NiCl}_2$ [8].

Experimental

GLC analysis of gases was made on a Crom-31 instrument with 1.5 m \times 5 mm columns at 170 $^\circ\text{C}$, 100 mesh Porapak-Q was used as filler. The rate of carrier gas (nitrogen) was 60 ml/min. The IR spectra (KBr pellets) were recorded on an UR-10 instrument. The ^1H NMR spectra were registered on a Perkin-Elmer R-32 spectrometer operated at 90 MHz with tetramethylsilane as external standard. The ESR spectrum of $(\text{Ph}_3\text{P})_2\text{NiCl}$ was obtained on a Varian E-12 instrument at 77 K.

The starting materials, the σ -ethylnickel derivatives $\text{EtNi}[\text{P}(\text{C}_6\text{H}_{11})_3](\text{acac})$ and $\text{EtNi}(\text{PPh}_3)_2\text{Cl}$, were prepared as described elsewhere ([9] and [6], respectively).

All synthetic and isolation experiments were carried out under argon in absolute solvents distilled in argon flow prior to use.

Reaction of Ethyl(acetylacetonato)(tricyclohexylphosphine)nickel with Diethylaluminium Chloride

An ether solution of diethylaluminium chloride (0.86 ml, 7.58 mmol) was added to $\text{EtNi}[\text{P}(\text{C}_6\text{H}_{11})_3]$ -

(acac) (3.54 g, 7.58 mmol) and tricyclohexylphosphine (4.22 g, 15.16 mmol) at -78°C . The mixture was stirred at -25°C for 2 hr. The yellow crystalline precipitate formed was isolated by filtration and recrystallized from ether to give $[(\text{C}_6\text{H}_{11})_3\text{P}]_2\text{Ni}(\text{H})\text{Cl}$ (3.10 g, 62.5%), m.p. $147\text{--}149^{\circ}\text{C}$ (dec.) [3]. The ^1H NMR spectrum (in C_6H_6) contained the hydride proton signal at $\delta -25.1$ ppm (triplet) [3].

Reaction of Ethyl(acetylacetonato)(tricyclohexylphosphine)nickel with Diethylaluminium Bromide

An ether solution of diethylaluminium bromide (0.32 ml, 2.46 mmol) was added to a solution of $\text{EtNi}[\text{P}(\text{C}_6\text{H}_{11})_3](\text{acac})$ (1.15 g, 2.46 mmol) and tricyclohexylphosphine (1.33 g, 4.92 mmol) in 20 ml ether at -40°C . The mixture was stirred at 22°C for 1 hr. According to GLC, the gas evolved during stirring contained ethylene (87%) and ethane (13%). The reaction mixture was evaporated, the precipitate formed was isolated by filtration and recrystallized from ether to give $[(\text{C}_6\text{H}_{11})_3\text{P}]_2\text{Ni}(\text{H})\text{Br}$ (1.61 g, 94%), m.p. $154\text{--}156^{\circ}\text{C}$ (dec.) [3]. The IR spectrum of the product (KBr) showed an absorption at 1922 cm^{-1} due to Ni-H stretches [3]. The ^1H NMR spectrum (in C_6H_6) contained the hydride proton signal at $\delta -23.61$ ppm [3].

Reaction Between Ethylbis(triphenylphosphine)nickel Chloride and Acetic Acid

Glacial acetic acid (3 ml) was added to $\text{EtNi}(\text{PPh}_3)_2\text{Cl}$ (0.5 g, 0.77 mmol). The mixture was heated at 60°C for 15 min. According to GLC, the evolved gas mixture (17.5 ml) contained ethane (61%), ethylene (35%), and hydrogen (5%). Blue precipitate isolated by filtration was $(\text{Ph}_3\text{P})_2\text{NiCl}_2$ (0.22 g, 83%), m.p. $246\text{--}248^{\circ}\text{C}$ (dec.) [8].

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