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

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Recently we reported the isolation of the new nickel hydride complex, $(Ph_3P)_3Ni(H)Br$, 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, $[(C_6H_{11})_3P]_2Ni(H)X$ (X is Cl, Br), containing two molecules of tricyclohexylphosphine:

$$EtNi[P(C_6H_{11})_3](acac) + Et_2AlX + P(C_6H_{11})_3 \longrightarrow [(C_6H_{11})_3P]_2Ni(H)X + C_2H_6 + C_2H_4$$

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 $EtNi(PPh_3)(acac)$ and Et_2AlBr yields a nickel hydride stabilized by three triphenylphosphine molecules:

$$EtNi(PPh_3)(acac) + Et_2AlBr + 2PPh_3 \longrightarrow (Ph_3P)_3Ni(H)Br$$

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, $[(C_6H_{11})_3P]_2Ni(H)X$ (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.* $EtNi(PPh_3)_2Cl$, containing two triphenylphosphine molecules:

$$EtNi(PPh_3)(acac) + Et_2AlCl + PPh_3 \longrightarrow EtNi(PPh_3)_2Cl$$

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, $(Ph_3P)_2NiCl$ [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 $(Ph_3P)_2NiCl_2$ [8].

Experimental

GLC analysis of gases was made on a Crom-31 instrument with 1.5 m × 5 mm columns at 170 °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 $(Ph_3P)_2NiCl$ was obtained on a Varian E-12 instrument at 77 K.

The starting materials, the σ-ethylnickel derivatives $EtNi[P(C_6H_{11})_3](acac)$ and $EtNi(PPh_3)_2Cl$, 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 $EtNi[P(C_6H_{11})_3]$-

(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 $[(C_6H_{11})_3P]_2Ni(H)Cl$ (3.10 g, 62.5%), m.p. 147–149 °C (dec.) [3]. The ^1H NMR spectrum (in C_6H_6) contained the hydride proton signal at δ –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 $EtNi[P(C_6H_{11})_3](acac)$ (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 $[(C_6H_{11})_3P]_2Ni(H)Br$ (1.61 g, 94%), m.p. 154–156 °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 δ –23.61 ppm [3].

Reaction Between Ethylbis(triphenylphosphine)nickel Chloride and Acetic Acid

Glacial acetic acid (3 ml) was added to $EtNi(PPh_3)_2Cl$ (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 $(Ph_3P)_2NiCl_2$ (0.22 g, 83%), m.p. 246–248 °C (dec.) [8].

References

1 A. N. Nesmeyanov, L. S. Isaeva, L. N. Lorens, V. S. Kolesov, *Dokl. Akad. Nauk SSSR, 223,* 1140 (1975).

2 J. D. Druliner, A. D. English, J. P. Jesson, P. Meakin, C. A. Tolman, *J. Am. Chem. Soc., 98,* 2156 (1976).

3 M. L. H. Green, T. Saito, P. J. Tanfield, *J. Chem. Soc. A,* 152 (1971).

4 H. Imoto, H. Moriyama, T. Saito, Y. Sasaki, *J. Organomet. Chem., 120,* 453 (1976).

5 A. Tolman, *Chem. Rev., 77,* 313 (1977).

6 A. N. Nesmeyanov, L. S. Isaeva, L. N. Lorens, *J. Organomet. Chem., 129,* 421 (1977).

7 P. Heimbach, *Angew. Chem. Int. Ed., 3,* 648 (1964); V. V. Saraev, F. K. Shimdt, L. V. Mironova, V. A. Gruznykh, *Koordinatsionnaya Khim., 2,* 1949 (1976) (Russ.).

8 L. M. Venanzi, *J. Chem. Soc.,* 719 (1958).

9 A. N. Nesmeyanov, L. S. Isaeva, L. N. Lorens, V. S. Kolesov, *Dokl. Akad. Nauk SSSR, 219,* 877 (1974).