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REACTIONS OF ETHYL(ACETYLACETONATO)(TRIPHENYLPHOSPHINE)NICKEL(II). A NEW HYDRIDE NICKEL COMPLEX, $(Ph_3P)_3Ni(H)Br$

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Summary

The reactions of $EtNi(PPh_3)(acac)$ with various reagents have been discussed; the reaction with $NaFe(CO)_2Cp$ or $Fe(CO)_5$ occurs via nickel(II) reductive carbonylation while $EtNi(PPh_3)(acac)$ and Et_2AlCl afford the unstable $EtNi(PPh_3)_2Cl$. The cleavage of the Ni—C bond with evolution of ethylene and ethane is observed when $EtNi(PPh_3)(acac)$ reacts with CS_2, $HgCl_2$ and Et_2AlBr. A new nickel hydride complex, $(Ph_3P)_3Ni(H)Br$, has been obtained from $EtNi(PPh_3)(acac)$ and Et_2AlBr and its properties have been studied. Another method of synthesis of this hydride complex directly from $Ni(acac)_2$ and Et_2AlBr has been proposed.

Introduction

At the present time few examples of σ-alkylnickel derivatives [1] stabilized by strong field ligands, are known.

σ-Ethylnickel(II) complexes, $EtNi(PR_3)(acac)$ (where $R = C_6H_5$ or cyclo-C_6H_{11}) have been prepared recently by alkylating nickel acetylacetonate with triethylaluminum or diethylaluminum ethoxide at low temperature (—30°C) in the presence of [2,3] or with subsequent addition of tertiary phosphine [4]. The structures of these compounds have been discussed in a number of papers [3,5] on the basis of X-ray analysis and NMR spectroscopy. However, practically no information is available on their chemical behaviour.

In this work we have studied the reactivity of ethyl(acetylacetonato)(triphenylphosphine)nickel, prepared for the first time the nickel hydride complex, $(Ph_3P)_3Ni(H)Br$, and described its properties.

Results and discussion

We have shown that ethyl(acetylacetonato)(triphenylphosphine)nickel undergoes reductive carbonylation with Ni—C bond cleavage, in the presence of reagents such as $NaFe(CO)_2Cp$ and $Fe(CO)_5$ [6].

The formation of gaseous products and the precipitation of a small quantity of solid is observed when THF solutions of ethyl(acetylacetonato)(triphenylphosphine)nickel, triphenylphosphine and $NaFe(CO)_2Cp$ are mixed at room temperature. GLC analysis of the gas evolved showed ethane, ethylene and traces of hydrogen. Bis(triphenylphosphine) dicarbonylnickel (50%) and the unstable triphenylphosphine derivative, $Cp_2Fe_2(CO)_3PPh_3$, were isolated from the reaction mixture by chromatography on alumina. The latter compound was obtained for the first time analytically pure and identified by elemental analysis, NMR and mass spectra.

$$EtNi(PPh_3)(acac) + NaFe(CO)_2Cp + 2\ PPh_3 \rightarrow C_2H_4 + C_2H_6 + (Ph_3P)_2Ni(CO)_2 + Cp_2Fe_2(CO)_3PPh_3 + Na(acac) \quad (1)$$

The formation of the zerovalent nickel complex, $(Ph_3P)_2Ni(CO)_2$, shows that a redox process occurs in which the π-cyclopentadienyliron dicarbonyl anion acts as a donor of electrons and CO groups simultaneously. The carbonyl ligand transfer may proceed via an unstable intermediate complex containing both nickel and iron. In fact, by the careful chromatographic separation of the reaction products we succeeded in isolating a small quantity of a red-brown substance with 4.60% Ni and 6.70% Fe. Its IR spectrum contains the CO ligand stretching modes at 1858 and 1870(sh) cm^{-1}. Its NMR spectrum in benzene solution shows a signal at δ 3.90 ppm with $J(^{31}P—H) \leqslant 1.5$ Hz which could be due to the C_5H_5 protons. The compound may be an intermediate binuclear iron—nickel complex. Similar compounds have been obtained from $NaFe(CO)_2Cp$ and nickelocene or $CpNi(PPh_3)X$ [7].

When ethyl(acetylacetonato)(triphenylphosphine)nickel was allowed to reacts with $Fe(CO)_5$ instead of $NaFe(CO)_2Cp$ it gave $(Ph_3P)_2Ni(CO)_2$ (37%), mono- and diphosphinic $Fe(CO)_5$ derivatives.

$$EtNi(PPh_3)(acac) + Fe(CO)_5 + 4\ Ph_3P \rightarrow (Ph_3P)_2Ni(CO)_2 + (Ph_3P)Fe(CO)_4 + (Ph_3P)_2Fe(CO)_3 \quad (2)$$

Previously, the reductive and carbonylating abilities of $Fe(CO)_5$ have been used for the synthesis of some transition metal carbonyls: W, Mo, Co and Rh [8].

We have also studied the reactions of ethyl(acetylacetonato)(triphenylphosphine)nickel with CS_2 and $HgCl_2$. The composition of the gaseous products generated in these reactions agrees with the β-elimination mechanism commonly adopted for a decomposition of σ-alkyl transition metal compounds containing β-hydrogen [9a].

The action of carbon disulfide on ethyl(acetylacetonato)(triphenylphosphine)nickel produced ethylene (70%) and ethane (30%) as well as the nickel carbon disulfide complex, $[Ni(CS_2)PPh_3]_2$, reported in [10]:

$$2\ EtNi(PPh_3)(acac) + 2\ CS_2 \rightarrow C_2H_4 + C_2H_6 + [Ni(CS_2)PPh_3]_2 \quad (3)$$

Similarly, the treatment of ethyl(acetylacetonato)(triphenylphosphine)nickel with a solution of mercuric chloride at room temperature gives ethylene, ethane and hydrogen, in a ratio of 50 : 32 : 18, nickel acetylacetonate and the complexes of mercuric chloride with triphenylphosphine:

$$\mathrm{EtNi(PPh_3)(acac) + HgCl_2 \rightarrow C_2H_4 + C_2H_6 + H_2 + Ni(acac)_2 + HgCl_2(PPh_3)_2 + (HgCl_2)_2(PPh_3)_2} \quad (4)$$

We detected no organomercury compounds in the reaction mixture. This is an interesting point in this reaction for usually mercuric chloride acts as an electrophilic agent causing the cleavage of the alkyl—transition metal σ-bond and the formation of organomercury compounds [9b].

The β-elimination in the reaction of ethyl(acetylacetonato)(triphenylphosphine)nickel with triethylaluminium also proceeds in a peculiar manner. The reaction was carried out at —40° C in the presence of triphenylphosphine; π-ethylenebis(triphenylphosphine)nickel(0) (52%) was isolated as the main product:

$$\mathrm{EtNi(PPh_3)(acac) + Et_3Al + Ph_3P \rightarrow C_2H_4Ni(PPh_3)_2} \quad (5)$$

Probably the reaction involves an intermediate formation of the phosphine derivative of diethylnickel [11] which is unstable and may decompose into zerovalent nickel, ethylene and ethane. The ethylene generated coordinates with the zerovalent nickel producing $C_2H_4Ni(PPh_3)_2$.

The treatment of ethyl(acetylacetonato)(triphenylphosphine)nickel with diethylaluminum chloride under the same conditions caused instant precipitation of an orange crystalline substance, extremely unstable in solid and solution. Elemental analysis and thermal decomposition (C_2H_4 and C_2H_6 evolution) of this compound demonstrated that it is a new σ-ethylnickel complex, ethyl(triphenylphosphine)nickel chloride:

$$\mathrm{EtNi(PPh_3)(acac) + Et_2AlCl + PPh_3 \rightarrow EtNi(PPh_3)_2Cl} \quad (6)$$

Thus this reaction involves an exchange between the acetylacetonate anion and chloride, instead of Ni—C bond cleavage.

At the same time the reaction of ethyl(acetylacetonato)(triphenylphosphine)-nickel with diethylaluminum bromide gives ethylene and ethane (3 : 2) along with the dark-red crystalline compound which is a new nickel hydride complex, $(Ph_3P)_3Ni(H)Br$:

$$\mathrm{EtNi(PPh_3)(acac) + Et_2AlBr + 2\ Ph_3P \rightarrow (Ph_3P)_3Ni(H)Br + C_2H_4 + C_2H_6} \quad (7)$$

The reaction may occur via the formation of the unstable bromine-containing σ-ethylnickel complex which decomposes to metal hydride with olefin elimination. Hydridotris(triphenylphosphine)nickel bromide is poorly soluble in common organic solvents. Upon dissolving in acetone it decomposes with the evolution of hydrogen identified by GLC, and the formation of the paramagnetic tris(triphenylphosphine)nickel bromide, $(Ph_3P)_3NiBr$ [13]. This nickel hydride complex is highly sensitive to air oxygen. In argon however it decomposes completely at 100—140° C with hydrogen evolution. The reaction with carbon tetrachloride is a specific indicator of the hydride hydrogen in the complexes. Treatment of hydridotris(triphenylphosphine)nickel bromide with CCl_4 in toluene afforded 82% of $CHCl_3$ in the reaction mixture (GLC analysis).

The same nickel hydride complex, $(Ph_3P)_3Ni(H)Br$, was obtained directly from nickel acetylacetonate and diethylaluminum bromide. One may assume that nickel acetylacetonate and diethylaluminum bromide react with the formation of σ-ethylnickel complex which decomposes into an olefin and nickel hydride complex by a β-elimination mechanism. Depending on the ratio of the reagents this reaction may also afford bis(triphenylphosphine)nickel dibromide, $(Ph_3P)_2NiBr_2$. Thus with the ratio 1 : 3 : 1 of nickel acetylacetonate, triphenylphosphine and diethylaluminum bromide, the mixture found contains bright-red $(Ph_3P)_3Ni(H)Br$ (31%) and dark-green $(Ph_3P)_2NiBr_2$ (69%):

$$Ni(acac)_2 + 3\ Ph_3P + Et_2AlBr \rightarrow (Ph_3P)_3Ni(H)Br \qquad (8)$$

$$Ni(acac)_2 + 2\ Ph_3P + 2\ Et_2AlBr \rightarrow (Ph_3P)_2NiBr_2 \qquad (9)$$

For directing the reaction predominantly according to eqn. 8 the quantity of diethylaluminum bromide should be considerably reduced and a 1 : 1 : 0.16 ratio of reagents used. The ratio 1 : 3 : 2 yields $(Ph_3P)_2NiBr_2$ quantitatively. Further, it should be noted that $(Ph_3P)_2NiBr_2$ is not an intermediate in reaction 8, since it does not react with diethylaluminum bromide under these conditions.

When the mixture of organoaluminum compounds, diethylaluminum ethoxide and diethylaluminum bromide (4 : 1), was used as an alkylating agent of nickel acetylacetonate we isolated the nickel hydride complex, $(Ph_3P)_3Ni(H)Br$, and ethyl(acetylacetonato)(triphenylphosphine)nickel (71 and 60% respectively).

Experimental

All reactions were carried out under argon, in absolute solvents previously distilled in argon. IR spectra were taken on a UR-20 spectrophotometer. The NMR spectra were recorded on a Hitachi Perkin—Elmer R-20 instrument at 60 MHz. GLC analysis of gases was performed on a Crom-31 chromatograph with 1.5 m × 5 mm columns at 170°C, 100 mesh Paropak-Q was used as filler. The rate of gas-carrier (nitrogen) was 60 ml/min.

Reactions of ethyl(acetylacetonato)(triphenylphosphine)nickel

(1) With π-cyclopentadienyliron dicarbonyl sodium salt. The THF solution of $NaFe(CO)_2Cp$ prepared from 1.1 ml of Hg, 6 mg-atom of Na and 2 mmol of $[CpFe(CO)_2]_2$ [14] was added to 4 mmol of $EtNi(PPh_3)(acac)$ and 8 mmol of PPh_3 in 30 ml of THF. The reaction mixture was stirred at 22°C for 3.5 h then evaporated to dryness and the residue chromatographed on an alumina column (2 × 20 cm) (the alumina was preliminary heated in vacuo to 200°C and cooled under argon stream). Consecutive elution with petroleum ether/benzene mixtures (9 : 1 and 1 : 1) gave 1.71 g of crude $(Ph_3P)_2Ni(CO)_2$, its recrystallization from benzene afforded 1.28 g (50% theory) of the product, m.p. 198—200°C, $\nu(CO)$ 1955, 2010 cm^{-1} (hexane) [15]. Then 0.17 g of a red-brown substance was eluted with benzene, $\nu(CO)$ 1858, 1870(sh) cm^{-1} (KBr) and 0.09 g (7% theory) of $Cp_2Fe_2(CO)_3PPh_3$, the dark-green substance recrystallized from acetone. (Found: C, 63.57; H, 4.64; Fe, 18.43; P, 5.39. $C_{31}H_{25}Fe_2O_3P$ calcd.: C, 63.31; H, 4.29; Fe, 18.99; P, 5.27%). The NMR spectrum ($(CD_3)_2CO$) has absorptions at δ 4.33 (C_5H_5, d, J 1.5 Hz) 4.55 (s, C_5H_5), 7.20—8.00 ppm (m, C_6H_5). The mass-spectrum taken on an MX-1303 instrument at 40°C and 30 V ionizing voltage contains the heaviest ion at m/e 588. The IR spectrum: $\nu(CO)$

1745, 1940 and 1963 cm^{-1} (cyclohexane) [16].

(2) With iron pentacarbonyl. A solution of 30 mmol of $Fe(CO)_5$ in THF was added to 3 mmol of $EtNi(PPh_3)(acac)$ and 6 mmol of PPh_3 in 25 ml of THF at 22°C. After 3.5 h the solution was evaporated in vacuo and the residue was separated on alumina column (2 × 20 cm). Consecutive elution with petroleum ether and petroleum ether/benzene mixtures (9 : 1, 4 : 1 and 1 : 1) afforded the following substances: 1.20 g of $(Ph_3P)Fe(CO)_4$, m.p. 198—199°C (benzene), ν(CO) 1938, 1981 and 2057 cm^{-1} (KBr) [17]; 0.70 g (37% theory) of $(Ph_3P)_2Ni(CO)_2$, m.p. 199—201°C (benzene), ν(CO) 1955, 2010 cm^{-1} (hexane) [15] and 0.32 g of $(Ph_3P)_2Fe(CO)_3$, m.p. 268—270°C (acetone), ν(CO) 1890 cm^{-1} ($CHCl_3$) [17].

(3) With carbon disulfide. 3.9 mmol of $EtNi(PPh_3)(acac)$ was dissolved in 10 ml of carbon disulfide. GLC analysis of the gaseous products evolved showed 70% of C_2H_4 and 30% of C_2H_6. The precipitated nickel complex was filtered, washed with pentane and dried in vacuo. 1.22 g of $[Ni(CS_2)PPh_3]_2$ (80% theory) was obtained. Its IR spectrum in vaseline oil contains the strong band ν(CS) at 1122 cm^{-1} which is in agreement with the literature data [10].

(4) With mercuric chloride. A suspension of 15.2 mmol of $HgCl_2$ in 50 ml of benzene was added to 6 mmol of $EtNi(PPh_3)(acac)$. Intensive gas evolution was observed. GLC analysis of the gaseous products (116 ml) showed 50% of C_2H_4, 32% of C_2H_6 and 18% of H_2. The reaction mixture was stirred at room temperature for 2 days. The light solid was separated from unreacted $HgCl_2$, the mother liquid evaporated to dryness and the residue crystallized from ethanol, 0.22 g of nickel acetylacetonate was obtained. The filtered solid (3.25 g) was placed in a Soxhlet apparatus and extracted repeatedly with benzene. After the evaporation of the benzene extract 1.09 g of $HgCl_2(PPh_3)_2$ was isolated, m.p. 266—268°C (benzene) [18]. The solid remaining after extraction with benzene was washed repeatedly with hot glacial acetic acid to give 0.51 g of $(HgCl_2)_2(PPh_3)_2$, m.p. 306—309°C [19].

(5) With triethylaluminum. A solution of 4.4 mmol of Et_3Al in pentane was added dropwise at —40°C to a solution of 4.4 mmol of $EtNi(PPh_3)(acac)$ and 4.4 mmol of PPh_3 in 10 ml of ether. The mixture was stirred at —40°C for 33 h. The yellow precipitate was filtered, repeatedly washed with ether and dried in vacuo. 1.40 g of $C_2H_4Ni(PPh_3)_2$ (52% theory) was obtained, m.p. 108—110°C (dec.). (Found: C, 74.76; H, 5.62; Ni, 8.99. $C_{38}H_{34}NiP_2$ calcd.: C, 74.66, H, 5.61; Ni, 9.60%). NMR spectrum: δ 2.55 (s, C_2H_4) (benzene).

(6) With diethylaluminum chloride. An ethereal solution of 3.82 mmol of Et_2AlCl was added to 3.82 mmol of $EtNi(PPh_3)(acac)$ and 7.64 mmol of PPh_3 in 30 ml of ether at —40°C. After stirring for 30 min the orange precipitate was filtered, washed with ether and dried. 2.00 g (82% theory) of $EtNi(PPh_3)_2Cl$ was obtained, m.p. 60°C (dec.). (Found: C, 70.26; H, 5.59; Ni, 8.62. $C_{38}H_{35}ClNiP_2$ calcd.: C, 70.47; H, 5.45; Ni, 9.06%).

(7) With diethylaluminum bromide. An ethereal solution of Et_2AlBr (4.65 mmol) was added at —40°C to a solution of $EtNi(PPh_3)(acac)$ (4.65 mmol) and PPh_3 (9.3 mmol) in 60 ml ether. The mixture was stirred for 30 min at —20°C. Gradual gas evolution and precipitation of a solid were observed. GLC analysis of the gas (57 ml) showed 57% of C_2H_4, 40% of C_2H_6 and 3% of H_2. The red crystalline solid was filtered, washed with ether and dried. 3.72 g (86.5% theory)

of $(Ph_3P)_3Ni(H)Br$, m.p. 79°C (dec.) (ether) was obtained. (Found: C, 69.62; H, 5.62; Br, 9.62; P. 9.33. $C_{48}H_{46}BrNiP_3$ calcd.: C, 70.16; H, 5.00; Br, 8.64; P, 10.03%).

The reaction of nickel acetylacetonate with diethylaluminum bromide

An ethereal solution of Et_2AlBr (3.1 mmol) was added at −20°C to a solution of $Ni(acac)_2$ (3.1 mmol) and PPh_3 (9.3 mmol) in 40 ml of ether. The mixture was stirred for 16 h at −10°C. The flocky green solid formed gradually turned into a mixture of red and dark-green crystalline substances which were filtered. A multiple extraction with ether afforded 0.89 g (31% theory) of $(Ph_3P)_3Ni(H)Br$, bright-red crystals, m.p. 80°C (dec.)(ether). The residue from ether extraction was 0.79 g $(Ph_3P)_2NiBr_2$ (69% theory) which was crystallized from acetone, m.p. 214—218°C [20].

At a 1 : 1 : 0.16 molar ratio of $Ni(acac)_2$, PPh_3 and Et_2AlBr only $(Ph_3P)_3Ni(H)Br$ was obtained (94% theory).

The reaction of bistriphenylphosphinenickel dibromide with diethylaluminum bromide

An ethereal solution of 0.47 mmol of Et_2AlBr was added at −40°C to 3 mmol of $(Ph_3P)_2NiBr_2$ and 3 mmol of PPh_3 in 30 ml of ether. The mixture was stirred at −10°C for 13 h. Then the starting complex was isolated quantitatively by filtration.

The reaction of nickel acetylacetonate with a mixture of organoaluminum compounds

An ethereal solution of a 1 ml mixture of Et_2AlOEt and Et_2AlBr (molar ratio 4.2 : 1) was added at −40°C to 10 mmol of $Ni(acac)_2$ and 10 mmol of PPh_3 in 40 ml of ether. The mixture was stirred at −15°C for 5 h. The red precipitate was filtered, washed with ether and dried. 1.02 g (71% theory) of $(Ph_3P)_3Ni(H)Br$ was obtained. The mother liquid was allowed to stay at −10°C. After 4 h it was evaporated to a minimum volume and cooled to −78°C. The yellow crystalline solid was filtered and crystallized from ether. 1.44 g of $EtNi(PPh_3)(acac)$ (60% theory) was obtained, m.p. 90—95°C (dec.) [3,4].

The reaction of hydridotristriphenylphosphinenickel bromide with acetone

15 ml of acetone was added to 2.1 mmol of $(Ph_3P)_3Ni(H)Br$. The suspension was heated to 50—60°C for 1.5 h. 20 ml of hydrogen evolved (86.5% theory, GLC). 1.36 g (71% theory) of $(Ph_3P)_3NiBr$ was obtained, yellow crystalline solid, m.p. 110°C (dec.) (ether-benzene) [13]. (Found: C, 70.22; H, 5.37. $C_{48}H_{45}BrNiP_3$ calcd.: C, 70.16; H, 4.90%).

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References

1 A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida and A. Misono, J. Amer. Chem. Soc., 87 (1965) 4652; H.F. Klein and H.H. Karsch, Chem. Ber., 105 (1972) 2628; ibid., 106 (1973) 1433.

2 P.W. Jolly, K. Jonas, C. Krüger and Y.-H. Tsay, J. Organometal. Chem., 33 (1971) 109.

3 A. Yamamoto, T. Yamamoto, T. Saruyama and Y. Nakamura, J. Amer. Chem. Soc., 95 (1973) 4073.

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

5 F.A. Cotton, B.A. Frenz and D.L. Hunter, J. Amer. Chem. Soc., 96 (1974) 4820.

6 A.N. Nesmeyanov, L.S. Isaeva and L.N. Lorens, Dokl. Akad. Nauk SSSR, 229 (1976) 634.

7 J.F. Tilney-Bassett, Proc. Chem. Soc., (1960) 419; K. Yasufuku and H. Yamazaki, J. Organometal. Chem., 38 (1972) 367.

8 A.N. Nesmeyanov, K.N. Anisimov, E.P. Mikheev, V.L. Volkov and Z.P. Valueva, Zh. Neorg. Khim., 4 (1959) 249; Zh. ibid., 4 (1959) 503; B.L. Booth, M.J. Else, R.Fields, H. Goldwhite and R.N. Haszeldine, J. Organometal. Chem., 14 (1968) 417.

9 (a) S. Otsuka, A. Nakamura, T. Yoshida, M. Naruto and K. Ataka, J. Amer. Chem. Soc., 95 (1973) 3180; M.C. Baird, J. Organometal. Chem., 64 (1974) 289; R.P.A. Sneeden and H.H. Zeiss, J. Organometal. Chem., 22 (1970) 713.
(b) L.J. Dizikes and A. Wojcicki, J. Amer. Chem. Soc., 97 (1975) 2540; G.N. Schrauzer, J.H. Weber, T.M. Bechman and R.K.Y. Ho, Tetrahedron Lett., (1971) 275.

10 M.C. Baird and G. Wilkinson, J. Chem. Soc. A, (1967) 865.

11 G. Wilke and G. Herrman, Angew. Chem., Int. Ed., 1 (1962) 549; K. Fischer, K. Jonas, P. Misbach, R. Stabba and G. Wilke, Angew. Chem., Int. Ed., 12 (1973) 943.

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

13 P. Heimbach, Angew. Chem., Int. Ed., 3 (1964) 648.

14 T.S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 3 (1956) 104.

15 M. Bigorgne and A. Zelwer, Bull. Soc. Chim. Fr., (1960) 1986.

16 R.J. Haines and A.L. du Preez, Inorg. Chem., 8 (1969) 1459.

17 A.F. Clifford and A.K. Mukherjee, Inorg. Chem., 2 (1963) 151.

18 G.E. Coates and A. Lauder, J. Chem. Soc., (1965) 1857.

19 R.C. Evans, F. Mann, H.S. Peiser and D. Purdie, J. Chem. Soc., (1940) 1209.

20 G. Yagypsky, W. Mowat, A. Shortland and G. Wilkinson, J. Chem. Soc. Chem. Commun., (1970) 1369.