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Interaction of Nickel Acetylacetonate with Diethylaluminum Chloride

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The interaction of $Ni(acac)_2$ with diethylaluminum chloride in the presence of triphenylphosphine has been studied. Complexes of nickel, $[(Ph_3P)_3NiCl]_2$ and $Ni(acac)_2PPh_3$ not so far described, have been isolated. Thermal decomposition of $[(Ph_3P)_3NiCl]_2$ has yielded $(Ph_3P)_2NiCl_2$, $NiCl_2$, and metallic Ni. Dissociation of $[(Ph_3P)_3NiCl]_2$ in THF solution has been studied by the ESR method. A new Ni(I) complex, $[(Ph_3P)_3Ni(CH_3CN)]BF_4$, has been obtained by interaction of $[(Ph_3P)_3NiCl]_2$ with acetonitrile in the presence of $TlBF_4$. The structure of penta-coordinate complex of nickel, $Ni(acac)_2PPh_3$ has been established by IR and NMR (^1H, ^{13}C, and ^{31}P) spectroscopy.

The reaction of $Ni(acac)_2PPh_3$ with diethylaluminum bromide has been shown to yield $(Ph_3P)_3Ni(H)Br$ and $(Ph_3P)_2NiBr_2$.

Introduction

The literature gives scattered and conflicting information about the composition and structure of the products of the reaction of nickel salts with alkylaluminum halides; these products play an important role in homogeneous catalysis of olefins [1].

Feldblyum and co-workers [2] have shown that gaseous products of the reaction of nickel oleate with ethylaluminum sesquichloride consist of ethane, hydrogen, and traces of ethylene. On this basis, it has been suggested that nickel hydrides are formed as the intermediates of the reaction. However, Ewers [3] believes that nickel is mainly in a zerovalent oxidation state. While investigating such catalytic systems by the ESR method Shmidt and coworkers [4] have discovered paramagnetic compounds of nickel of different geometric configuration.

We have recently started an investigation of the unstable intermediates formed in such systems. Thus, we have obtained the new hydride complex, $(Ph_3P)_3Ni(H)Br$, from the reaction of nickel acetylacetonate with diethylaluminum bromide in the presence of triphenylphosphine and investigated its properties [5]. The present paper considers the reaction of nickel acetylacetonate with diethylaluminum chloride.

Results and Discussion

The reaction of nickel acetylacetonate with diethylaluminum chloride in the presence of triphenylphosphine proceeds only at room temperature and is accompanied by the evolution of ethane, ethylene, and hydrogen in the ratio 6:3:1, respectively. A yellow crystalline precipitate is produced, which probably has a structure of a dimer of a monovalent nickel chloride, $[(Ph_3P)_3NiCl]_2$. The compound $Ni(acac)_2PPh_3$, has been also isolated from the reaction mixture:

$$Ni(acac)_2 + Et_2AlCl + PPh_3 \rightarrow [(Ph_3P)_3NiCl]_2 + Ni(acac)_2PPh_3 + C_2H_6 + C_2H_4 + H_2 \quad (1)$$

The reagents, $Ni(acac)_2$, Et_2AlCl, and PPh_3, are used in the ratio 6:1:6, which, as has been shown earlier [5], is an optimum one for the synthesis of nickel hydride, $(Ph_3P)_3Ni(H)Br$. We have, however, failed to perform reaction (1) at −10 °C, as it is reported for nickel acetylacetonate and diethylaluminum bromide [5]; this may be due to a lower reactivity of diethylaluminum chloride as compared with the bromide. A higher proportion of diethylaluminum chloride in comparison with the bromide, considerably accelerates the reaction and results in the precipitation of metallic nickel. It is proposed that the reaction of nickel acetylacetonate with diethylaluminum chloride involves the formation σ-ethyl compound, which decomposes *via* the unstable nickel hydride under these conditions giving $[(Ph_3P)_3NiCl]_2$ and the mixture of ethane, ethylene and hydrogen. This assumption is cofirmed by the composition of the evolved gaseous products. Besides, treating the known σ-ethyl compound, $EtNi(PPh_3)(acac)$, with diethylaluminum chloride at −40 °C, we obtain another σ-ethyl derivative of nickel, $EtNi(PPh_3)_2Cl$ [5, 14]:

$$EtNi(PPh_3)(acac) + Et_2AlCl + PPh_3 \rightarrow EtNi(PPh_3)_2Cl \qquad (2)$$

When dissolved in benzene $EtNi(PPh_3)_2Cl$ decomposes with the evolution of ethane and ethylene (1:1) and formation of a monovalent nickel complex, $(Ph_3P)_2NiCl$.

The obtained dimer of tris(triphenylphosphine)-nickelchloride in the solid state is thermally stable under argon atmosphere.

On heating to 140–180 °C the complex decomposes with the formation of bis(triphenylphosphine)nickeldichloride, nickeldichloride and metallic nickel:

$$2[(Ph_3P)_3NiCl]_2 \rightarrow (Ph_3P)_2NiCl_2 + NiCl_2 + 2Ni + 10PPh_3 \qquad (3)$$

An increase in temperature probably causes dissociation of dimer to monomer, which in turn disproportionates giving zero-valent nickel and compounds of bivalent nickel.

It should be noted that according to GLC analysis the gaseous phase does not contain hydrogen after thermal decomposition of the complex. This result confirms the supposed structure of dimer $[(Ph_3P)_3NiCl]_2$ and excludes an alternative structure of $(Ph_3P)_3Ni(H)Cl$.

As it has been reported [6], compounds of nickel-(I), $[(Ph_3P)_3NiBH_4]_2$ and $[(Ph_3P)_3Ni]_2(PF_6)_2$, dimeric with Ni–Ni bond are diamagnetic. $[(Ph_3P)_3NiCl]_2$ complex in a solid state is practically diamagnetic, but in THF solution at 22 °C the dimer is completely dissociated. The measured concentration of radicals is close to the double concentration of parent dimer. At temperature below −10 °C the monomer ESR spectrum in THF is a poorly resolved triplet ($a^P = 57$ Gauss, $g = 2.205$). With a temperature decrease to −70 °C the ESR signal disappears, which suggested the monomer dimerization under these conditions. The last conclusion is also confirmed by the ^{31}P NMR spectrum of $[(Ph_3P)_3NiCl]_2$. Its spectrum recorded in THF at −70 °C shows a singlet at δ 25.38 ppm, which disappears at 22 °C.

Metal oxidation state (+1) remains constant in the reaction of $[(Ph_3P)_3NiCl]_2$ with acetonitrile in the presence of thallium borofluoride. Addition of a small excess of acetonitrile and $TlBF_4$ to THF solution of $[(Ph_3P)_3NiCl]_2$ results in the formation of thallium chloride and a monovalent nickel paramagnetic compound, $[(Ph_3P)_3Ni(CH_3CN)]BF_4$, not described yet:

$$[(Ph_3P)_3NiCl]_2 + 2CH_3CN + 2TlBF_4 \rightarrow 2[(Ph_3P)_3Ni(CH_3CN)]BF_4 + 2TlCl \qquad (4)$$

The obtained tetra-coordinate complex of nickel, containing triphenylphosphine and acetonitrile as ligands, is a pale-yellow crystalline substance soluble in polar solvents and stable under argon. The Raman spectrum of this complex shows a peak at 2274 cm^{-1} corresponding to ν(C≡N), which confirms the presence of coordinate aetonitrile in $[(Ph_3P)_3Ni(CH_3CN)]BF_4$. A shift of ν(C≡N) in the complex towards high frequencies by 20 cm^{-1} as compared with free acetonitrile molecule [7] is typical of nitrile molecule coordination with the metal atom through a lone electron pair of the nitrogen atom [8].

The ESR spectra of $[(Ph_3P)_3Ni(CH_3CN)]BF_4$ recorded both in acetone and in the solid state at 22 °C show a broad signal ($\Delta H \cong 1200$ Gauss, $g = 2.158$). Besides, it was shown that with a temperature decrease to −70 °C the intensity of the ESR signal in THF falls down. This allowed us to observe the singlet at 27.17 ppm in the ^{31}P NMR spectrum of this complex in THF. However, this signal disappears at 22 °C. Perhaps $[(Ph_3P)_3Ni(CH_3CN)]BF_4$ is dimerized at the low temperature.

Special emphasis should be given on properties of nickel acetylacetonate complex, $Ni(acac)_2PPh_3$. We obtained this complex for the first time when treating the mixture of nickel acetylacetonate and triphenyl phosphine with diethylaluminum chloride at 22 °C (see eqn. 1). We have found that nickel acetylacetonate does not react with triphenylphosphine without Et_2AlCl. It can be suggested that bis(acetylacetonato)(triphenylphosphine)nickel is formed by disproportionation of an unstable intermediate σ-ethyl nickel compound. This assumption is in accordance with the literature data; as it was shown earlier [15] pyridine reacts with $EtNi(PPh_3)(acac)$ to give $Ni(acac)_2 \cdot 2py$ and $(\pi\text{-}C_2H_4)Ni(PPh_3)_2$ alongside with the ethane elimination.

Similar compounds of Pt and Pd, containing acetylacetonate ligand coordinated to the metal in a uni- or bidentate fashion have been described quite recently [9]. They are usually obtained by the action of tertiary phosphine on the acetylacetonates of the corresponding metals.

The data of the elemental analysis and cryoscopic determination of the molecular weight of the nickel complex obtained agree well with the suggested formula, $Ni(acac)_2PPh_3$.

The spectral data indicate that $Ni(acac)_2PPh_3$ is a penta-coordinate complex in which acac-ligand is coordinated to the nickel atom in a bidentate chelate mode.

The IR spectrum of $Ni(acac)_2PPh_3$ fits well the supposed structure. It contains bands 1592, 1532 cm^{-1} (stretching vibrations C=O), 1190 cm^{-1} (defor-

TABLE I. Parameters of $^{13}C-\{^1H\}$ NMR Spectra of Ni(acac)$_2$PPh$_3$ for Acac-ligand.

Solvent	Temperature °C	Chemical shifts (δ) in ppm		
		CH_3	CH	C···O
Benzene	20	26.58	100.98	191.04
Acetone	30	26.40	100.93	191.31
	–50	26.27	101.06	191.18
Ether	–50	26.34	100.48	190.47

mation C–H vibration), 1030, 935, 770, 660, 580 cm^{-1} characteristic of chelate complexes of acetylacetonate. The given frequencies are close to those of acetylacetonate ligand in Ni(acac)$_2$ [10]. The spectrum also contains bands of triphenylphosphine ligand; the most pronounced bands appear at 695 and 720 cm^{-1} and refer to the out-of-plane deformation vibrations C–H of the phenyl substituent.

The PMR spectrum of Ni(acac)$_2$PPh$_3$ recorded in benzene ($\delta_{C_6H_6}$ = 7.37 ppm) shows two singlet signals at δ = 1.87 and δ = 5.56 ppm assigned to protons of CH_3 and CH groups of acetylacetonate anion, with an intensity ratio 6:1.

The ^{13}C NMR spectrum of this compound shows signals of methyl group carbons δ = 26.58 ppm [J($^{13}C-^1H$) = 128.0 Hz], ketone group carbons δ = 191.04 ppm and methine group carbon δ = 100.98 ppm [J($^{13}C-^1H$) = 163.3 Hz].

Table I gives chemical shifts of the acac-ligand carbon atoms of Ni(acac)$_2$PPh$_3$ complex. The data of these spectra unambiguously prove the presence in the complex of acetylacetonate ligand in the enolate chelate form and correlate well with the $^{13}C-\{^1H\}$ NMR spectrum of palladium acetylacetonate [9]. Examination ^{13}C and ^{31}P NMR spectra of Ni(acac)$_2$-PPh$_3$ in different solvents and at different temperatures reveals the dynamic behaviour of the triphenylphosphine ligand. In fact, the triphenylphosphine signals appear in ^{13}C NMR spectrum only after decreasing the temperature to –50 °C and they are weaker than the acac-ligand signals. The ^{31}P NMR spectrum recorded in ether at –80 °C shows one signal at δ 23.38 ppm, while two signals (25.88 and –9.97 ppm) are observed in the spectrum recorded in acetone under the same conditions. A less intense signal (25.88) corresponds to coordinated triphenylphosphine and a more intense one (–9.97) to free triphenylphosphine. Spectrum recorded in toluene at –80 °C demonstrates, along with the intense signal of the triphenylphosphine ligand at δ = 23.79 ppm, a broad signal centered at δ = 22.05 ppm.

With a temperature decrease by 5 °C the distance between signals increases to 2.34 ppm and their width decreases. Such a spectroscopic pattern points to exchange processes even at low temperature (–80 to –85 °C) between the triphenylphosphine ligand and free PPh$_3$, the content of the latter in the solution being significantly lowered. Similar dynamic behaviour of the triphenylphosphine ligand is also observed in alkyl compounds of nickel, RNi(acac)-(PR$'_3$)$_n$ [11].

It is of interest to note that we failed to isolate bis(acetylacetonato)(triphenylphosphine)nickel in the reaction of nickel acetylacetonate with Et$_2$AlBr carried out in a broader temperature range (–30 °C–+20 °C).

However, it may be assumed that this complex is formed as an intermediate, since Ni(acac)$_2$PPh$_3$ reacts with Et$_2$AlBr in the presence of triphenylphosphine to yield (Ph$_3$P)$_3$Ni(H)Br and (Ph$_3$P)$_2$·NiBr$_2$. Earlier the same nickel complexes have been obtained from the reaction of nickel acetylacetonate with diethylaluminum bromide [5].

Experimental

The PMR spectra were recorded on a Perkin-Elmer R-12 spectrometer at 60 MHz. The ^{13}C and ^{31}P NMR spectra were obtained with a Bruker HX-90 spectrometer with frequencies 22.635 MHz and 36.46 MHz, respectively. Chemical shifts in ^1H and ^{13}C NMR spectra were measured from TMS; for ^{31}P NMR spectra 85% H$_3$PO$_4$ was used as external reference.

Infrared spectra in the region 4000–250 cm^{-1} were recorded with a Perkin-Elmer-457 spectrometer as nujol mulls (prepared under argon atmosphere). Raman spectra were registered on a Coderg-PHO laser spectrometer at 6328 Å line excitation of He/Ne laser. Samples were sealed in a capillary under argon. ESR spectra were registered on a Varian-E12A spectrometer equipped with a standard temperature unit.

All experiments were carried out under argon in absolute solvents distilled also under argon just before the experiments.

Reactions of Nickel Acetylacetonate with Diethylaluminum Chloride in the Presence of Triphenylphosphine

Ether solution of 0.4 g (3.35 mmol) of diethylaluminum chloride was added to the suspension of 5.0 g (20 mmol) of Ni(acac)$_2$ and 5.2 g (20 mmol) of triphenylphosphine in 60 ml of ether at –40 °C. The reaction mixture was stirred for 4 hours at room temperature. The reaction was accompanied with gas evolution and formation of a yellow precipitate. According to GLC data the gas evolved (35 ml) contained C_2H_6, C_2H_4 and H_2 in the ratio 6:3:1, respectively. The precipitated substance was filtered, washed with ether, and dried *in vacuo*. 2.88 g (98%) of [(Ph$_3$P)$_3$NiCl]$_2$ was obtained, m.p. 144–145 °C (dec.) (ether). *Anal.* (Found: C, 73.23; H, 5.52; Ni, 7.04; Cl, 4.30%. Calcd. for $C_{54}H_{45}ClNiP_3$: C, 73.53; H, 5.15; Ni, 6.67; Cl, 4.02%. $[(Ph_3P)_3NiCl]_2$ is a yellow crystalline substance, readily soluble in THF and benzene and poorly soluble in ether.

After 15 hours the mother liquor was concentrated to a minimum volume. The red-brown precipitate was filtered and recrystallized from ether; 1.60 g (30.9%) of $Ni(acac)_2PPh_3$ was obtained, m.p. 101–105 °C (dec.) (ether); 110–113 °C (benzene). *Anal.* Found: C, 67.86; H, 5.71. Calcd. for $C_{28}H_{29}NiPO_4 \cdot C_6H_6$: C, 68.37; H, 6.04%. Molecular weight, cryoscopy in benzene, found: 539.28; calcd.: 519.27.

Thermal Decomposition of $[(Ph_3P)_3NiCl]_2$

2.21 g (1.26 mmol) of $[(Ph_3P)_3NiCl]_2$ were heated in an ampoule to 140–180 °C. Metallic nickel gradually settled on the walls of the ampoule. After 1 hour, the reaction mixture was cooled and the residue consecutively washed with ether, CH_2Cl_2, and water. After evaporation 1.63 g (99.5%) of triphenylphosphine, m.p. 79 °C (ethanol), 0.40 g (97.7%) of $(Ph_3P)_2NiCl_2$, m.p. 246–248 °C (dec.) (acetic acid) [12] and 0.07 g (87.5%) of $NiCl_2$ were obtained. The remaining insoluble precipitate was metallic nickel (0.07 g, 94.7%).

Reaction of $[(Ph_3P)_3NiCl]_2$ with Acetonitrile in the Presence of $TlBF_4$

2 ml (38.2 mmol) of acetonitrile and 0.89 g (3.06 mmol) of $TlBF_4$ were added to 2.25 g (1.28 mmol) of $[(Ph_3P)_3NiCl]_2$ in 20 ml of THF. The reaction mixture was stirred for an hour at 22 °C. The precipitate of TlCl was filtered. The THF solution was evaporated to dryness and the tarry residue dissolved in 5 ml of acetone and treated with a small amount of absolute ether at –78 °C. The precipitated substance was filtered off and recrystallized from acetone. 1.60 g (64.5%) of $[(Ph_3P)_3Ni(CH_3CN)]BF_4$ was obtained, m.p. 183 °C (dec.) (acetone). *Anal.* Found: C, 69.35; H, 5.27; F, 7.52%. Calcd. for $C_{56}H_{48}BF_4NNiP_3$: C, 69.02; H, 4.97; F, 7.80%.

Reaction of $Ni(acac)_2PPh_3$ with Diethylaluminum Bromide in the Presence of Triphenylphosphine

Ether solution of 0.35 g (2.1 mmol) of diethylaluminum bromide was added at –40 °C to the suspension of 1.09 g (2.1 mmol) of $Ni(acac)_2PPh_3$ and 1.09 g (4.2 mmol) of triphenylphosphine in 30 ml of ether. The reaction mixture was stirred for 3 hours at –10 °C; this was accompanied by reddening of the solution and precipitation of a mixture of red and dark-green crystalline substances. Repeated ether extraction yielded 0.61 g (31.2%) of $(Ph_3P)_3Ni(H)Br$. The Raman spectrum of the product showed an absorption at 2115 cm^{-1} due to Ni–H stretching [16]. The remaining residue was recrystallized from acetone. 0.53 g (68.2%) of $(Ph_3P)_2NiBr_2$ was obtained, m.p. 215–218 °C [13].

References

1 V. Sh. Feldblyum and N. V. Obeshchalova, *Uspekhi Khimii, 37,* 1835 (1968); C. A. Tolman, in 'Transition metal hydrides', Muetterties (ed.), Marcel Dekker Inc., New York (1971) vol. 1, p. 271.

2 N. V. Obeshchalova, V. Sh. Feldblyum and N. M. Pashchenko, *J. Org. Khimii, 4* 1014 (1968).

3 J. Ewers, *Erdol und Kohle, 21,* 763 (1968).

4 V. S. Tkach, F. K. Schmidt, V. V. Saraev and A. V. Kalabina, *Kinetika i Kataliz., 15,* 617 (1974); V. V. Saraev, F. K. Shmidt, L. V. Mironova and V. A. Gruznikh, Koord. Khimiya, 2, 1249 (1976).

5 A. N. Nesmeyanov, L. S. Isaeva, L. N. Lorens and V. S. Kolesov, *Dokl. Acad. Nauk SSSR, 223,* 1140 (1965); *ibid. J. Organometal. Chem., 129,* 421 (1977).

6 D. G. Holah, A. N. Hughes, B. C. Hui and C. T. Kan, *Can. J. Chem., 56,* 2552 (1978).

7 J. N. Stolz, G. R. Dobson ahd R. K. Sheline, *Inorg. Chem., 2,* 323 (1963).

8 M. Kilner, *Adv. Organometal. Chem., 10,* 115 (1972).

9 T. Ito, T. Kariyama and A. Yamamoto, *Bull. Chem. Soc. Japan, 49,* 3250 (1976); *ibid. Chem. Letters,* 835 (1976).

10 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', New York, London (1963).

11 T. Yamamoto, T. Saruyama, Y. Nakamura and A. Yamamoto, *Bull. Chem. Soc. Japan, 49,* 589 (1976).

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

13 G. Yagupsky, W. Mowat, A. Shortland and G. Wilkinson, *J. Chem. Soc., Chem. Commun.,* 1369 (1970).

14 A. N. Nesmeyanov, L. S. Isaeva and L. N. Morozova, *Inorg. Chim. Acta, 33,* L 173 (1979).

15 A. Yamamoto, T. Yamamoto, T. Saruyama and Y. Nakamura, *J. Am. Chem. Soc., 95,* 4073 (1973).

16 A. N. Nesmeyanov, L. S. Isaeva, G. I. Drogunova and L. N. Morozova, *J. Organometal. Chem., 195,* C13 (1980).