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Preliminary communication

A NEW CATIONIC HYDRIDE COMPLEX OF NICKEL, $[(Ph_3P)_3Ni(H)(CH_3CN)]BF_4$

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Summary

A new cationic hydride nickel complex, $[(Ph_3P)_3Ni(H)(CH_3CN)]BF_4$, was obtained in the reaction of neutral nickel hydride, $(Ph_3P)_3Ni(H)Br$ with acetonitrile in the presence of $TlBF_4$. The NMR and Raman spectra of the obtained complex are discussed.

Previously, we reported the preparation of the pentacoordinated nickel complex, $(Ph_3P)_3Ni(H)Br$, and showed that the Ni—H bond in this compound is readily cleared by such organic solvents as carbon tetrachloride, acetone and trifluoroacetic acid [1].

In this work we studied the behaviour of this nickel hydride in reactions which do not involve the Ni—H bond. With this aim we substituted the coordinated halide ligand in $(Ph_3P)_3Ni(H)Br$ by a neutral ligand in the presence of a noncoordinating anion. It was established that addition of acetonitrile to a tetrahydrofuran solution of hydridotris(triphenylphosphine)nickel bromide in the presence of thallium borofluoride at −78°C resulted in precipitation of thallium bromide, and a change in colour of the reaction mixture from dark-red to yellow. A new pentacoordinated nickel hydride was isolated from the mother liquor:

$$(Ph_3P)_3Ni(H)Br + CH_3CN + TlBrF_4 \rightarrow [(Ph_3P)_3Ni(H)(CH_3CN)]BF_4 + TlBr$$

The obtained cationic nickel hydride, $(Ph_3P)_3Ni(H)(CH_3CN)\,BF_4$, is an orange crystalline substance, readily soluble in polar solvents, insoluble in pentane and ether and sensitive to atmospheric oxygen. In an argon atmosphere $[(Ph_3P)_3Ni(H)(CH_3CN)]BF_4$ is thermally stable and decomposes only when heated to 220°C with liberation of hydrogen and formation of metallic nickel.

The presence of hydride hydrogen in $[(Ph_3P)_3Ni(H)(CH_3CN)]BF_4$ was confirmed by spectral studies. Thus, the Raman spectrum of this compound exhibits a line at 2050 cm^{-1} which may be assigned to ν(Ni—H). In the spectrum of the initial neutral nickel hydride, $(Ph_3P)_3Ni(H)Br$, this line is in the region of

2115 cm^{-1}. The Raman spectrum also displays a line at 2275 cm^{-1} which belongs to C≡N stretching vibrations of the acetonitrile ligand coordinated through the unshared pair of the nitrogen atom [2].

The proton NMR spectrum of $[(Ph_3P)_3Ni(H)(CH_3CN)]BF_4$ recorded in acetone at 34°C contains a broad signal for the hydride ion at τ 20.89 ppm. Broadening of the signal is presumably due to dynamic effects in nonrigid pentacoordinated nickel complexes [3].

It should be noted that in cationic pentacoordinated nickel hydrides of the type $[(Ph_2PCH_2CH_2PPh_2)_2NiH]^+X^-$ ($X = AlCl_4$, BF_4 HCl_2) the hydride ion signal is displayed in the NMR spectra at $\tau \sim 23$ ppm and in the IR spectra ν(Ni—H) at ~1950 cm^{-1} [4].

When the reaction of hydridotris(triphenylphosphine)nickel bromide with acetonitrile and thallium borofluoride was carried out at room temperature, evolution of gas is observed along with formation of TlBr and a change of colour. According to GLC data the gas was hydrogen. From the reaction mixture we were able to isolate a yellow crystalline product, comprising a mixture of three substances. The ^{31}P NMR spectrum of the product recorded in tetrahydrofuran at −70°C displays three signals at δ −8.71, 17.34 and 29.57 ppm.

The signal at δ −8.71 ppm corresponds to free triphenylphosphine and the broader signal at δ 17.34 ppm should presumably be assigned to coordinated triphenylphosphine ligand in the cationic nickel hydride, $[(Ph_3P)_3Ni(H)(CH_3CN)]BF_4$. The signal at δ 29.57 ppm belongs to the fourcoordinated nickel complex without hydride hydrogen, $[(Ph_3P)_3Ni(CH_3CN)]BF_4$, which we were able to isolate in pure form by double crystallization of the obtained crude product. Additionally, we obtained the same univalent nickel complex by treating acetonitrile with the dimeric compound $[(Ph_3P)_3NiCl]_2$ in the presence of $TlBF_4$.

Preparation of $[(Ph_3P)_3Ni(H)(CH_3CN)]BF_4$

3.21 g (3.4 mmol) of $(Ph_3P)_3Ni(H)Br$ was added to a mixture containing 2.27 g (55.5 mmol) of acetonitrile, 1.35 g (4.6 mmol) of $TlBF_4$ and 40 ml of tetrahydrofuran under argon at —78° C. After one hour the precipitated TlBr was filtered off and the filtrate was evaporated to dryness. The resinous residue was dissolved in a minimal amount of acetone at −78°C. The crystalline substance formed was filtered, washed with ether and dried under vacuum to yield 1.70 g (50%) of $[(Ph_3P)_3Ni(H)(CH_3CN)]BF_4$ (from acetone), decomposition temperature 191—195°C. Found: C, 68.96; H, 5.32; F, 7.2. Calcd for $C_{56}H_{48}BF_4NNiP_3$: C, 69.02; H, 4.97; F, 7.80%.

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