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FIXATION OF DINITROGEN AND ACETYLENE BY THE SYSTEM CrCl_2 —Mg. ISOLATION AND PROPERTIES OF CHROMIUM COMPLEXES WITH FIXED N_2 AND C_2H_2

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Summary

We found that in the system CrCl_2 —Mg—dppe—THF, N_2 and C_2H_2 fixation takes place yielding the complexes. $[\text{Cr}(\text{dppe})_2]_2\text{N}_2$ and $[\text{Cr}(\text{dppe})_2]_2\text{C}_2\text{H}_2$. Magnetic, EPR and IR investigations showed that nitrogen and acetylene are non-linearly fixed between the chromium atoms. Hydrolysis of the nitrogen complex yields a small amount of NH_3 and N_2H_4 , and that of the acetylene complex yields ethane. In the system CrCl_2 —Mg—THF the fixation of 0.5 N_2/Cr has also been shown, with formation of a product which under hydrolysis yielded NH_3 and N_2H_4 (yield 60% and 25% respectively, based on the fixed nitrogen).

Introduction

Studies of molecular nitrogen fixation by transition metal compounds have chiefly concentrated on the molybdenum compounds and molybdenum is basically responsible for nitrogen fixation by the biological systems. Chatt [1] has reported the results of his studies in non-aqueous solution, and the tungsten compounds were similarly investigated.

Very few papers devoted to direct nitrogen fixation by chromium compounds [2] have appeared.

We have undertaken studies on nitrogen fixation by the system CrCl_2 —Mg—THF and by the analogous system with bis(1,2-diphenylphosphine)ethane added.

Results

Reactions within the system CrCl_2 —Mg—THF

A solution of CrCl_2 in tetrahydrofuran (THF) was treated with metallic magnesium chips, molar ratio $\text{Mg} : \text{CrCl}_2 = 1 : 5$, under nitrogen. The solution

changed colour from white via green and blue to black. In a week some 0.5 N₂/Cr was fixed, and a black product of formula [Cr₂N₂Mg₄Cl₄(THF)₅] was obtained from the solution.



Hydrolysis yielded NH₃ (60%), N₂H₄ (25%) and N₂ (15%) based on the fixed nitrogen. Magnetic susceptibility measurements χ_g at 77–293 K indicated the $1/\chi_g$ linear temperature dependence, $\theta = -83$ K, $\mu_{\text{eff}} = 2.92$. The product undergoes slow decomposition in air and is partially soluble in benzene and in THF. Up to now we have not succeeded in isolating the pure compound of constant stoichiometric formula. The analogous reaction was carried out under argon, and examined by EPR. Several hours after the reaction had started a signal appeared at g 1.98. This signal decayed stepwise and after 7 days completely disappeared. Thus the system neither fixed the N₂ nor reacted with ketones, aldehydes [3] or nitrocompounds [4]. Neither had it any catalytic properties of olefine hydrogenation [5]. When the reaction was carried out under carbon monoxide, 6CO/Cr was fixed. The chromium carbonyl Cr(CO)₆ was isolated with a yield of about 60%. The molybdenum and tungsten carbonyls [6] were synthesized in the same way.



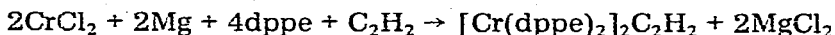
where $\text{MCl}_n = \text{CrCl}_2, \text{MoCl}_5, \text{WCl}_6$.

Reactions within the system CrCl₂—Mg—dppe—THF

The reaction was carried out under nitrogen with the molar ratio CrCl₂ : Mg : dppe = 1 : 5 : 2. The solution changed colour from white via green and blue to dark brown. In 7 days 0.5 N₂/Cr was fixed. After separation of Mg and densification under vacuum, the brown paramagnetic complex [Cr(dppe)₂]₂N₂ was formed. In an acid medium it decomposed with liberation of NH₃ (7%), N₂H₄ (1%) and N₂, based on the fixed nitrogen. The IR spectrum showed no frequency of the fixed N₂ molecule. Magnetic susceptibility measurements over 77–293 K indicated the weak temperature dependence of the magnetic moment. The μ_{eff} varied from 1.36 to 1.50 at 77 and 293 K, respectively. In the EPR spectrum (Fig. 1) of the complex [Cr(dppe)₂]₂N₂, in addition to the strong signal at $g = 1.98$ another signal at $H = 1600$ G was also observed, for which $D = 0.02$ cm⁻¹ and the exchange integral value $J \approx 300$ cm⁻¹.

Reaction with acetylene

The reaction with C₂H₂ was carried out in the same way as with N₂. The reaction yielded a grey compound of formula [Cr(dppe)₂]₂C₂H₂.



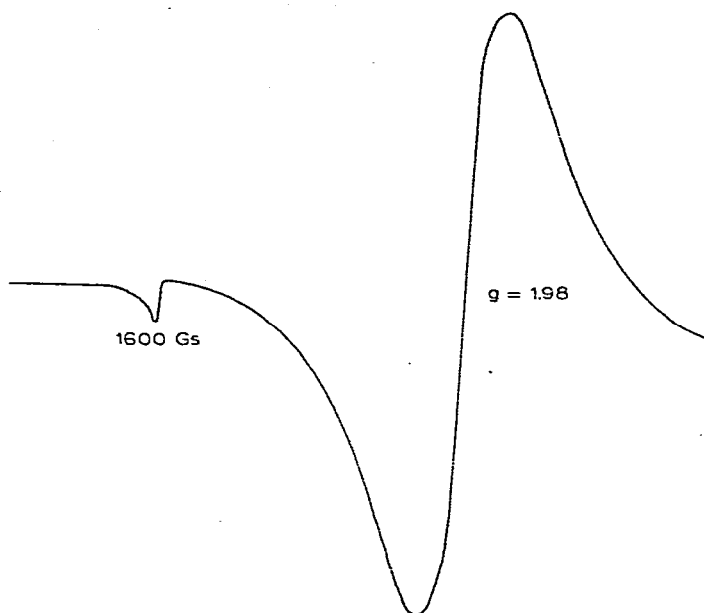


Fig. 1. Polycrystalline EPR spectrum of $[\text{Cr}(\text{dppe})_2]_2\text{N}_2$.

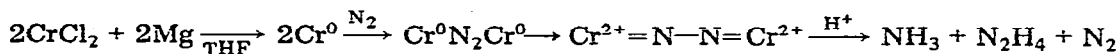
It decomposed in an acid medium and in air with liberation of ethane. The IR spectrum showed no frequency of the coordinated acetylene molecule. The temperature dependence of $1/\chi_g$ was linear and $\mu_{\text{eff}} = 4.98$. $\text{CrCl}_2\text{-Mg-dppe-THF}$ does not react with carbon monoxide.

Discussion

Our studies revealed that the nitrogen in the systems containing chromium was equally easily fixed as that in the systems containing molybdenum and tungsten. But the reaction mechanisms and the obtained compounds were different.

In the system $\text{CrCl}_2\text{-Mg-THF } 0.5 \text{ N}_2$ and six carbon monoxide molecules were fixed per one chromium atom. The formation of the $\text{Cr}(\text{CO})_6$ carbonyl revealed the reduction of Cr^{2+} to Cr^0 , which fixed and reduced the bridgedly coordinated nitrogen to N^{2-} , and oxidized itself to Cr^{2+} . The selfoxidation was indicated by the $\mu_{\text{eff}} = 2.92$.

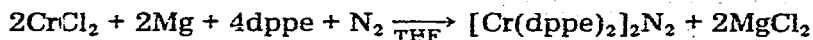
This value corresponds to two unpaired electrons on the chromium atom and to the t_{2g}^4 electronic configuration. The nitrogen fixation mechanism in the system $\text{CrCl}_2\text{-Mg-THF}$ could be written schematically:



EPR examination of the system $\text{CrCl}_2\text{-Mg-THF}$ under argon indicated the reduction of Cr^{2+} , via Cr^{1+} ($g = 1.98$) to Cr^0 . The system, after reduction under argon, did not fix nitrogen. It could be supposed that the system was deactivated because of the formation of dimers or polymers with chromium-chromium

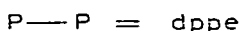
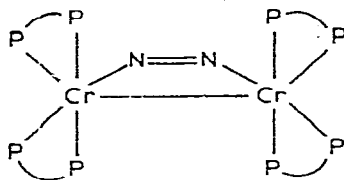
bonding and due to this the N_2 could not be bridgedly fixed.

The reaction within the system $CrCl_2-Mg-dppe-THF$ is similar, yielding the dimer $[Cr(dppe)_2]_2N_2$.

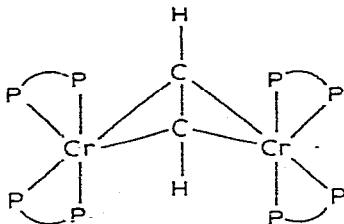


The μ_{eff} temperature dependence and the EPR signals at 1600 G at the forbidden line $\Delta M_s = 1$ indicate the dipole-dipole interaction between chromium atoms.

It could be concluded that the N_2 molecule was not linearly fixed between the chromium atoms. Assuming the unpaired electron on the chromium atom to be on the d_{xy}^1 orbital, the structure of a dimer could be presented as:



The formation of ethane in the hydrolysis of $[Cr(dppe)_2]_2C_2H_2$ indicated the bridge fixation of acetylene between chromium atoms.



The N_2 and C_2H_2 molecules react differently under similar conditions. In the case of acetylene fixation the reaction was four-electronic, in the case of N_2 -dielectronic.

Thus one should proceed with caution in comparing the various systems on the basis of their reactivity towards nitrogen and acetylene.

Experimental

Substrates

Chromium dichloride and bis(1,2-diphenylphosphine)ethane were obtained from Fluka AG. Metallic magnesium chips were the same as those used in the Grignard reaction. Tetrahydrofuran was distilled from $LiAlH_4$ immediately before each reaction. Nitrogen and argon gases were dried and deoxygenated by passing through a molecular sieve column and activated copper.

Synthesis of $[\text{Cr}_2\text{N}_2\text{Mg}_4\text{Cl}_4(\text{THF})_5]$

1.23 g CrCl_2 (0.01 mol) was dissolved under nitrogen in 50 ml THF, under stirring 1.21 g (0.05 mol) metallic magnesium (chips) was then added and the solution slowly changed colour from white via green and blue to black. The nitrogen fixation started when the solution was black. In 7 days 0.5 N_2 was fixed (based on the chromium). After the reaction the solution was filtered off from magnesium and evaporated under vacuum to dryness. Analysis of the residue: Found: C, 32.45; H, 5.62; N, 3.71; Cl, 19.50; Mg, 13.01; Cr, 13.95; $\text{C}_{10}\text{H}_{20}\text{NCl}_2\text{Mg}_2\text{O}_{2.5}\text{Cr}$ calcd.: C, 32.82; H, 5.47; N, 3.82; Cl, 19.42; Mg, 13.29; Cr, 14.22%.

Synthesis of $[\text{Cr}(\text{dppe})_2]_2\text{N}_2$

1.23 g CrCl_2 (0.01 mol) and 7.96 g bis(1,2-diphenylphosphino)ethane was dissolved under stirring in 50 ml THF under nitrogen. 1.21 g (0.05 mol) metallic magnesium chips were then added. The solution changed colour from white via green and blue to dark brown. In 7 days 0.7 N_2 was fixed (based on the chromium) After the reaction the solution was filtered off from magnesium and evaporated to 1/3 its volume. A polycrystal brown compound was obtained from the solution. Found; C, 71.95; H, 5.27; P, 14.06; N, 1.59; Cr, 5.95. $\text{C}_{52}\text{H}_{48}\text{P}_4\text{NCr}$ calcd.: C, 72.31; H, 5.56; P, 14.35; N, 1.62; Cr, 6.02%.

Synthesis of $[\text{Cr}(\text{dppe})_2]_2\text{C}_2\text{H}_2$

The reaction similar to the N_2 fixation one was carried out under acetylene, and yielded a grey compound. Found: C, 73.54; H, 5.57; P, 14.07; Cr, 5.91. $\text{C}_{53}\text{H}_{49}\text{P}_4\text{Cr}$ calcd.: C, 73.70; H, 5.67; P, 14.35; Cr, 6.02%.

IR measurements were made in Nujol mulls on a Perkin—Elmer 621, and the EPR measurements on a JEOL 3BX.

References

- 1 J. Chatt, *J. Organometal. Chem.*, 100 (1975) 17.
- 2 M.E. Volpin and V.B. Shur, *Dokl. Acad. Nauk*, 156 (1964) 1102; M.E. Volpin and V.B. Shur, *Vestn. Akad. Nauk SSSR*, (1965) 51; D. Sellman and G. Maisel, *Z. Naturforsch.*, 27b (1972) 465; D. Sellman and G. Maisel, *Z. Naturforsch.*, 27b (1972) 718.
- 3 S. Tyrlik and I. Wlochowicz, *Bull. Soc. Chim. Fr.*, (1973) 2147.
- 4 P. Sobota, *Rocz. Chem.*, 50 (1976) 1643.
- 5 P. Sobota, B. Jeżowska-Trebiatowska and J. Utko, *React. Kin. Catal. Letters*, 4 (1976) 113.
- 6 Polish patent No. 182594.