

PROPERTIES OF THE SYSTEM: TRANSITION METAL COMPOUND—MAGNESIUM, FIXATION AND ACTIVATION OF N₂, CO₂, CO, H₂ AND RELATED MOLECULES

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A. INTRODUCTION

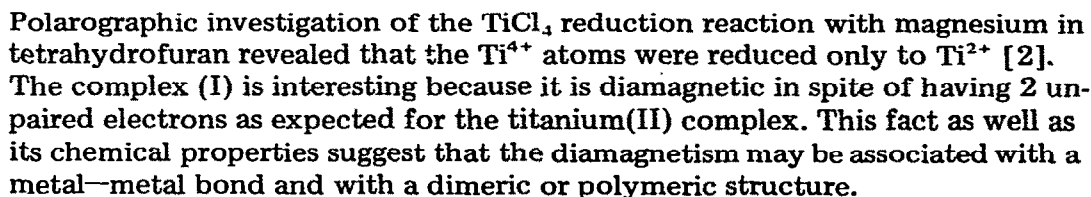
The detailed investigation of chemical reactions involving both transition metal compounds and main group I and II elements is a recent phenomenon. These elements usually function to reduce transition metals to lower oxidation states. It has been observed however, that these metals not only play the role of reductants, but also are able to form stable chemical compounds with new and interesting properties with the transition metals. Best known are the reactions of magnesium with titanium, vanadium, chromium, molybdenum and iron compounds in tetrahydrofuran.

Systems of the type MCl_n—Mg where MCl_n = TiCl_{3;4}, VCl_{3;4}, CrCl₂, MoOCl₃, FeCl₃ exhibit high reactivity in reduction reactions involving molecular nitrogen, carbon monoxide, carbon dioxide, acetylene, aldehydes and ketones and nitrocompounds.

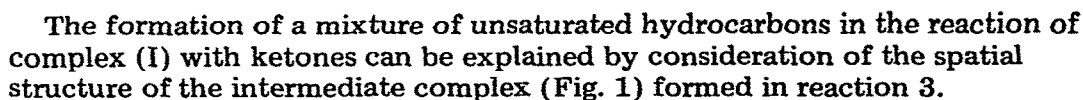
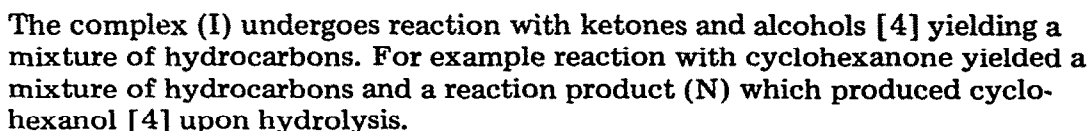
This paper reviews the latest achievements in this domain and provides an interpretation of some results.

B. THE SYSTEMS: TiCl_n—Mg AND VCl_n—Mg

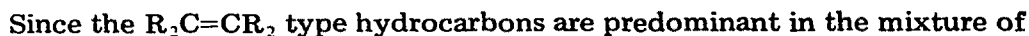
The reaction course of TiCl_n or VCl_n (*n* = 3; 4) with magnesium in tetrahydrofuran depends on the reaction time and atmosphere. In the TiCl₄—Mg—THF system under an argon atmosphere, reaction yields the black poly-



The complex (I) is a very strong reductant, due to its composition. The system was investigated with a view towards the fixation and reduction of N_2 , CO_2 , CO , H_2 and C_2H_2 . These reactions are polyelectronic because of the low oxidation state of titanium and magnesium. The reaction of complex (I) with nitrocompounds, is a good example for such a type of reaction yielding the azocompounds [3]



The ketone molecules are coordinated by the titanium atoms via the carbonyl oxygen groups giving rise to the formation of the intermediate complex. Rupture of the carbonyl oxygen group gives rise to the formation of the carbene R_2C : Various hydrocarbons arise depending on how the ketone molecules are coordinated to each other. With ketone coordination as shown in Fig. 1a, the isolated carbenes decay. They can stabilize either by mutual bonding, giving rise to the formation of the dimers $R_2C=CR_2$ or by the intermolecular migration of hydrogen to the carbene carbon from the adjacent carbon atom e.g. reaction with acetone gives $CH_3-\ddot{C}-CH_3$ which next may yield propylene.



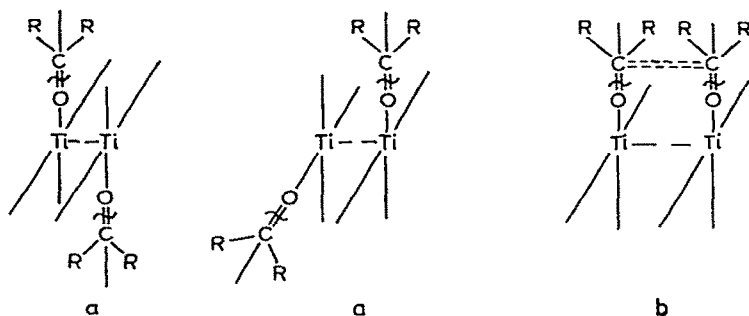
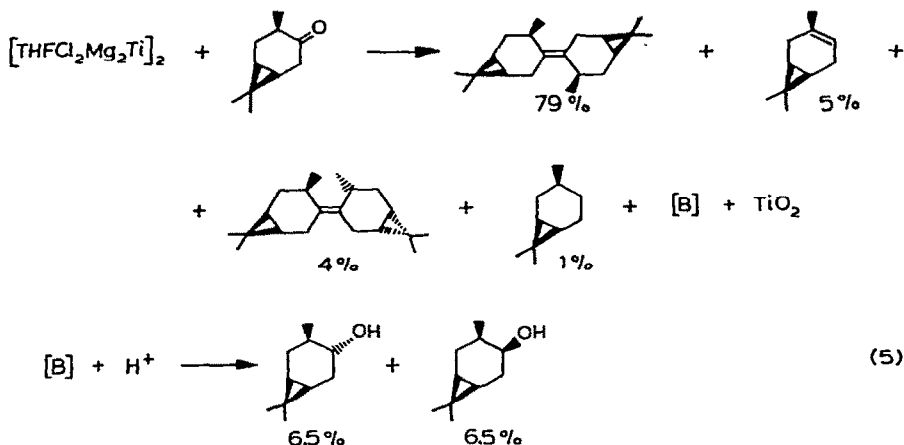


Fig. 1. Structure of the intermediate complexes formed in the reaction of $[\text{THFCl}_2\text{Mg}_2\text{Ti}]_2$ with ketones.

the reaction products of ketone with the complex (I) we suggest that syn-parallel ketone molecule coordination is most likely (Fig. 1b). Coordination of two ketone molecules initiates the simultaneous process of the rupture of the carbonyl group oxygen and the bonding of carbenes into dimers. The formation of cyclohexanol from the hydrolysis of reaction 3 product may suggest that a ketone is coordinated and reduced by the magnesium atoms in the complex (I). Cyclohexane, in reaction 3 is most likely to arise through cyclohexene hydrogenation. It was found that, under an argon atmosphere, 0.1 mol cyclohexene was hydrogenated per 1 mol of the complex (I) hydrogenated by the tetrahydrofuran hydrogen [5].

To confirm the proposed mechanism of the reaction of complex (I) with ketones, reaction with *trans*-caranone-4 was carried out [4]. The reaction was



stereospecific as expected and only one at the two possible isomers was formed, the *trans*oidal form of 4-caranylidenecarane in 79% yield. Stereospecificity of this reaction can easily be explained in terms of the structure of the transition complex (Fig. 2). *trans*-caranone-4 can only be located in the position given in

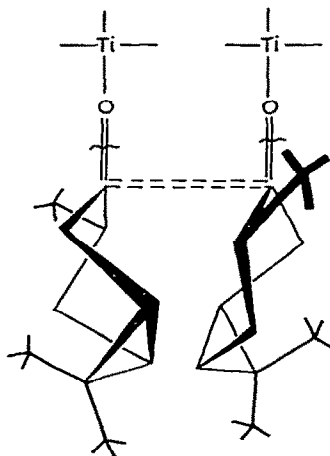
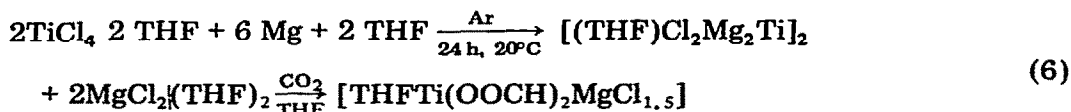


Fig. 2. Structure of the intermediate complex, the initial complex for the transoidal form of 4-caranylidene-carane.

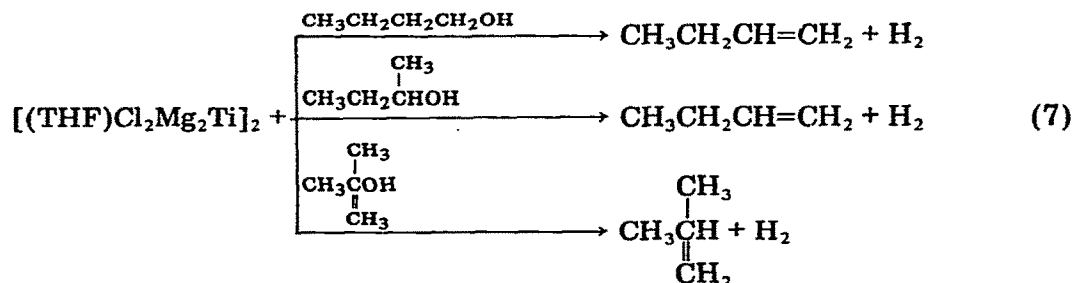
Fig. 2, because of the steric effects. Abstraction of oxygen of the C=O group results in formation of the transoidal form of a 4-caranylidene-carane.

Complex (I) also reacts with carbon dioxide [1].



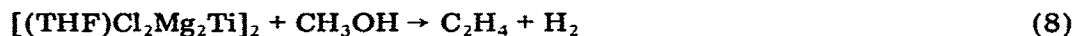
The reaction yields the black, diamagnetic complex $[\text{THFTi}(\text{OOCH})_2\text{MgCl}_{1.5}]$. Its IR spectrum exhibits the frequencies 1530, 1420 and 830 cm^{-1} , characteristic for a coordinated carboxyl group. Under hydrolysis the complex yielded formic acid, and in reaction with methyl iodide, methyl formate, products characteristic of this type of carbon dioxide complex [6].

Complex (I) also reacts with alcohols [4]. The reaction products are unsaturated hydrocarbons, independent of the alcohol and accompanied by hydrogen liberation. The liberation of hydrogen and the formation of un-



saturated hydrocarbons is proof for dehydration of the alcohols during the course of the reaction. An unsaturated hydrocarbon arises and Ti^{2+} is oxidized

to Ti^{3+} by water resulting in the liberation of hydrogen. Reaction with methanol was the proof for such a reaction.



The reaction products are ethylene and hydrogen, indicating formation of $:\text{CH}_2$ type carbenes as a result of methanol dehydration. The carbenes react with each other, giving rise to ethylene.

The course of reaction in the $\text{VCl}_3\text{—Mg—THF}$ system under argon was different [7]. The reaction produced the complex (III) $[\text{VHMgCl}_{1.5}(\text{THF})_{1.5}]$.

The presence of hydrogen was deduced from the amount of H_2 produced in iodolysis of (III). When $\text{VCl}_3(\text{THF})_3$ was reduced with excess magnesium in THF under hydrogen at ambient temperature and pressure, the system absorbed hydrogen slowly but steadily over a long period: 3.5 mol of H_2 were absorbed per mol of the vanadium complex (III) in 35 days. The diamagnetic vanadium complex (IV) isolated from the system was [7] $[\text{VH}_2\text{MgCl}(\text{THF})_2]$. In the $\text{VCl}_3\text{—Mg—THF}$ system the hydrogen fixation rate is higher [8,9]. When magnesium was introduced to the system dosewise, (1 mol Mg per 1 mol VCl_3), the ratio of reacted H_2/Mg was 0.93. In 50 h some 10 mol MgH_2 were produced per 1 mole VCl_3 . The complex (IV) reacted as a catalyst in the formation of magnesium hydride [9].

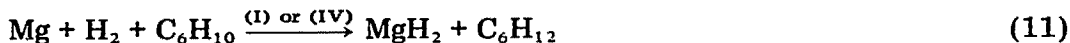


The course of reaction in the presence of complex (I) was similar [8].

In the presence of complexes (I) and (IV), catalytic hydrogenation of olefins was observed, e.g. reaction with cyclohexene yielded cyclohexane [5].



The yield of reaction (10) is low because of the water produced by dehydration of tetrahydrofuran by the titanium and/or vanadium compounds in low oxidation state. Reaction (10) in these systems in the presence of excess of metallic magnesium and olefin is directed towards the formation of the magnesium hydride $\text{MgH}_2 > \text{C}_6\text{H}_{12}$.



When carbon dioxide is introduced to the system with fixed hydrogen (reaction 9), the amount of fixed CO_2 depends upon the amount of H_2 fixed before the carbon dioxide is introduced. The fixed hydrogen ratio will be $\text{H}_2/\text{CO}_2 = 0.5$, with formation of magnesium formate [8]. When H_2 and CO_2 were introduced alternately to the system, the reaction lasted as long as free metallic magnesium was present. The formation of magnesium formate can be written [8].



Magnesium hydride is first formed, followed by reaction with carbon dioxide to yield $(\text{HCOO})_2\text{Mg}$.

Complex (I) does not fix molecular nitrogen. N_2 fixation takes place only when the $\text{TiCl}_4\text{--Mg--THF}$ system is reacted under a dinitrogen atmosphere from the very beginning [7].



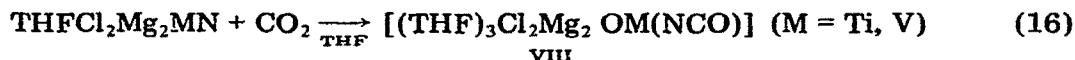
(M = Ti, V)

That complex (I) is unable to fix N_2 can be explained in terms of its structure. The complex $[\text{THFCl}_2\text{Mg}_2\text{Ti}]_2$ is a dimer or polymer with metal-metal bonding. Dinitrogen can be fixed by Ti^{2+} ions at the moment of their formation, before the metal-metal bond forms [10]. The process can be presented by [11]

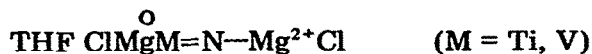


The amount of dinitrogen fixed in reaction (14) depends upon the amount of magnesium in the system. Dinitrogen fixation begins with an excess of magnesium over 0.5 atom/ MCl_3 -atom [7]. The maximum amount of N_2 is fixed at $\text{Mg} : \text{M} = 2.5$. Hydrolysis of complex (V) liberated all the fixed nitrogen as ammonia [7].

The magnesium atoms in the complex, $\text{TiNMg}_2\text{Cl}_2\text{THF}$, (Va), are in various oxidation states [7]. Part of the magnesium contained in (Va) was removed upon reaction of (Va) with pyridine to yield $\text{MgCl}_2(\text{py})_2$ and a black complex $\text{TiNMgCl}_{0.5}(\text{THF})$ (VI). Part of the magnesium in (Va) was also removed as a zerovalent complex by addition of 2,2'-dipyridyl. Reaction of (Va) with 2,2'-dipyridyl in THF yields reddish purple crystals identified as $\text{Mg}(\text{dipy})_3$ and complex (VII) with composition $\text{TiNMg}_{1.5}\text{Cl}_2(\text{dipy})_{1.5}$. The nitrogen in complex (V) has nitride character, confirmed by liberation of a stoichiometric amount of ammonia under hydrolysis [7], and by its reaction with carbon dioxide [11].



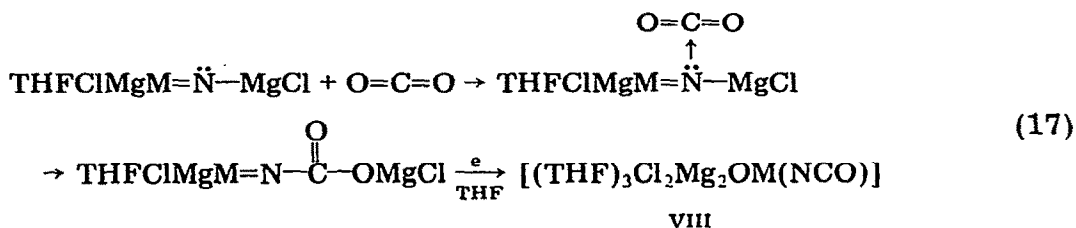
Reaction of carbon dioxide with complex (V) produced the isocyanate compound (VIII) which undergoes decomposition with liberation of NH_3 and CO_2 when treated with acid. Reaction with CH_3I produced methyl isocyanate, CH_3NCO . To explain the mechanism of reaction of carbon dioxide with complex (V), the following structure for $\text{THFCl}_2\text{Mg}_2\text{MN}$ was assumed [11]



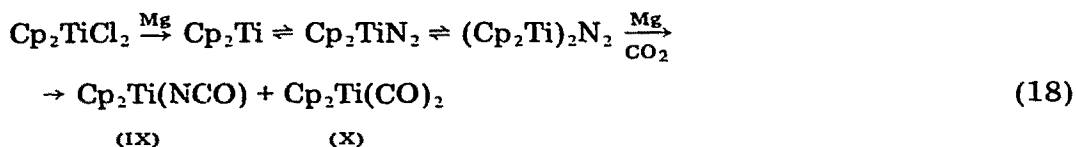
The carbon dioxide molecule, as the electron acceptor, is bound to the nitrogen atom by the free electron pair. The free nitrogen electron pair is transferred to the antibonding $2\pi_u$ orbital of the CO_2 molecule, which changes its

configuration from linear to angular and causes formation of the

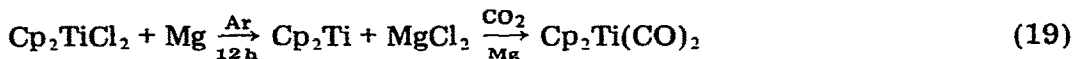
M=N-C(=O)-OMgCl bond. This bond is then reduced by magnesium or titanium (vanadium) atoms, which are in a low oxidation state (17).



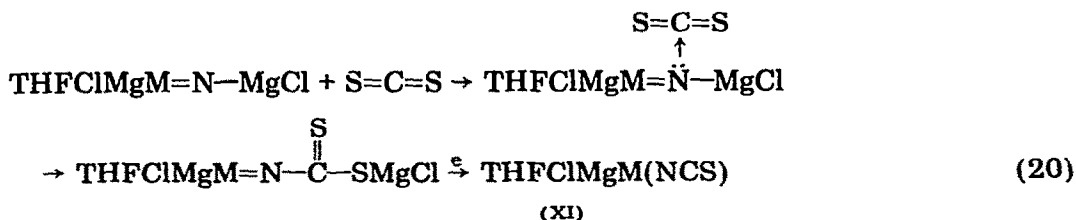
The course of reaction in the similar system [10] $\text{Cp}_2\text{TiCl}_2\text{--Mg--THF}$ is similar [11].



Reaction probably proceeds through an intermediate compound with nitrogen—magnesium bonding, $\text{Cp}_2\text{Ti}=\text{N}^--\text{MgCl}^+$, which then reacts with carbon dioxide. Moreover the reaction also produces the carbonyl $\text{Cp}_2\text{Ti}(\text{CO})_2$. The carbonyl also arose in the system $\text{Cp}_2\text{TiCl}_2-\text{Mg}-\text{THF}$, when reaction was carried out first under argon atmosphere and next under CO_2 [11].



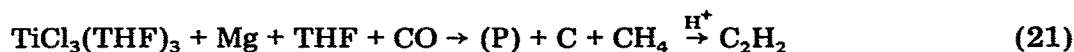
Reaction mechanism (17) was confirmed by the reaction of carbon disulphide, CS₂, yielding a structure similar to that of the carbon dioxide system. Reaction of the nitrogen complex (V) with CS₂ produces the complex THFCIMgM-(NCS), isolated in pure form [12]



CO₂ and CS₂ insertion into the nitrogen—metal bond [11,12] may be used to identify the nitrogen—metal bond of the reductant, since isocyanates and isothiocyanates exhibit strong absorption in the IR at about 2200 cm⁻¹ and 2080 cm⁻¹. Through studies carried out with these Ti and V systems with other metals of groups I and II it follows that they are capable of forming bonds with reduced nitrogen. As the result of the reduction of transition

metal compounds in a non-aqueous medium under a dinitrogen atmosphere, there appear in solution reductant cations or their halogenide compounds, which may play the role of a proton and combine with the reduced nitrogen [12].

In the Ti and V systems carbon monoxide fixation was also observed. With titanium reduction of carbon monoxide yielded carbon, and the hydrolysis of the reaction product (P) produced acetylene [13].



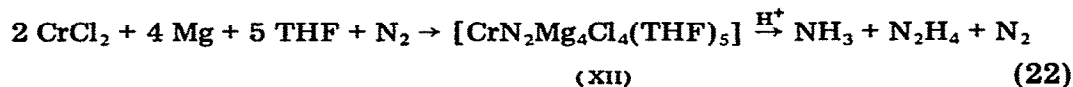
All the reactions in these systems were accompanied by hydrocarbon liberation, their main component being methane. Hydrocarbons arise in the reaction of the reduced titanium/vanadium atom with tetrahydrofuran. In these reactions tetrahydrofuran itself undergoes copolymerisation with acetylene. It has been stated that the introduction of acetylene to these systems results in the total reaction of tetrahydrofuran via copolymerisation [12].

C. THE SYSTEM: $\text{CrCl}_2\text{—Mg}$ [14]

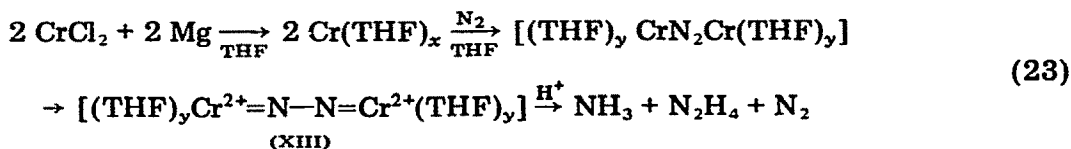
EPR investigation of the reduction of CrCl_2 with magnesium in tetrahydrofuran under an argon atmosphere indicated that the Cr^{2+} atoms are reduced to Cr^0 . As a result, a homogeneous solution of the zerovalent solvated chromium $\text{Cr}_n(\text{THF})_x$ was most probably obtained. The system $\text{Cr}_n(\text{THF})_x$ does not react with molecular dinitrogen indicating that the Cr^0 atoms most probably form either dimers or polymers.

The reduced chromium system under an argon atmosphere neither reacts with ketones and nitrocompounds nor catalyses the olefin hydrogenation reaction.

Under a dinitrogen atmosphere, however, 0.5 N_2 per chromium atom were fixed in one week, with liberation of the product (XII) of formula $[\text{Cr}_2\text{N}_2\text{Mg}_4\text{Cl}_4(\text{THF})_5]$



Hydrolysis of the product (XII) produced NH_3 60%, N_2H_4 25% and N_2 15% calculated per fixed dinitrogen. The magnetic moment of the chromium atom in the product (XII) is $\mu_{\text{eff}} = 2.93$ B.M., which corresponds to the t_{2g}^4 electronic configuration. Dinitrogen fixation in this system may be written as



The nitrogen molecule bridges two chromium atoms in the zero oxidation

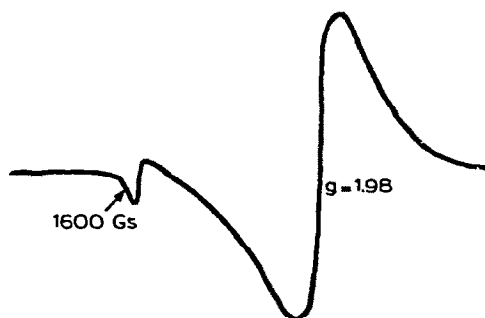
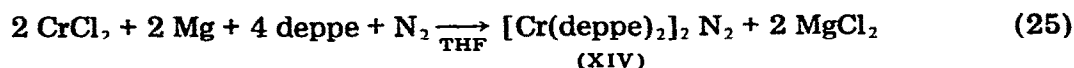


Fig. 3. Polycrystalline EPR spectrum of $[\text{Cr}(\text{dppe})_2]_2\text{N}_2$.

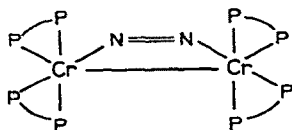
state. The chromium atoms reduced the nitrogen to N^{2-} and were oxidized to Cr^{2+} . The hydrolysis produced hydrazine, which next decomposed to ammonia and dinitrogen. In the chromium system under a carbon monoxide atmosphere chromium carbonyl $\text{Cr}(\text{CO})_6$ was formed, with a yield of 60%



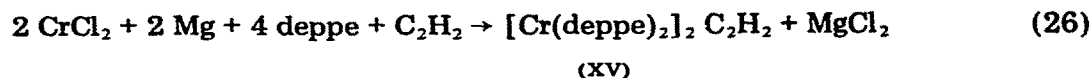
The analogous N_2 fixation reaction was carried out with the $\text{CrCl}_2\text{--Mg--THF}$ system while adding bis(1,2 diphenylphosphin) ethane (deppe).



The magnetic moment of the chromium atom in the complex (XIV) is temperature dependent. At liquid nitrogen temperature, $\mu_{\text{eff}} = 1.36$ and at 293 K, $\mu_{\text{eff}} = 1.50$ B.M. In the EPR spectrum of this complex, there is observed a line at $g = 1.98$ due to Cr(I) and another line at 1600 Gauss. This is the forbidden line for $\Delta M_s = 1$; $D = 0.02 \text{ cm}^{-1}$ and $J \approx 300 \text{ cm}^{-1}$ (Fig. 3). These parameters, together with the temperature dependent magnetic moment imply dipole—dipole interaction between the chromium atoms in a dimer. Thus, the dinitrogen in the complex (XIV) was not fixed linearly and the structure proposed is

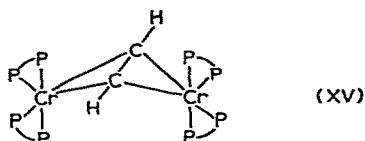


The same reaction was carried out with acetylene.



Reaction produced complex (XV) $[\text{Cr}(\text{deppe})_2]_2 \text{C}_2\text{H}_2$. Its hydrolysis yielded ethane. The magnetic moment of complex (XIV) is $\mu_{\text{eff}} = 4.98$ B.M. which corresponds to the $t_{2g}^3 e^1$ configuration. The structure of complex (XV) may be

presented as

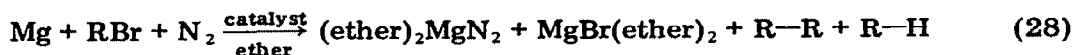


The acetylene molecule bridges two chromium atoms, forming two carbon—chromium bonds. The course of reaction of N_2 and C_2H_2 fixation in this system is different even under the same conditions. For N_2 fixation the reaction involves two electrons, and for acetylene four. Thus one should proceed with caution in comparing the systems on the basis of their reactivity versus N_2 and C_2H_2 .

D. THE SYSTEM: $MoOCl_3-Mg$

Under a dinitrogen atmosphere in this molybdenum system [15], some 5 N_2/Mo were fixed. Dinitrogen fixation was accompanied by liberation of hydrocarbons, mainly butane. Hydrolysis of the fixed dinitrogen product produced 10% ammonia. Further reduction of the dinitrogen fixed in the reaction product did not increase the amount of ammonia. Separation of the reaction products yielded an organic substance containing nitrogen. Chromatographic separation yielded a compound of mass about 1000, which proved to be a tetrahydrofuran polymer together with a compound containing nitrogen of mass about 500. Detailed examination of the nitrogen compound by IR and NMR methods indicated that the N_2 molecule was built into the chain of the open tetrahydrofuran ring. The amount of nitrogen incorporated depends upon the reaction conditions [15]. Catalytic N_2 fixation was also carried out in a modified molybdenum system.

Reaction in the system: $dppeMoCl_4-Mg-RBr-ether$ (where: $dppe = Ph_2PCH_2CH_2PPh_2$, $R = C_2H_5$, $n-C_3H_7$, $n-C_4H_9$, C_6H_5 , ether = tetrahydrofuran, diethyl ether) yielded a product which under hydrolysis produced diimide N_2H_2 [16]. The reaction was carried out as follows: the $dppeMoCl_4$ solution in ether was treated with excess metallic magnesium and the alkyl/aryl bromide was added dropwise under N_2 atmosphere under mild conditions. Besides dinitrogen fixation, liberation of $R-R$ and $R-H$ hydrocarbons was observed. The process can be written as



The amount of dinitrogen fixed depends only on the amount of RBr and Mg used in the reaction.

The maximum amount of dinitrogen fixed in the system: $dppeMoCl_4-$

$\text{C}_6\text{H}_5\text{Br-Mg-ether}$ was 106 N_2 molecules calculated per molybdenum atom. From the post-reaction solution a white product was isolated, which contained nitrogen, magnesium, bromine, carbon and hydrogen. Its hydrolysis produced diimide N_2H_2 . The presence of N_2H_2 was found by hydrolysis in the presence of allyl alcohol, whose carbon-carbon double bond undergoes hydrogenation under influence of diimide to 1-propanol [17]. Thus, the white product is a mixture of $\text{MgBr}_2(\text{ether})_2$ and most likely of a nitrogen compound with magnesium, of formula $(\text{ether})_2\text{MgN}_2$.

E. THE SYSTEM: $\text{FeCl}_3\text{-Mg}$

The course of reaction in the $\text{FeCl}_3\text{-Mg-THF}$ system under an argon atmosphere depends upon how it is carried out [18]. The reaction yielded a yellow product, being a mixture of the iron compounds — monomer (XVI) and the dimer (XVII). The monomer (XVI) was identified as $[\text{THFFeCl}_4]_2\text{Mg}(\text{THF})_2$. All attempts to isolate the pure dimer failed. In the ESR spectrum of the yellow reaction product there are observed monomer lines at $H = 3200$ Gauss, and dimer lines at $H = 480, 2880$ and 4800 Gauss. The dimer line intensity declines with lower temperature. The amount of dimer in the reaction product depends upon the mixing rate of the reaction mixture (Fig. 4). The temperature dependent variation of dimer line intensity indicates the presence

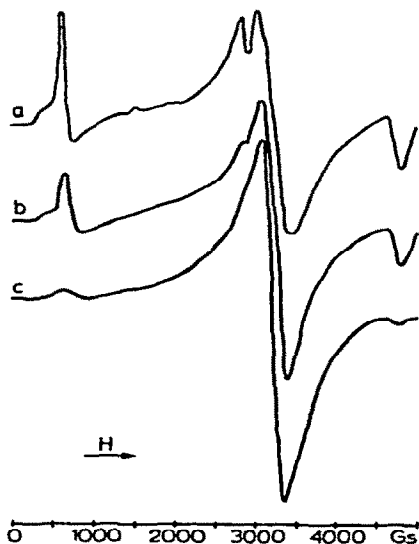
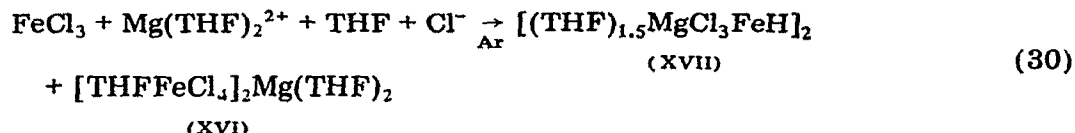
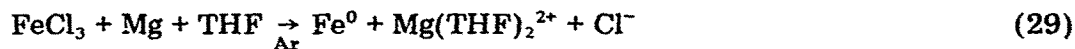


Fig. 4. EPR spectrum of the reaction mixture $\text{FeCl}_3 + \text{Mg} + \text{THF}$; (a) without mixing of substrates; (b) slow mixing of substrates; (c) fast mixing of substrates.

of a $\pi S_1 S_2$ interaction. The reaction course may be written as [18]



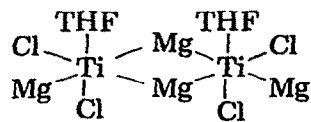
At first Fe^{3+} ions are reduced to Fe^0 , which settle on the metallic magnesium surface and $\text{Mg}(\text{THF})_2^{2+}$ and Cl^- ions are formed. These ions contribute to further reaction, giving rise to the complex $[\text{THFFeCl}_4]_2\text{Mg}(\text{THF})_2$, and most likely the hydride complex $[(\text{THF})\text{MgCl}_3\text{FeH}]_2$. With vigorous stirring of the reaction mixture the solution turned black, and the reaction course was different. Most probably the total amount of Fe^{3+} was reduced to Fe^0 . Under a dinitrogen atmosphere [18,19] the reaction yield was the product of general formula: $\text{FeCl}_3\text{N}_{0.5}\text{Mg}_{0.75}(\text{THF})_3$, partially soluble in benzene. From benzene the complex (XVIII) was separated, being a dimer with the dinitrogen molecule fixed between the iron atoms [19] $[(\text{THF})_{1.5}\text{MgCl}_3\text{FeN}_2\text{FeCl}_3\text{Mg}(\text{THF})_{1.5}]$. Hydrolysis produced a small amount of hydrazine. Formation of the Grignard compound is possible with vigorous stirring of the reaction substrates. The metallic magnesium reacts with the products of the open tetrahydrofuran ring, being the cause of the different reaction pathways. No dimer lines appear in the EPR spectrum of the complex (XVIII). It could be supposed that the reaction course is analogous to that in the earlier systems i.e. the dinitrogen molecule is bridged by the single iron atoms. The dimer formed under argon atmosphere is inactive in N_2 fixation.

F. CONCLUSIONS

Studies on the reaction of transition elements with magnesium allow the establishment of relationships between structure and reactivity of the compounds obtained, as well as the reaction mechanism. The course of reaction depends mainly upon the transition element compound, reaction time, atmosphere and the Mg/MCl_n ratio.

In the system $\text{TiCl}_4\text{--Mg}$ the compound (I) $[\text{THFCl}_2\text{Mg}_2\text{Ti}]_2$ is formed. The course of catalytic reaction (9) between H_2 and Mg under mild conditions, which yields MgH_2 is proof that the magnesium atoms in complex (I) are directly bound with the titanium atom, most likely by covalent coordination bonding.

The course of reaction (9) can be explained only by the reaction of H_2 molecule with magnesium in complex (I).



(I)

This gives rise to the formation of MgH_2 and to fixation of another magnesium atom which then reacts with hydrogen. The complex $[\text{THFCl}_2\text{Mg}_2\text{Ti}]_2$ exhibits unusual reactivity because of the presence of the titanium and magnesium atoms in low oxidation states. The reactivity permitted the design of a new synthetic method. Complex (I) reacts with ketones and with other molecules by their coordination in place of tetrahydrofuran forming an intermediate compound (Figs. 1 and 2). Recognition of the structure and properties of $[\text{THFCl}_2\text{Mg}_2\text{Ti}]_2$ also allowed an understanding of the molecular dinitrogen fixation mechanism and of the structure of the nitrogen complex formed in the system: $\text{TiCl}_4\text{--Mg}$. This allowed us to design for the first time a new method to synthesize isocyanates and isothiocyanates directly from N_2 and CO_2 or CS_2 .

The course of reactions in the system: $\text{VCl}_4\text{--Mg}$ is similar to the system containing titanium tetrachloride: N_2 fixation and reduction reactions, olefin hydrogenation, formation of MgH_2 and the insertion of CO_2 and CS_2 into the magnesium–nitrogen bond.

In the system: $\text{VCl}_3\text{--Mg}$ vanadium compounds are formed with magnesium in the zero oxidation state, e.g. $[\text{VHHgCl}_{1.5}(\text{THF})_{1.5}]$. It could be supposed that the difference in properties in these systems is basically due to the difference in the magnesium content in the titanium and vanadium complex compounds.

The course of reaction in the other three systems is different. In the $\text{CrCl}_2\text{--Mg}$ system reaction under argon atmosphere yields larger $\text{Cr}_x(\text{THF})_n$ molecules. They do not contain magnesium. This system is only active in the fixation of N_2 , C_2H_2 and CO . The fixation and reduction of molecular nitrogen and acetylene is influenced by the chromium atoms. Magnesium is not involved and thus the nitrogen atoms are reduced by chromium atoms only to $\text{--N}^{1-}=\text{N}^{1-}$ in the diphosphine complex, the phosphine stabilizing the lower oxidation state of the chromium atom. In the absence of the phosphine ligand dinitrogen is reduced to $=\text{N}^{2-}-\text{N}^{2-}$ (reaction 23). The formation of $\text{Cr}(\text{CO})_6$ in the system $\text{CrCl}_2\text{--Mg}$ under a carbon monoxide atmosphere also indicates the lack of chromium–magnesium bonding.

Reaction in the $\text{MoCl}_5\text{--Mg}$ system is more complicated than in the $\text{CrCl}_2\text{--Mg}$ system because of the reaction between MoCl_5 and tetrahydrofuran. The products of the THF ring rupture have a strong influence on the N_2 fixation process. The water formed in this process inhibits catalytic dinitrogen fixation and olefin hydrogenation.

Catalytic dinitrogen fixation in the $\text{dppeMoCl}_4\text{--Mg--ether--RBr}$ system is different to that observed in the Volpin–Shur systems: transition metal compound–reductor–ether [20]. Such a system under hydrolysis produced ammonia from the fixed N_2 . In our system the reaction was catalytic only if RBr was added dropwise to the $\text{dppeMoCl}_4\text{--Mg--ether}$ mixture under a dinitrogen atmosphere. The reaction product under hydrolysis produced the diimide N_2H_2 .

In the $\text{FeCl}_3\text{--Mg}$ system reaction leads mainly to the formation of the mono-

mer $[\text{THFFeCl}_4]_2\text{Mg}(\text{THF})_2$, which is inactive in the molecule activation process. The amount of active form could be estimated as 10%. For this reason the fixation reaction efficiency is very low.

In the systems: $\text{TiCl}_4\text{—Mg}$, $\text{VCl}_4\text{—Mg}$, $\text{MoCl}_5\text{—Mg}$ and $\text{FeCl}_3\text{—Mg}$ the liberation of hydrocarbons — mainly methane — was observed, due to reaction between the THF molecule and the elements in low oxidation states. Opening of the THF ring facilitates the formation of magnesium—organic compounds which could then facilitate reduction of the transition element compounds.

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