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REACTION MECHANISM AND PROPERTIES OF THE COMPOUNDS FORMED IN THE SYSTEM: $FeCl_3+Mg+THF+N_2$

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SUMMARY

A binuclear complex with fixed molecular nitrogen $[(THF)_{1.5}MgCl_3Fe]_2N_2$ (III) and the complexes $[(THF)FeCl_4]_2Mg(THF)_2$ (II), $[C_4H_5FeCl_5Mg(THF)_2 \cdot 6H_2O]$ (IV) and $[(C_4H_5)_2FeCl_7Mg_2(THF)_46H_2O]$ (V) have been isolated from the system: $FeCl_3+THF+N_2+Mg$. Reaction of the nitrogen complex (II) with hydrochloric acid leads to the reduction of the nitrogen to hydrazine. In addition, the introduction of anhydrous ferric chloride into the system causes dehydration of the tetrahydrofuran. As a result of this decomposition an unsaturated hydrocarbon is formed which undergoes σ-bonding with the iron atom of the complex or, alternatively, in the presence of metallic magnesium forms the corresponding Grignard compound.

INTRODUCTION

As we have shown in a previous paper[1], passage of molecular nitrogen slowly through the system (A): ferric chloride ($FeCl_3$)/tetrahydrofuran/metallic magnesium, under mild conditions gives rise to a yellow product (I). This product contains fixed nitrogen and has the general formula $FeCl_3N_{1.2}Mg_{0.75}(THF)_3$. It is stable at room temperature under a nitrogen atmosphere and EPR and magnetic susceptibility measurements have shown that it consists of a mixture of monomeric and dimeric compounds. Shilov and co-workers[2-5] have also obtained the binuclear iron dinitrogen complex $(PPh_3)_2RHFeN_2FeR(Ph_3P)_2$ and the titanium complex $[(C_5H_5)_2RTi]_2N_2$ by the reaction of the Grignard compound RMgCl with $(PPh_3)_2FeCl_3$ or $(C_5H_5)_2TiCl$ in ether. The nitrogen in these complexes may be reduced to hydrazine in the presence of HCl.

RESULTS AND DISCUSSION

In the present work we have studied the separation of the product (I) and the mechanism of the reaction occurring in system (A). The product (I) was found to be soluble in anhydrous benzene while a dark-yellow paramagnetic complex also isolated is insoluble in the same solvent.

The IR spectrum of this latter compund exhibits the characteristic frequency ν

TABLE 1

OBSERVED IR FREQUENCIES IN CM^{-1}

Compounds	*ν(Fe–Cl)*	*ν(FeCl$_4$)$^-$*	*ν(Fe–C)*	*ν(C=C)*	*ν(H$_2$O)*	*Other bands (cm^{-1})*
$[(THF)FeCl_4]_2Mg(THF)_2$ (II)		350 vs				1342 m, 1310 w, 1293 w, 1245 m, 1185 m, 1165 m, 1070 m, 1040 m, 1100 vs, 958 m, 915 s, 882 vs, 850 vs, 715 m, 670 m, 310 s
$[(THF)_{1.5}MgCl_3Fe]_2N_2$ (*III*)	385 vs					1346 m, 1310 w, 1295 m, 1250 m, 1175 m, 1075 m, 1025 vs, 1020 vs, 960 w, 920 s, 885 vs, 720 m, 670 m, 310 s
$[C_4H_5FeCl_5Mg(THF)_2\ 6H_2O]$ (IV)	375 vs		465 w	1640 s	3450 s, 1610 s	1345 m, 1296 m, 1244 m, 1196 m, 1070 s, 1023 vs, 916 vs, 878 vs, 718 vs, 683 s, 620 m, 310 s
$[(C_4H_5)_2FeCl_7Mg_2(THF)_4\ 6H_2O]$ (V)	380 vs		470 w	1670 s, 1640 s		1345 m, 1296 s, 1244 m, 1196 m, 1070 s, 918 vs, 878 vs, 720 s, 620 m, 310 s
oily product in system oil-$FeCl_3$ + THF + n-pentane	375 vs		460 w	1655 m	3470 m, 1600 m	1345 m, 1175 s, 1135 w, 1135 s, 1010 vs, 955 m, 915 s, 852 vs, 840 vs, 715 m, 665 s, 568 m

of the $[FeCl_4]^-$ ion[6] and from IR studies and chemical analysis it is possible to assign the formula $[(THF)FeCl_4]_2Mg(THF)_2$ (II) to this complex. In addition, we have succeeded in isolating a further complex (III) from the benzene solution. This complex, which was light-yellow in colour, contained fixed nitrogen in the molar ratio Fe/N = 1/1 but exhibited no bands corresponding to the fixed nitrogen *i.e.*, $\nu(N{\equiv}N)$, in its IR spectrum. When compound (II) is treated with an aqueous solution of hydrochloric acid reduction of the fixed nitrogen to hydrazine occurs. On the basis of this data and on chemical analysis we suggest that compound (III) is a symmetric dimer of formula $[(THF)_{1.5}MgCl_3Fe]_2N_2$. During the chemical reaction occurring in system (A) the liberation of a gas was observed and chromatographic examination proved that it consists essentially of one hydrocarbon.

If, after separation of the product (I) from system (A), the resulting solution is treated with n-pentane a further complex (IV) is liberated. If, however, benzene is added to the solution, complex (V) is formed. The IR spectra of both these complexes (Table 1) exhibit stretching vibration frequencies which may be assigned to $\nu(C{=}C)$, $\nu(H_2O)$ and $\nu(Fe{-}C)$ respectively, in addition to frequencies which may be attributed to coordinated molecules of tetrahydrofuran and $\nu(Fe{-}Cl)$. The existence of these additional frequencies indicates that complexes (IV) and (V) contain both coordinated water molecules and unsaturated hydrocarbon molecules linked directly to the iron atom through σ-bonding. Complexes (IV) and (V) were assigned the formulae $[C_4H_5FeCl_5(THF)_2Mg\ 6H_2O]$ and $[(C_4H_5)_2FeCl_7(THF)_4Mg_2\ 6H_2O]$, respectively, on the basis of chemical analysis, IR spectra, thermogravimetric analysis and magnetic susceptibility measurements. When anhydrous ferric chloride was dissolved in tetrahydrofuran and n-pentane was added, a tawny coloured oil separated from the solution. The IR spectrum of this oil exhibits frequencies corresponding to $\nu(C{=}C)$, $\nu(H_2O)$ and $\nu(Fe{-}C)$. This suggests that the tetrahydrofuran ring is dehydrated[7,8] under the influence of ferric chloride giving rise to a water molecule and an unsaturated hydrocarbon which forms a σ-bond with the iron atom.

Magnetic susceptibility studies of complexes (IV) and (V) have been made over the temperature range from liquid nitrogen temperature to room temperature. The magnetic moments thereby calculated from the Curie law (Table 2) are in good agreement with the magnetic moment corresponding to the ground state $^6A_1$ of the $t_{2g}^3\ e^2$ configuration.

TABLE 2

THE EFFECTIVE MAGNETIC MOMENTS OF Fe^{3+} COMPLEXES

Compounds	μ_{eff}
$[C_4H_5FeCl_5(THF)_2Mg\ 6H_2O]$ (IV)	5.69
$[(C_4H_5)_2FeCl_7(THF)_4Mg_2\ 6H_2O]$ (V)	5.72

The magnetic moments of complexes (II) and (III) were not determined since insufficient amounts of these complexes were available. The temperature-dependent magnetic moment[1] of product (I) was obtained, however, and at liquid nitrogen temperature this was found to equal 3.57 BM whereas at room temperature a value of −4.64 BM was measured.

π-Bonding between the iron atoms and unsaturated hydrocarbons in complexes (IV) and (V) is not observed because of the low value of the electron density of the Fe^{3+} atom.

Liberation of a gas during the initial reaction in system (A) and the fact that complexes $[C_4H_5FeCl_5(THF)_2Mg\ 6H_2O]$ (IV) and $[(C_4H_5)_2FeCl_7(THF)_4Mg_2\ 6H_2O]$ (V) differ from one another in terms of a $C_4H_5Mg(THF)_2Cl_2$ group indicate that a Grignard compound is formed in the system $MeCl_n + THF + N_2$.

To verify this suggestion we have undertaken a similar reaction in system (B), *i.e.* $TiCl_3\ 3THF$, metallic magnesium and tetrahydrofuran, under a nitrogen[9] or argon atmosphere. By means of the characteristic reactions with the Michler's ketone it is possible to show that in this system also a Grignard compound is formed. In system (A), however, the formation of a Grignard compound could not be verified and it must therefore be assumed that if a Grignard compound is formed in this latter system it is probably partially employed in the reduction of Fe^{3+} and in the formation of complexes (IV) and (V). If tetrahydrofuran is replaced by ether in either system (A) or (B) no reaction is observed. In general, therefore the process of nitrogen fixation in system (A) may be expressed as:

$$\begin{tikzcd}
FeCl_3 + RMgCl + THF \arrow[r] & {[(THF)_{1.5}MgCl_3FeN_2FeCl_3(THF)_{1.5}]} \arrow[d, "H^+"] \\
 & N_2H_4
\end{tikzcd}$$

Furthermore, on the basis of the above data, it is reasonable to suppose that the Grignard compound formed in the reaction of ferric chloride, $FeCl_3$, or $TiCl_3$ with tetrahydrofuran and metallic magnesium is the principal reductor in both systems (A) and (B) and causes the fixation of nitrogen in both iron and titanium compounds. Similar results were obtained when magnesium was replaced by calcium in system (A).

EXPERIMENTAL

Product (*I*). 2 g of anhydrous ferric chloride $FeCl_3$ dissolved in 50 ml of tetrahydrofuran was placed in a bowl with a porous bottom and gaseous nitrogen was passed slowly through the solution. Next, 4 g of metallic magnesium was added and after 15 min a yellow product of general formula $FeCl_3N_{1.2}Mg_{0.75}(THF)_3$ was isolated. The results of EPR magnetic susceptibility measurements and IR spectra of this product have been reported previously[1].

Compounds (*II*) *and* (*III*). When product (I) was extracted with anhydrous benzene an insoluble residue which consisted of the dark-yellow complex (II) remained, and this was separated and dried in vacuo. The benzene solution was evaporated under vacuo to yield the light-yellow complex (III). After separation from the solution, complex (III) was dried in an argon atmosphere. Analysis: Compound (II) found: C, 27.30; H, 4.77; Cl, 39.69; Fe, 15.92; Mg, 3.39%. $C_{20}H_{22}Cl_8Fe_2MgO_4$ calcd.: C, 27.50; H, 4.57; Cl, 40.69; Fe, 16.63; Mg, 3.43%. Compound (III) found: C, 23.03; H, 4.37; Cl, 34.09; Fe, 18.15; Mg, 7.74; N, 4.13. $C_{15}H_{15}Cl_6Fe_2Mg_2N_2O_6$ calcd.: C, 23.90; H, 3.96; Cl, 35.34; Fe, 18.55; Mg, 7.82; N, 4.55%.

Compounds (*IV*) *and* (*V*). If the remaining solution is treated with n-pentane, after separation of product (I), a light-yellow paramagnetic compound (IV) is isolated.

Treatment with benzene, however, results in the isolation of the light-yellow paramagnetic complex (V). Both compounds after separation from the solution were dried in an argon atmosphere. Analysis: Complex (IV) found: C, 24.95; H, 5.77; Cl, 30.72; Fe, 8.97; Mg, 4.24. $C_{12}H_{28}Cl_5FeMgO_{10}$ calcd.: C, 25.44; H, 5.85; Cl, 31.37; Fe, 9.77; Mg, 4.26%. Thermographic measurements indicated that complex (IV) decomposes with the liberation of two molecules of THF over the temperature range 50–120°; Six molecules of H_2O at 120–150° and one molecule of C_4H_5 at 150–190°. Analysis: Complex (V) found: C, 34.25; H, 5.77; Cl, 29.45; Fe, 6.89; Mg, 5.82. $C_{24}H_{36}Cl_7FeMg_2O_5$ calcd.: C, 33.75; H, 6.23; Cl, 28.99; Fe, 6.68; Mg, 5.64%. With complex (V) the following thermographic results were obtained: four molecules of THF were liberated over the temperature range 50–125°, six molecules of H_2O at 125–150° and two molecules of C_4H_5 at 150–195°.

In order to convert the fixed nitrogen in dimer (III) into hydrazine the dimer was treated first with an aqueous solution of hydrochloric acid (1/1) and then with an alkali. After separation of $Fe(OH)_3$ the solution was neutralized and treated with benzaldehyde which resulted in the precipitation of a yellow crystalline precipitate of the hydrazine derivative (m.p. 92.0°).

Magnetic susceptibility measurements were performed using Gouy's method, IR spectra were recorded on a Perkin–Elmer 621 spectrophotometer in Nujol. Samples for measurements were prepared in an argon atmosphere.

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