REACTION OF TETRAHYDROFURAN WITH TRANSITION METAL COMPOUNDS IN LOW OXIDATION STATES PART I

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Summary

The reaction of the transition metal compounds MCl_n (MCl_n = $TiCl_4$; VCl_4; $CrCl_2$ or $_3$; $MoOCl_3$, WCl_6 and $FeCl_3$) with magnesium and tetrahydrofuran yields organometallic cluster compounds. These compounds, upon hydrolysis with H_2O, D_2O, DCl and $NaOD$, produce a mixture of hydrocarbons and dihydrogen. The composition of the liberated gas suggests that the reaction between the reduced clusters M_x ($x \geqslant 2$) and THF gives metallocyclic compounds, which then undergo α or β C—C cleavage, hydrolysis and hydride elimination.

Introduction

Reductions of the transition metal compounds MCl_n with organometallic compounds or with group I and II elements are usually carried out in tetrahydrofuran (THF). Such reactions almost always proceed in the homogeneous phase because of the specific properties of THF. The system of the type MCl_n-reductant-THF exhibits a high reactivity in the reduction reaction of dinitrogen, carbon dioxide, carbon monoxide, aldehydes, ketones, azocompounds etc [1—3] because of the lack of ligands stabilizing the low oxidation state of the reduced transition metal atoms. The final product of these reactions depends greatly upon the reaction conditions, the reaction mode, and reductant.

In the system MCl_n-Mg-THF (MCl_n = $TiCl_4$, VCl_4, $CrCl_2$ or $_3$, $MoOCl_3$, WCl_6 and $FeCl_3$), tetrahydrofuran not only plays the role of the solvent, but contributes to the reaction [3]. In this paper we react the investigation of the reaction occurring between the reduced transition metal compound, magnesium and tetrahydrofuran.

TABLE 1

COMPOSITION OF THE HYDROCARBONS LIBERATED DURING THE REACTIONS OF THE SYSTEMS MCl_n-Mg-THF UNDER AN ARGON ATMOSPHERE

System	Hydrocarbons liberated [a] (%)				Σ hydrocarbons
	CH_4	C_2H_6	C_3H_8	C_4H_{10}	MCl_n
$TiCl_4$-Mg-THF	83.0	16.5	t	t	0.06
VCl_3-Mg-THF	91.0	9.0	—	—	0.07
$CrCl_2$-Mg-THF	77.1	22.9	—	—	0.01
$MoOCl_3$-Mg-THF	31.5	10.5	t	57.8	0.05
WCl_6-Mg-THF	31.0	13.0	—	48.0	0.06
$FeCl_3$-Mg-THF	t	t	—	t	t

[a] t-trace.

Results

The reduction reaction of transition metal compounds MCl_n (MCl_n = $TiCl_4$, VCl_4, $CrCl_2$ or $_3$, $MoOCl_3$, WCl_6 and $FeCl_3$) with an excess of metallic magnesium in THF under argon, dinitrogen or dihydrogen atmosphere is exothermic, and the mixture becomes black. During the reaction small amounts of hydrocarbon are liberated, and their identities and yields are shown in Table 1. After 24 h of reaction, the excess of metallic magnesium was separated and the post-reaction mixture was frozen and treated with H_2O under vacuum. After the post-reaction mixture reached room temperature, the amount of liberated gas was measured and its composition was determined. It was shown to be a mixture of dihydrogen and hydrocarbons. The results are presented in Table 2. To establish the course of the reaction it was necessary to carry out an isotopic examination of the liberated methane and hydrogen. For that purpose the post-reaction mixture obtained under argon was separated from magnesium and evaporated to dryness under vacuum. The residue was hydrolysed with D_2O, DCl and NaOD. Methane and dihydrogen from the liberated gas were examined by mass spectrometry. The results are given in Table 3. In the case of the vanadium and chromium systems, liberation of gas was observed only during the hydrolysis of the solid reaction product under dinitrogen. Isotopic analysis

TABLE 2

COMPOSITION OF THE HYDROCARBONS LIBERATED AFTER HYDROLYSIS OF THE POST-REACTIONS MIXTURES

System	Hydrocarbons liberated (%)						Σ hydrocarbons	Σ H_2
	CH_4	C_2H_6	C_2H_4	C_3H_8	C_4H_{10}	C_5H_{12}	MCl_n	MCl_n
$TiCl_4$-Mg-THF [a]	22.4	59.7	4.3	2.8	1.1	3.1	0.63	1.47
VCl_4-Mg-THF	46.7	39.2	5.6	4.7	3.7	—	0.44	1.22
$CrCl_2$-Mg-THF	80.0	20.0	—	—	—	—	0.36	1.22
$MoOCl_3$-Mg-THF	19.8	18.4	—	8.8	52.2	—		
WCl_6-Mg-THF	4.8	16.0	t	17.6	49.6	6.4	0.41	1.59
$FeCl_3$-Mg-THF	62.0	12.2	—	10.0	15.5	—	0.17	0.24

[a] A trace of acetylene was liberated in this reaction.

revealed that the liberated dihydrogen was a mixture of HD, D_2 and H_2, and the methane was a mixture of CH_4, CH_3D, CH_2D_2, CHD_3 and CD_4. For the system $TiCl_4$-Mg-THF small amounts of CD_2O, $DCOOD$, $CH_2(OD)_2$, $DOCH_2CH_2OD$, CH_3OD and furan were also detected.

Discussion

Hydrolysis of the reaction products obtained in the system MCl_n-Mg-THF produced a mixture of hydrocarbons and dihydrogen. The amount of the liberated gas as well as its composition depends greatly on the transition metal. The formation of hydrocarbons upon hydrolysis indicates that organometallic compounds are formed from the reaction of the reduced transition metal compounds, tetrahydrofuran and magnesium. In the systems involving titanium, vanadium and chromium, the main component of the liberated mixture was ethane, with methane of isotopic composition CH_2D_2. In the molybdenum and tungsten systems, it was butane.

A mechanism for the reactions can be proposed on the basis of the analysis of the composition of the liberated hydrocarbons (Table 1 and 2) and upon the isotopic analysis of methane and dihydrogen (Table 3). In reaction in the system MCl_n-Mg-THF the reduced atoms or transition metal ions, because of the lack of ligands, react with each other to form metal clusters by metal—metal bonding [3].

$$2 \, MCl_n + n \, Mg \xrightarrow[\text{THF}]{} 2 \, M + n \, MgCl_2 \tag{1}$$

$$x M \xrightarrow[\text{THF}]{} M_x \qquad (x \geqslant 2) \tag{2}$$

The tetrahydrofuran molecule is coordinated by the cluster M_x via the oxygen atom, and this results in its destabilisation and decomposition.

$$\tag{3}$$

$$\tag{4}$$

The newly formed metallocycle compound $M_{x-1}C_4H_8$ could be the subject of further reactions [4—6]: a) hydrolysis, b) α or β carbon—carbon bond cleavage, c) hydride elimination. The formation of hydrocarbons during the hydrolysis indicates that the oxidizing agent produces an intermediate cation which undergoes rapid α and β C—C cleavage or hydrolysis. Such a reaction yields methane, ethylene, propylene and butane (Scheme 1). Pentane is probably formed in the reaction between the metal-carbene species $M_{x-1}CH_2$ and metallocycle compounds.

$$M_{x-1}CH_2 + M_{x-1}C_4H_8 \rightarrow M_{x-1}C_5H_{10} + M_{x-1} \xrightarrow{2H^+} C_5H_{12} \tag{5}$$
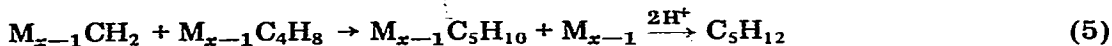
Isotopic analysis of the gas liberated upon hydrolysis revealed that, in addition to hydrocarbons, it contained a mixture of deuterium and hydrogen D_2, HD and H_2. For example, hydrolysis of the $TiCl_4$-Mg-THF reaction product with

TABLE 3

ISOTOPIC ANALYSIS OF DIHYDROGEN AND METHANE LIBERATED UPON HYDROLYSIS OF THE PRODUCTS OBTAINED IN REACTIONS OF THE MCl_n-Mg-THF SYSTEMS

System	Hydrolysis agent	Isotopic composition (%)								
		H_2	HD	D_2	Total amount of D	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
$TiCl_4$-Mg-THF [a]	D_2O	10.39	62.88	26.72	58.2 ± 0.4	6.66	10.10	35.05	14.32	33.87
	DCl	10.90	68.50	20.60	54.9 ± 0.5	8.16	13.88	33.56	16.97	27.43
	NaOD	7.03	64.99	27.98	60.5 ± 0.4	7.08	17.19	32.33	13.24	30.17
$TiCl_4$-Mg-THF [b]	D_2O	15.26	60.36	24.37	54.6 ± 0.4	8.38	10.29	29.77	12.48	39.08
	DCl	23.00	65.32	11.68	44.3 ± 0.4	13.82	10.69	35.01	9.30	31.18
	NaOD	7.24	67.22	25.54	59.2 ± 0.4	10.20	14.52	51.67	18.63	4.98
VCl_4-Mg-THF [b]	D_2O	10.09	69.48	20.43	55.2 ± 0.4	13.54	13.28	32.55	20.05	20.58
	DCl	9.85	75.94	14.21	52.2 ± 0.5	9.97	15.09	33.22	17.43	24.29
	NaOD	13.85	67.20	18.95	52.6 ± 0.5	13.72	14.12	32.39	16.77	23.60
$CrCl_2$-Mg-THF [b]	D_2O	22.30	50.27	27.43	52.6 ± 0.4	19.69	27.56	35.85	15.75	2.36
	NaOD	11.10	60.17	28.68	58.7 ± 0.5	55.36	13.89	16.67	5.36	8.33
$MoOCl_3$-Mg-THF [a]	D_2O	12.93	52.45	34.52	60.8 ± 0.4	43.96	15.93	21.43	10.44	8.24
WCl_6-Mg-THF [a]	D_2O	15.03	42.00	42.97	64.0 ± 0.4	20.89	24.14	29.14	16.94	8.94
	DCl	20.74	45.07	34.19	56.7 ± 0.4	20.82	27.34	28.93	15.55	7.36
	NaOD	13.65	42.47	43.88	65.1 ± 0.3	20.14	22.18	29.54	17.30	10.21

[a] Argon atmosphere; [b] dinitrogen atmosphere.

SCHEME 1
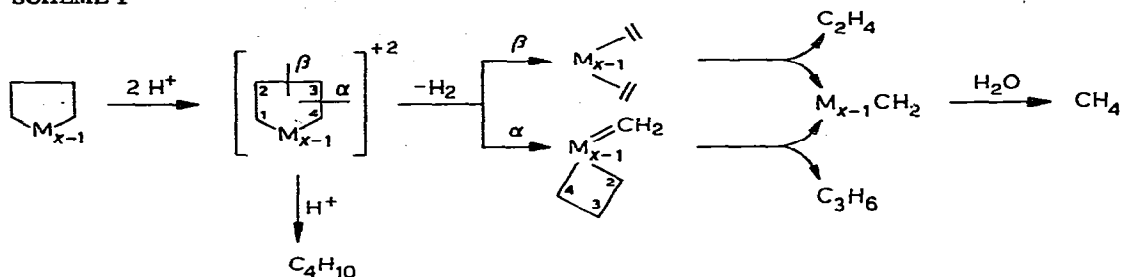
D_2O produced 58.2% deuterium and 41.8% hydrogen (Table 3), which amounts to 0.85 and 0.62 moles per Ti atom, respectively (Table 2). This amount is equivalent to 1.24 moles per Ti of hydrogen fixed in the form of hydride. From the total amount of liberated hydrocarbons it could be calculated that the amount of tetrahydrofyran consumed was 0.27 moles per Ti. Comparison of these amounts indicates that the hydride elimination from $M_{x-1}CH_2$ is accompanied by dehydrogenation of the solvent tetrahydrofuran.
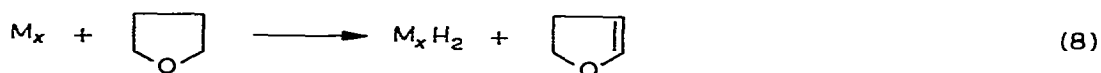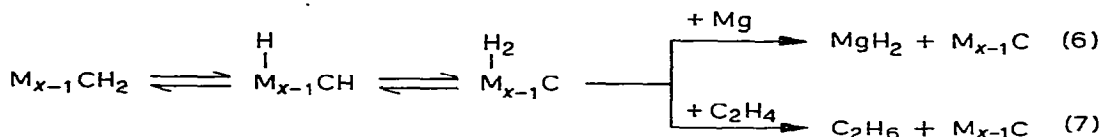
The hydride elimination and dehydrogenation of THF results in formation of transition metal hydrides, which may then react with metallic magnesium [7] or with unsaturated hydrocarbons [8].

Along with hydrocarbons and dihydrogen, the D_2O hydrolysis of the reaction products considered above also gives H_2O, HDO, CD_2O, DCOOD, CH_2-$(OD)_2$, $DOCH_2CH_2OD$, CH_3OD and their hydrogen analogs. The additional organic compounds are probably formed in the reaction between the products from the α and β C—C bond cleavage of the metallocycle compounds (Scheme 1). The mechanism of these reaction will be the subject of further investigations.

Experimental

All manipulations were carried out under pure, dry argon or dinitrogen using standard Schlenk-tube and vacuum line techniques. Tetrahydrofuran was purified before use by distillation under argon from sodium and benzophenone. The transition metal chlorides $TiCl_4$, VCl_4, $CrCl_3$, $CrCl_2$, $MoCl_5$, WCl_6 and $FeCl_3$ were obtained commercially from Fluka AG and the Grignard magnesium turnings from POCh-Gliwice.

In the titanium system the $TiCl_4$ 2 THF compound was used because the reaction between $TiCl_4$, THF and magnesium was too violent. $TiCl_4$ 2 THF was obtained by very slow addition (2 h) of $TiCl_4$ (25 cm³) to tetrahydrofuran (50

cm^3) under argon with stirring. The yellow product was recrystallised from tetrahydrofuran, dried under vacuum and stored under argon (yield 70%). MoOCl$_3$ 2 THF was obtained from molybdenum pentachloride (20 g), which was added slowly (3 h) to tetrahydrofuran (50 cm^3). The polymerisation products of the THF were filtered from the green MoOCl$_3$ 2 THF precipitate. The precipitate was washed with THF (3 × 10 cm^3) dried under vacuum and stored under argon (yield 30%).

The concentration of the transition metal chlorides TiCl$_4$ 2 THF, VCl$_4$, CrCl$_3$, CrCl$_2$, WCl$_6$ in tetrahydrofuran during the reduction was 0.06 M and for MoOCl$_3$ 2 THF and FeCl$_3$ 0.2 M, respectively. At concentrations below 0.001 M, the measurement of volume of the liberated gases is difficult. At higher concentrations the reductions are strongly exothermic and polymerisation of THF occurs, and so cooling is necessary. The reaction with chromium chlorides was the slowest (3—4 days).

The amount of liberated gas was determined from the changes of gas volume over the reaction mixture (Table 1 and 2). Measurements were taken at constant pressure and room temperature. The composition of the gas (relative ratios) was determined by GLC on a 2 m silica gel column. Isotopic analyses (Table 3) were performed after hydrolysis of dry, Mg free, residues with the appropriate reagent, viz. D$_2$O, DCl, or NaOD the reaction being carried out in a vacuum apparatus linked to a mass spectrometer. A typical example of a reduction reaction in the MCl$_n$-Mg-THF systems is as follows. TiCl$_4$ 2 THF (or VCl$_4$; VCl$_3$; CrCl$_2$; CrCl$_3$; MoOCl$_3$ 2 THF; WCl$_6$; FeCl$_3$), 1.0 g, was dissolved in tetrahydrofuran (50 cm^3) under argon and an excess of magnesium turnings (4 g) was added with stirring. During the exothermic reaction the mixture turned black and hydrocarbons were liberated; their identities and relative yields are given in Table 1. After 24 h the magnesium was filtered using a Schlenk filter and the filtrate was divided into two parts. The first was cooled in liquid nitrogen and H$_2$O was added in vacuo. The mixture was allowed to warm to room temperature, the amount of liberated gas was measured and its contents were analysed (Table 2). The second part was evaporated to dryness in vacuum. The residue was hydrolysed with D$_2$O, DCl or NaOD and the liberated gases (methane and hydrogen) were determined by mass spectrometry. Their yields and compositions are given in Table 3.

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