

Catalytic properties of cluster Grignard reagents

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Abstract

Cluster Grignard reagents $C_6H_5Mg_4F$ have been obtained by direct magnesium cluster insertion into C–F bond in fluorobenzene with magnesium vapors co-condensates at low temperature. The appearance of metal cluster in organomagnesium molecule leads to unusual non-transition metal cluster compounds catalytic properties studied on halogen exchange reaction $RF + R'Cl \rightarrow RCl + R'F$ as example. Cluster Grignard reagents catalyze the fluorobenzene reaction with alkyl chlorides due to reversible magnesium cluster insertion into C–F and C–Cl bonds. © 2002 Elsevier Science B.V. All rights reserved.

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Grignard reagents (RMgX) have been known for over 100 years. They represent a useful and important class of reagents to synthetic organic chemistry [1]. It can be expected that during this long period, all the significant questions regarding the formation and activity of these reagents might have been answered, but in practice, this is not the case. For example, in some systems, notably involving fluorohydrocarbons, Grignard reagents appear to be impossible produced by classical way. However, in MVS conditions, when reactions proceed in reagents co-condensates deposited onto the cooled surface, all organic halides react with magnesium [2,3]. MVS in the systems C_6H_5X-Mg ($X = Br, Cl$ and even F) leads to the formation of cluster Grignard reagents, which present the first example of novel type of organometallic clusters obtained by direct metal cluster insertion into strong interatomic bond [4]. The presence of metal cluster nucleus in organometallic molecules results in unusual organomagnesium compounds properties,

in particular catalytic activity appearance. Here we report the first results of cluster Grignard reagents catalytic properties study.

1. Experimental

Cluster Grignard reagents synthesis was carried out in reactor similar to that described in [3]. Magnesium was evaporated by resistive heating. Metal vapor was co-condensed with C_6H_5F excess onto a surface cooled to about 77 K. Co-condensation areas were 200 cm² in glass reactor and 0.5 m² in metal reactor, C_6H_5F/Mg molar ratios were 40–1000. The matrices formed at 77 K were dark brown, became colorless at 100–130 K and melted when warmed to ambient temperature. Phenyltetramagnesium fluoride solutions in fluorobenzene excess were filtered to exclude the presence of aggregated magnesium. Reaction with organic halides was carried out at temperatures 253–293 K ($[C_6H_5Mg_4F] = 0.1 \times 10^{-3} - 2.1 \times 10^{-3} M$, $[C_8H_{17}Cl] = 3.0 \times 10^{-2} - 0.7 M$, $[C_6H_5F] = 0.4 \times 10^{-2} - 2.1 \times 10^{-1} M$). Deuterolysis of $C_6H_5Mg_4F$

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proceeds with C_6H_5D formation in accordance with [4,5]. Reaction mixture gave C_6H_5D and $C_8H_{17}D$ on deuterolysis. Product composition was detected by GC, GC/MS. Organomagnesium compounds were identified by MALDI–TOF MS (matrix assisted laser desorption ionisation–time of flight mass spectrometry). Mass spectrometry measurements were performed at room temperature. Samples of the compounds in organic halide solution (RX) were put on the target, and after RX evaporation were introduced into mass spectrometer whose inlet system was isolated by a dry box. MALDI–TOF mass spectra were recorded by a Vision 2000 mass spectrometer.

1.1. Catalytic activity of $C_6H_5Mg_4F$

Classical Grignard reagents interaction with organic halides leads to the formation of cross-coupling reaction products [5]:



However, for cluster Grignard reagents RMg_nX there are two ways of the reaction [6]. Only bromo-substituted clusters enter to the reaction (1). In the case of chloro- and fluoropolymagnesium halides, halogen exchange is observed [6]:



Apart from reaction (2), halogen exchange between organic halides



was found to be realized in the presence of phenyltetramagnesium fluoride in catalytic regime. The yields of $R'F$ were found to be up to 21 mol per mol of organomagnesium cluster. The data are presented in the Tables 1 and 2. The tables show that catalytic activity of phenyltetramagnesium fluoride does not depend on reagents ratio in co-deposition procedure.

The catalytic reaction (3) viewed as halogen exchange possibly proceed via magnesium cluster exchange:

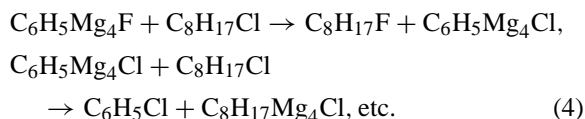


Table 1

$C_8H_{17}F$ yields ($[C_8H_{17}F]/[C_6H_5Mg_4F]$, mol/mol) for interaction of $C_8H_{17}Cl$ with C_6H_5F in the presence of $C_6H_5Mg_4F$ obtained by MVS in the systems C_6H_5F –Mg at different C_6H_5F/Mg ratio ($[C_6H_5Mg_4F] = 2.1 \times 10^{-3} M$, $[C_8H_{17}Cl] = 3.6 \times 10^{-2} M$)

C_6H_5F/Mg in MVS	$[C_8H_{17}F]/[C_6H_5Mg_4F]$	
	1 h	20 h
117	0.20	17.6
258	0.21	17.3
370	0.22	17.5
583	0.20	17.5

The scheme assumes reversible metal clusters insertion into different C–X bonds confirmed by MALDI–TOF MS. Organomagnesium compounds composition data are presented in the Tables 3 and 4 for the interaction with chlorobenzene and alkyl chloride. As it is shown in Table 3, there are four $C_6H_5Mg_4F$ peaks at $m/z = 193$ – 196 Da in the spectrum before the reaction, and these peaks were present in all samples irrespective of reagent ratio in the preparation procedure. We attributed them to so-called “quasi-molecular” ion $[C_6H_5Mg_4F + H]^+$ [4]. The intensities of these four peaks are in a good agreement with the theoretical isotope distribution for $C_6H_5Mg_4F$ molecule. After the reaction with chlorobenzene was ended they disappeared. Simultaneously, five peaks of the phenyltetramagnesium chloride protonated molecules at $m/z = 209$ – 213 Da was shown [4]. MS data for the phenyltetramagnesium fluoride interaction with octyl chloride are presented in the Table 4. Before the reaction there are four peaks of $C_6H_5Mg_4F$ protonated molecules at $m/z = 193$ – 196 Da. After the reaction there are five peaks of the phenyltetramagnesium chloride protonated molecules at $m/z =$

Table 2

Halogen exchange reaction products yields, $C_8H_{17}F$ and C_6H_5Cl , for interaction of $C_8H_{17}Cl$ with C_6H_5F catalysed by $C_6H_5Mg_4F$ at different concentrations, $[C_6H_5Mg_4F]$, $[C_8H_{17}Cl] = 0.7 M$, reaction time 20 h

$[C_6H_5Mg_4F]$, $10^{-3} M$	$[C_8H_{17}F]/$ $[C_6H_5Mg_4F]$	$[C_6H_5Cl]/$ $[C_6H_5Mg_4F]$
0.15	23.7	21.5
0.30	25.6	19.1
0.41	27.3	18.2
0.48	27.5	18.3

Table 3

MALDI–TOF MS data for products of C₆H₅Cl reaction with C₆H₅Mg₄F obtained by MVS in the systems C₆H₅F–Mg at different C₆H₅F/Mg ratio

C ₆ H ₅ F/Mg in synthesis	C ₆ H ₅ Mg ₄ F (before reaction)		After reaction with C ₆ H ₅ Cl	
	<i>m/z</i> (Da)	Molecular ion	<i>m/z</i> (Da)	Molecular ion
63	193–196	[C ₆ H ₅ Mg ₄ F + H] ⁺	209–213	[C ₆ H ₅ Mg ₄ Cl + H] ⁺
117	193–196	[C ₆ H ₅ Mg ₄ F + H] ⁺	209–213	[C ₆ H ₅ Mg ₄ Cl + H] ⁺
328	193–196	[C ₆ H ₅ Mg ₄ F + H] ⁺	209–213	[C ₆ H ₅ Mg ₄ Cl + H] ⁺
475	193–196	[C ₆ H ₅ Mg ₄ F + H] ⁺	209–213	[C ₆ H ₅ Mg ₄ Cl + H] ⁺
518	193–196	[C ₆ H ₅ Mg ₄ F + H] ⁺	209–213	[C ₆ H ₅ Mg ₄ Cl + H] ⁺
760	193–196	[C ₆ H ₅ Mg ₄ F + H] ⁺	209–213	[C ₆ H ₅ Mg ₄ Cl + H] ⁺

Table 4

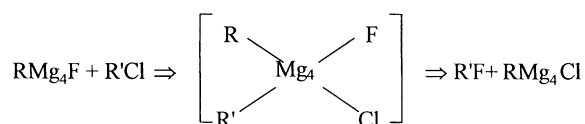
MALDI–TOF MS data for products of C₈H₁₇Cl reaction with C₆H₅F in the presence of C₆H₅Mg₄F obtained by MVS in the systems C₆H₅F–Mg at different C₆H₅F/Mg ratio

C ₆ H ₅ F/Mg in synthesis	C ₆ H ₅ Mg ₄ F (before reaction)		After reaction with C ₈ H ₁₇ Cl	
	<i>m/z</i> (Da)	Molecular ion	<i>m/z</i> (Da)	Molecular ion
75	193–196	[C ₆ H ₅ Mg ₄ F + H] ⁺	209–213 244–250	[C ₆ H ₅ Mg ₄ Cl + H] ⁺ [C ₈ H ₁₇ Mg ₄ Cl + H] ⁺
136	193–196	[C ₆ H ₅ Mg ₄ F + H] ⁺	209–213 244–250	[C ₆ H ₅ Mg ₄ Cl + H] ⁺ [C ₈ H ₁₇ Mg ₄ Cl + H] ⁺
374	193–196	[C ₆ H ₅ Mg ₄ F + H] ⁺	209–213 244–250	[C ₆ H ₅ Mg ₄ Cl + H] ⁺ [C ₈ H ₁₇ Mg ₄ Cl + H] ⁺
493	193–196	[C ₆ H ₅ Mg ₄ F + H] ⁺	209–213 244–250	[C ₆ H ₅ Mg ₄ Cl + H] ⁺ [C ₈ H ₁₇ Mg ₄ Cl + H] ⁺
540	193–196	[C ₆ H ₅ Mg ₄ F + H] ⁺	209–213 244–250	[C ₆ H ₅ Mg ₄ Cl + H] ⁺ [C ₈ H ₁₇ Mg ₄ Cl + H] ⁺
780	193–196	[C ₆ H ₅ Mg ₄ F + H] ⁺	209–213 244–250	[C ₆ H ₅ Mg ₄ Cl + H] ⁺ [C ₈ H ₁₇ Mg ₄ Cl + H] ⁺

209–213 Da and seven peaks at *m/z* = 244–250 Da attributed to quasi-molecular ions of octyltetramagnesium chloride protonated molecules. Consequently, phenyltetramagnesium chloride and alkyltetramagnesium chloride have been obtained in the reaction (4) independently on cluster Grignard reagent MVS conditions. The formation of the organomagnesium compounds mentioned have been confirmed by C₆H₅D and C₈H₁₇D getting on reaction mixture deuterolysis. Phenyl- and alkyltetramagnesium chloride formation appear to be proceeded due to magnesium cluster exchange. This fact demonstrates the possibility of reversible magnesium cluster insertion in various C–X bonds with conservation of cluster nuclearity.

Consequently, organopolymagnesium halides can act as magnesium clusters source. Detail mechanism

of the clusters exchange reaction is not yet clear. We can assume that reaction proceeds throughout organic chloride oxidative addition and organic fluoride reductive elimination:



This mechanism is similar to the classical addition–elimination scheme known for catalytic reactions on transition metals. The mechanism mentioned has been discussed for the organomagnesium cluster compounds interaction with hydrocarbons [7]. It should be noted that transformation takes place even at low temperature. The product yields for the

Table 5

Halogen exchange reaction product, C₈H₁₇F, yields (C₈H₁₇F/Mg, mol/atom) at various temperatures for the interaction of C₈H₁₇Cl with C₆H₅F in the presence of C₆H₅Mg₄F obtained by MVS in the systems C₆H₅F–Mg at different C₆H₅F/Mg ratio ([C₆H₅Mg₄F] = 2.1 × 10⁻³ M, [C₈H₁₇Cl] = 3.0 × 10⁻² M, reaction time 1 h)

C ₆ H ₅ F/Mg in MVS	C ₈ H ₁₇ F, yields (C ₈ H ₁₇ F/Mg, mol/atom) at various temperatures		
	253 K	273 K	293 K
117	0.18	0.19	0.20
258	0.19	0.21	0.22
370	0.19	0.20	0.21
583	0.20	0.21	0.22

cluster exchange reaction (4) at various temperatures are presented in Table 5. The yields almost do not depend on temperature. Accordingly, data obtained process proceeds with low activation energy.

2. Conclusions

Cluster Grignard reagents present the first example of hypovalent magnesium derivatives. Metal clusters composing are able to act as active centers in catalysis. They possess comparatively high stability and can retain their nuclearity in the course of chemical and catalytic transformations. Magnesium clusters exchange allows to obtain polymagnesium species not only in MVS conditions but in solution at ambient temperatures. Moreover, cluster Grignard reagents reactivity and catalytic activity are determined by their valent and coordination unsaturation.

First representatives of a new type of organometallic derivatives of hypovalent non-transition metals got in the course of this work exhibit quite unusual properties. Thus, they participate in C–X bond activation processes including catalytic reactions. Concept about

the origin of reactivity and catalytic activity of organomagnesium clusters will be developed.

Acknowledgements

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