Synthesis of Cluster Alkyl and Aryl Grignard Reagents in Solution

Ljudmila A. Tjurina,*[†] Vladimir V. Smirnov,[†] Denis A. Potapov,[†]
Sergei A. Nikolaev,[†] Stanislav E. Esipov,[‡] and Irina P. Beletskaya[†]

M.V. Lomonosov Moscow State University, Leninskie Gory,
119992 Moscow, Russian Federation, and Shemyakin and
Ovchinnikov Institute of Bioorganic Chemistry, Russian Academy of Sciences,
Mikluho-Makla'a Street, 16/10, 117871 Moscow, Russian Federation

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Cluster alkyl Grignard reagents, alkyltetramagnesium chlorides, have been obtained by exchange reaction between phenyltetramagnesium fluoride and organic halides in excess halide solution at room temperature. Transmetalation between PhCl, PhBr, and phenyltetramagnesium fluoride with the formation of $PhMg_4X$ ($X = Cl$, Br) has been shown to occur.

Introduction

The possibility of obtaining and stabilizing magnesium cluster derivatives has been the subject of much controversy until recently. Klabunde et al. have suggested that under metal-vapor synthesis (MVS) at low temperature not atoms but small magnesium clusters reacted with methyl halides.[1,2] On the other hand, the presence of a filled 2s-shell in magnesium, the absence of valence p-electrons, and the substantial energy gap between 2s- and 2p-sublevels gave no grounds for relying on the high stability of neutral clusters Mg_n. Their relatively low rigidity is also predicted by quantum-chemical calculations.[3,4] Reaction of isolated magnesium atoms with organic halides in an inert gas matrix, when their aggregation into clusters is impossible, does not result in the formation of compounds with Mg−Mg bonds.[5] Under experimental conditions, in which metal cluster formation is inhibited by diluting with 10 000-fold quantities of inert gas, reaction with methyl halides led to methylmagnesium halides. However, MVS in Mg−PhX systems proceeds with the formation of cluster analogues of Grignard reagents, namely, phenyltetramagnesium halides $PhMg_4X$, which are stable at room temperature both in the solid phase and in solutions.[6,7] Individuality of these compounds was confirmed mass-specrtometrically by the MALDI-TOF MS method. The presence in such cluster reagents of C−Mg and Mg−Mg bonds was confirmed by the formation of monodeuteriobenzene (or benzene) and deuterium (or hydrogen) upon deuteriolysis and hydrolysis, respectively (eq 1).[6]

$$C_6H_5Mg_4X + 7D_2O = C_6H_5D + Mg(OD)X + 3Mg(OD)_2 + 3D_2 \quad (1)$$

The problem of preparing cluster Grignard reagents in solution under usual conditions is of paramount importance. On one hand, it would open novel possibilities of utilizing these unusual compounds in organic and organometallic synthesis. On the other hand, it would give additional supportive evidence that compounds containing Mg−Mg bonds are intermediates in the formation of classical Grignard reagents in solution.[8]

In this paper we first report the synthesis of cluster Grignard reagents in a solvent of excess organic halide at room temperature by means of exchange reactions between phenyltetramagnesium halides and aryl and alkyl halides (eq 2).

$$PhMg_4X + RY \rightarrow RMg_4Y + PhX \quad (2)$$

where X is F or Cl, R is Ph or alkyl, and Y is Cl or Br.

Experimental Section

Phenylpolymagnesium halides were prepared by the MVS method in reaction between halobenzenes and magnesium. The organic halide was condensed with magnesium vapor, which was obtained by resistive heating at 623−873 K. The metal vapor was condensed onto the interior surface of the evacuated glass reactor, which was cooled by liquid nitrogen. The area in which the reagents condensed was about 200 cm^2; the condensation time was from 0.5 to 4 h. Dark brown layers of the reagent mixtures were formed on the glass surface of the reactor during this time. Magnesium ((10^{-5} −1.9) × 10^{-3} mol) and halobenzene (0.1−0.001 mol) were introduced into the reactor. After completion of the condensation the reaction mixture was warmed to room temperature. Decolorization and melting of samples occurred during the warmup period. As previously shown,[6,7] solutions of phenyltetramagnesium ha-

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* Corresponding author. Fax: 7-095-939-36-18. E-mail: tyurina@kinet.chem.msu.ru.

[†] M.V. Lomonosov Moscow State University.

[‡] Shemyakin and Ovchinnikov Institute of Bioorganic Chemistry, RAS.

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Table 1. MALDI-TOF MS Data for the Reaction $PhMg_4F + PhCl = PhMg_4Cl + PhF$ at Various Reagent Ratios, Reaction Time 1 h at 298 K

starting reagents ratio in reaction mixture and molecular ions observed				molecular ions after reaction mixture hydrolysis	
quantity of $PhMg_4F$, mol × 10^{-5}	quantity of PhCl, mol × 10^{-5}	*m*/*z*, Da	molecular ion	*m*/*z*, Da	molecular ion
37.5	39.0	193−196	$[C_6H_5Mg_4F + H]^+$	60−63	$[Mg(OH)F + H]^+$
		209−213	$[C_6H_5Mg_4Cl + H]^+$	59−61	$[Mg(OH)_2 + H]^+$
				77−81	$[Mg(OH)Cl + H]^+$
35.2	39.0	193−196	$[C_6H_5Mg_4F + H]^+$	60−63	$[Mg(OH)F + H]^+$
		209−213	$[C_6H_5Mg_4Cl + H]^+$	59−61	$[Mg(OH)_2 + H]^+$
				77−81	$[Mg(OH)Cl+ H]^+$
8.1	98	209−213	$[C_6H_5Mg_4Cl + H]^+$	59−61	$[Mg(OH)_2 + H]^+$
				77−81	$[Mg(OH)Cl + H]^+$

lides $PhMg_4X$ (X = fluorine or chlorine) are formed. They are stable under usual conditions in an excess of halobenzene. Subsequently, 1×10^{-4} to 1×10^{-3} mol of organic halide RY was added to the above solutions, and the homogeneous reaction mass was maintained for 1−3 h at room temperature. Then it was either hydrolyzed or, after proper workup, spectrophotometrically analyzed. The composition of products was analyzed by GLC and mass spectrometry by the MALDI-TOF method.[9] Anthracene was utilized as a matrix, 1×10^{-4} to 1×10^{-3} mol of which in the dry chamber was added to the solution of organomagnesium compound. A portion of the solution was applied to a special target and was evaporated under an inert atmosphere to remove volatile components. The target was placed in a vessel filled with inert gas and transferred to an inert atmosphere box which interfaced with a mass spectrometer. The target was inserted into the target holder of the mass spectrometer and injected into the mass spectrometer.

Mass spectra were obtained on a “Vision 2000” spectrometer (Thermo Bioanalysis Corp., England) equipped with a nitrogen laser ($\lambda = 337$ nm), impulse capacity 0.25 mJ 3 ns.

Results and Discussion

Adding an excess of chlorobenzene to a solution of phenyltetramagnesium fluoride in fluorobenzene solution led to the formation of phenyltetramagnesium chloride (eq 3).

$$PhMg_4F + PhCl \rightarrow PhMg_4Cl + PhF \qquad (3)$$

The formation of phenyltetramagnesium chloride in reaction 3 was confirmed by MALDI-TOF MS data. Prior to reaction only peaks at $m/z = 193-196$ Da of the protonated molecules $PhMg_4F$ were present in the mass spectrum of phenyltetramagnesium fluoride.[6] After the addition of chlorobenzene in excess these peaks disappeared and peaks at $m/z = 209-213$ Da due to molecular ions $[PhMg_4Cl + H]^+$ simultaneously appeared. Mass spectra of phenyltetramagnesium halides were identical to those previously obtained.[6] The ratio of peak intensities in the mass spectra of phenyltetramagnesium halides is in good agreement with the theoretical isotopic distribution for their protonated ions, as previously mentioned.[6] Gas chromatographic analysis of the volatile products shows that they are a mixture of fluoro- and chlorobenzene with no other compounds being detected.

When more than a 10-fold excess of chlorobenzene is used, the reaction eventually goes to completion in 20−40 min. An equilibrium is established when a smaller excess of chlorobenzene is present in the solution. This was shown by the simultaneous detection of both cluster magnesium derivatives by the MALDI-TOF MS method, and basic salts of magnesium chloride and bromide were simultaneously identified in products of hydrolyzed samples (Table 1).

A reaction occurs between phenyltetramagnesium fluoride and bromobenzene. On adding a large excess of bromobenzene (>10), peaks of protonated molecules of phenyltetramagnesium fluorides at $m/z = 193-196$ Da disappeared in the mass spectrum and peaks at $m/z = 253-258$ Da due to quasi molecular ions $[PhMg_4Br + H]^+$ appeared. However, with a smaller excess of bromobenzene, peaks of protonated molecules of both organomagnesium clusters were observed.

Transmetalation of bromobenzene with magnesium cluster Mg_4 proceeds similarly to both phenyltetramagnesium fluoride and phenyltetramagnesium chloride. In both reactions phenyltetramagnesium bromide and phenylmagnesium bromide are formed as well as a certain quantity of biphenyl. The mass spectrum of the PhMgBr thus produced is identical to that of a sample synthesized in diethyl ether solution according to the classical procedure.[7] It should be stressed that the formation of biphenyl and the Grignard reagent along with its cluster analogue is characteristic only of the reaction of organomagnesium clusters with bromobenzene; it does not occur with chloro- or fluorobenzene. Undoubtedly that should be attributed to the relative reactivity of the halobenzenes and ability of the corresponding C−X bonds to be reduced. That is why disproportionation of the type in eq 4 proceeds only in the case of bromobenzene.

$$C_6H_5Mg_4Br + 3C_6H_5Br = 4C_6H_5MgBr \qquad (4)$$

We have found that transmetalation without loss of the cluster nature of magnesium also proceeds with alkyl halides. Reactions of $PhMg_4X$ (X = F, Cl, Br) with alkyl halides led to quantitative formation of organomagnesium compounds of the type $AlkMg_4Cl$ (eq 5):

$$C_6H_5Mg_4X + AlkCl = AlkMg_4Cl + C_6H_5X \qquad (5)$$

$$X = F, Cl, Br; AlkCl = C_7H_{15}, C_8H_{17}$$

Convincing evidence of this was provided with monitoring of the reactions by mass spectrometry when an excess of the alkyl chlorides was used: the protonated $PhMg_4X$ species disappeared and peaks due to the protonated alkyl Mg_4X species were observed. Along with the formation of the cluster species, classical Grignard reagent AlkMgCl also was produced, as in the

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Table 2. MALDI-TOF MS Data for Phenyltetramagnesium Bromide Preparation by the Reaction $PhMg_4X + PhBr = PhMg_4Br + PhX$ (X = F, Cl) at Various Reagent Ratios, Reaction Time 1 h at 298 K

$PhMg_4X$ and starting reagents quantities in reaction mixture			molecular ions in reaction mixture	
$PhMg_4X$	quantity of $PhMg_4X$, mol × 10^{-5}	quantity of PhBr, mol × 10^{-5}	m/z, Da	molecular ion
$PhMg_4F$	12.5	7.7	193−196	$[C_6H_5Mg_4F + H]^+$
			253−258	$[C_6H_5Mg_4Br + H]^+$
			181−185	$[C_6H_5MgBr + H]^+$
$PhMg_4F$	8.3	96.0	253−258	$[C_6H_5Mg_4Br + H]^+$
			181−185	$[C_6H_5MgBr + H]^+$
			155	$[(C_6H_5)_2 + H]^+$
$PhMg_4F$	10.6	48.0	253−258	$[C_6H_5Mg_4Br + H]^+$
			181−185	$[C_6H_5MgBr + H]^+$
			155	$[(C_6H_5)_2 + H]^+$
$PhMg_4Cl$	15.4	7.7	209−213	$[C_6H_5Mg_4Cl + H]^+$
			253−258	$[C_6H_5Mg_4Br + H]^+$
			181−185	$[C_6H_5MgBr + H]^+$
			155	$[(C_6H_5)_2 + H]^+$
$PhMg_4Cl$	12.7	9.6	209−213	$[C_6H_5Mg_4Cl + H]^+$
			253−258	$[C_6H_5Mg_4Br + H]^+$
			181−185	$[C_6H_5MgBr + H]^+$
			155	$[(C_6H_5)_2 + H]^+$
$PhMg_4Cl$	12.9	48.0	253−258	$[C_6H_5Mg_4Br + H]^+$
			181−185	$[C_6H_5MgBr + H]^+$
			155	$[(C_6H_5)_2 + H]^+$
C_6H_5MgBr obtained in $(C_2H_5O)_2$ solution at 283 K			181−185	$[C_6H_5MgBr + H]^+$

Table 3. MALDI-TOF MS Data for Octyltetramagnesium Chloride Obtained in Reaction 5 at Various Reagent Ratios, Reaction Time 1 h at 298 K

$PhMg_4X$ and starting reagents quantities in reaction mixture			molecular ions in reaction mixture	
$PhMg_4X$	quantity of $PhMg_4X$, mol × 10^{-5}	quantity of octyl chloride, mol × 10^{-4}	m/z, Da	molecular ion
$PhMg_4F$	9.5	6.0	193−196	$[C_6H_5Mg_4F + H]^+$
			245−249	$[C_8H_{17}Mg_4Cl + H]^+$
			173−176	$[C_8H_{17}MgCl + H]^+$
$PhMg_4Cl$	8.2	12.0	245−249	$[C_8H_{17}Mg_4Cl + H]^+$
			173−176	$[C_8H_{17}MgCl + H]^+$
$PhMg_4Cl$	9.3	12.0	245−249	$[C_8H_{17}Mg_4Cl + H]^+$
			173−176	$[C_8H_{17}MgCl + H]^+$
$PhMg_4Br$	2.6	6.0	245−249	$[C_8H_{17}Mg_4Cl + H]^+$
			173−176	$[C_8H_{17}MgCl + H]^+$
$C_8H_{17}Cl/Mg$ for MVS in $C_8H_{17}Cl{-}Mg$ system				
33.2			173−176	$[C_8H_{17}MgCl + H]^+$
51.8			173−176	$[C_8H_{17}MgCl + H]^+$
112.0			173−176	$[C_8H_{17}MgCl + H]^+$

case of chlorobenzene transmetalation. MALDI-TOF MS data are in accordance with the destructive analysis results, analogous to those previously described.[6,7,1010−13] However, it has been assumed previously on the basis of destructive analysis data[7,10] for products of direct MVS synthesis in AlkCl−Mg systems that clusters containing magnesium dimers $AlkMg_2Cl$ are components of the alkylpolymagnesium halides that we formed. According to hydrolysis data, alkyldimagnesium halides are unstable and exist in solutions containing the alkyl halide in excess only for 15−30 min. The MALDI-TOF MS spectrum of MVS products in alkyl chloride−magnesium systems, which is recorded over 30 min after the reaction, contains only protonated molecule peaks of the classical alkylmagnesium halide. Stable alkyltetramagnesium halides can be obtained only by transmetalation.

We have demonstrated that tetranuclear magnesium clusters in cluster Grignard reagents posess significant stability. Organomagnesium clusters have a propensity to transmetalate C−X bonds in solution under ambient conditions without loss of nuclearity. Herewith, as in the case of MVS, phenyltetramagnesium halides are formed. It has been found that the above compounds could serve as sources of magnesium clusters. Transmetalation in solution at room temperature has made it possible to obtain cluster Grignard reagents bearing alkyl substituents.

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Supporting Information Available: This material (2 tables) is available free of charge via the Internet at http://pubs.org.

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