# Cluster Grignard Reagents

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*Received January 18, 2001*

*Summary: Cluster Grignard reagents, $C_6H_5Mg_nX$, have been obtained by metal vapor synthesis. Their composition has been established by MALDI−TOF MS and supporting hydrolysis studies.*

Grignard reagents, RMgX, are some of the most important synthetic reagents, but although they have been used for over a century, investigations of their structures, the mechanisms of their formation, and reactivity are still continuing and new ideas are still appearing.[1] One intriguing hypothesis discussed in the literature[2−9] is the possibility of the existence of “cluster Grignard reagents”, particularly under conditions of metal vapor synthesis (MVS). However, up to now there has been no direct evidence in favor of this hypothesis. Here we report the first evidence of cluster Grignard reagents $C_6H_5Mg_nX$. These compounds were obtained by MVS from $C_6H_5X$, where X = Br, Cl, and even F.

Phenylpolymagnesium halides were obtained through the reaction of magnesium and phenyl halides at 100−130 K. The interaction was performed in co-condensates of reagent vapors on the surface of a evacuated reactor cooled with liquid nitrogen. In all experiments, magnesium vapor was co-deposited with an excess of an $C_6H_5X$ ($C_6H_5X$/Mg = 50−500) at 77 K. The co-condensation areas were equal to 200 cm$^2$ in a glass reactor and 0.5 m$^2$ in a metal reactor. Condensation rates of magnesium were equal to $10^{-2}$−$10^{-5}$ M/h, condensation times 1−5 h. The matrixes formed at 77 K were dark brown but became colorless liquids when warmed to ambient temperature after the deposition had ended. These solutions were filtered in a drybox to exclude the possibility of the presence of aggregated Mg. The excess of RX was then evaporated, leaving colorless microcrystals of organomagnesium compounds. The latter were identified by MALDI−TOF MS (matrix-assisted laser desorption ionization−time-of-flight mass spectrometry). In these studies, samples of the compounds in excess of $C_6H_5X$ solution were put on the target and after $C_6H_5X$ evaporation were placed in a mass spectrometer whose inlet system was isolated by a drybox. MALDI−TOF mass spectra were recorded using a Vision 2000 spectrometer.

These compounds were found to undergo hydrolysis by the addition of water at room temperature, and the yields of the products were determined by GC. Quantitative analysis of Mg was carried out after hydrolysis by titration with Trilon B.

The MALDI−TOF MS spectra indicated the formation of cluster Grignard reagents having *four* magnesium atoms, and a typical spectrum of $C_6H_5Mg_4F$ is presented in Figure 1 of the Supporting Information. There are four peaks at *m*/*z* 193−196, and these peaks were present in all samples irrespective of reagent ratio in the preparation procedure). These four peaks we attributed to so-called “quasi molecular” ions $[C_6H_5Mg_4F + H]^+$. The formation of similar protonated molecules is a general feature of the ionization process in MALDI−TOF MS.[10] The intensities of these four peaks are in a good agreement with the theoretical isotope distribution for the molecule $C_6H_5Mg_4F$. Elemental analysis leads to the same formula, $C_6H_5Mg_4F$ (Table 1). After $C_6H_5$-$Mg_4F$ hydrolysis by water, only the quasi molecular ions $[Mg(OH)_2 + H]^+$ and $[Mg(OH)F + H]^+$ of the hydrolysis products were observed. However, unlike the classic Grignard reagent, the hydrolysis of $C_6H_5Mg_4F$ gives not only benzene but also hydrogen.

The ratio of total magnesium to benzene formed ([Mg]/[$C_6H_6$]) was found to be 4:1, and the ratio of hydrogen to benzene ([$H_2$]/[$C_6H_6$]) was found to be 3:1. This leads to the hydrolysis equation

$$C_6H_5Mg_4F + 7H_2O = C_6H_6 + Mg(OH)X + 3Mg(OH)_2 + 3H_2 \quad (1)$$

Thus MALDI−TOF MS, elemental analysis, and hydrolysis all lead to the same formula, $C_6H_5Mg_4F$.

Analogous studies involving the other aryl halides led to formulations $C_6H_5Mg_4Cl$ and $C_6H_5Mg_4Br$. Typical spectra of $C_6H_5Mg_4Cl$ and $C_6H_5Mg_4Br$ are presented in

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10.1021/om0100380 CCC: $20.00

**Table 1. Elemental Analysis Data for $C_6H_5Mg_4F$ Obtained by MVS in the System $C_6H_5F$−Mg at Various Reagent Ratio**

| $C_6H_5F$/Mg in MVS | % C | % Mg | % F | % H | *n* |
|---|---|---|---|---|---|
| 173 | 37.9 | 49.9 | 9.1 | 3.1 | 4 |
| 512 | 37.0 | 50.0 | 9.6 | 3.4 | 4 |
| 84 | 38.0 | 49.9 | 9.0 | 3.1 | 4 |
| theoretical | 37.5 | 50 | 9.9 | 2.6 | 4 |

Figures 2 and 3 in the Supporting Information. For these compounds the MALDI−TOF MS showed the quasi molecular ion $[C_6H_5Mg_4Cl + H]^+$ peaks at *m*/*z* 209−213 and $[C_6H_5Mg_4Br + H]^+$ peaks at *m*/*z* 253−258, respectively. In both cases, the observed intensities are in a good agreement with the theoretical isotope distributions for the molecules $C_6H_5Mg_4X$ (X = Cl, Br).

Thus MALDI−TOF MS leads to the same value of nuclearity, "*n* = 4", for all three cluster Grignard reagents, and these compounds can be identified as $C_6H_5Mg_4X$ (X = Br, Cl, F).

For X = Cl a similar value of the nuclearity was additionally obtained from destructive analysis, where the value of "*n*" from hydrolysis data was found to be 3.6. In the case of phenylpolymagnesium bromide, destructive analysis could not be used to confirm nuclearity. Here, the "*n*" value obtained from hydrolysis data was consistently found to be 2.1 and thus significantly less than the value obtained from MS data. This difference is believed to arise as result of reaction of $C_6H_5Mg_nBr$ with an excess of $C_6H_5Br$:

$$C_6H_5Mg_nX + C_6H_5X = C_6H_5Mg_{n-1}X + C_6H_5MgX$$

$$C_6H_5MgBr + C_6H_5Br = C_6H_5{-}C_6H_5 + MgBr_2$$

Support for this scheme comes from the observation that in the MALDI−TOF MS spectra of bromide systems not only were the quasi molecular ions $[C_6H_5Mg_4Br + H]^+$ from $C_6H_5Mg_4Br$ observed, but also the protonated ions $[C_6H_5MgBr + H]^+$ and even the ions $[(C_6H_5)_2 + H]^+$ arising from biphenyl, the formation of which was confirmed by GC analysis. It should be noted that the similar protonated species $[C_6H_5MgBr + H]^+$ was found to be observed in the MALDI−TOF MS spectra of $C_6H_5MgBr$ prepared in $(C_2H_5)_2O$ solution at 283 K.

It is therefore possible that phenyltetramagnesium halides are obtained initially from all $C_6H_5X$ (X = Br, Cl, F) systems, but that this initial product reacts with the excess of phenyl halide in the case of the most reactive system, $C_6H_5Mg_4Br$−$C_6H_5Br$. In contrast, for the relatively inert system $C_6H_5Mg_4F$−$C_6H_5F$ organopolymagnesiumfluorides can be isolated from $C_6H_5F$ solution as polycrystalline solids stable in a vacuum for a few weeks.[5,6]

Another point of interest is why only tetramagnesium clusters appear to be formed. One possible explanation can be sought from theoretical studies of the various structures of $C_6H_5Mg_nX$. In Table 2 the stabilization energies and ionization potentials (from MP2/6-31G** calculations) are presented for a range of organomagnesium clusters, and it would seem that the "magic" value of *n* = 4 seems to be observed as a result of the increasing stabilization energy for tetrahedral $Mg_4$ nuclei and simultaneous decreasing of the ionization potential with nuclearity *n*.

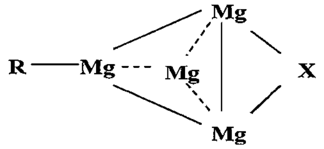

**Figure 1.** Possible structure of $C_6H_5Mg_4X$.[11]

**Table 2. Stabilization Energy, $E_s$,[11] and Ionization Potential, *I*, for $Mg_n$**

| | *n* | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| $E_s$, kcal/mol | | 3.7 | 3.0 | 14.8 |
| *I*, eV | 7.4[11] | 6.7[11] | 6.3 | 6.5 |
| | 7.6[4] | 6.7[4] | | 5.4 |

The structure of $C_6H_5Mg_4X$ predicted on the basis of the results of a theoretical study[11] is presented in Figure 1.

The decrease of the ionization potential for magnesium clusters may explain the differences between Grignard reagent formation in solution and under MVS conditions. In MVS there is a possibility for magnesium atoms to aggregate into clusters, and the lower value of the ionization potential in these clusters then allows $Mg_n$ insertion, even into the C−F bond of fluorobenzene,[12] which has resulted in a rare case of perfluoroarenes[13] in solution.

It should be noted that direct Mg atom insertion into a C−X bond is prevented by orbital symmetry restrictions. Indeed, the classic Grignard reaction has not been observed in the gas phase at either high or low temperatures.[14] In contrast, excited Mg atoms have been found to react with organic halides. In particular, Andrews[6] obtained the classic Grignard reagent from the reaction of laser-ablated $^3P$ Mg atoms with methyl halides in an argon matrix.

The results described here may be useful not only as a new synthetic approach but also in the understanding of classic Grignard reagent formation. It has recently been proposed that the "di-Grignard reagent" RMgMgX[15] may be a precursor of RMgX in heterogeneous Grignard preparations.

In conclusion, the present work demonstrates the existence of cluster Grignard reagents and provides the first example of a new type of organomagnesium cluster.

**Acknowledgment.** This work was supported by grant no. RFBR 01-03-32784. We express thanks to Professor S. Ogden for a polishing of our English.

**Supporting Information Available:** This material (3 figures, 4 tables) is available free of charge via the Internet at http://pubs.acs.org.

OM0100380

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