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Unusual magnesium–anthracene adduct

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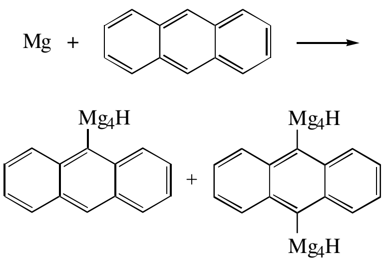
Under conditions of metal vapour synthesis (MVS) in the magnesium–anthracene system, magnesium clusters are inserted into a C–H bond to form organomagnesium compounds containing one or two C–Mg_4H fragments at the 9,10-positions.

Previously,[1] we found that magnesium gives Grignard-like compounds with the general formula $PhMg_4Hal$ in reactions with halobenzenes, including fluorobenzene, under conditions of metal vapour synthesis (MVS). In this work, we demonstrate that, under analogous conditions, magnesium clusters can also insert into the C_{sp^2}–H bond of an anthracene molecule. Magnesium reacts with anthracene in films obtained by the combined condensation of magnesium vapour with an excess of anthracene at 80 K. As the temperature was increased up to 100–130 K, a mixture of products **1**, **2** of mono- and di-insertion of magnesium into the C_9,C_{10}–H bonds of anthracene was formed.[†]



1 **2**

Note that, according to deuterolysis data, the reaction of magnesium with anthracene occurs only in co-condensates. Finely dispersed magnesium formed in the layer-by-layer condensation of the reactants does not enter the reaction, and the deuterolysis of such mixtures does not give deuterated compounds.

The structures of the prepared products were supported by the elemental composition and hydrolysis and deuterolysis data. The quantitative analysis of MVS products is difficult to perform because of their high chemical activity and the possibility of partial degradation in the course of the removal of an excess of anthracene. Although these factors impair the accuracy of analysis, we found that in all cases the metal content was many times higher than that for the equimolar ratio between magnesium and hydrocarbon. The value of *n* in the formula $C_{14}H_{10}Mg_n$, which was calculated from analytical data, varied from 4 to 8 in different experiments. This result with data[1] allowed us to assume the presence of magnesium clusters (probably, tetranuclear clusters) in the products. Hydrogen was released in the hydrolysis of combined condensates regardless of the initial ratio between components and of the presence of unreacted metal. The release of hydrogen, which was also found previously in the cluster analogues of Grignard reagents,[1] is also indicative of the presence of Mg–Mg bonds in low-temperature reaction products. In accordance with the proposed structures of **1**, **2**, deuterolysis affords a mixture of mono- and dideuterated anthracenes **3**, **4**. Their appearance unambiguously indicates the presence of C–Mg bonds in MVS products. Table 1 summarises the yields and compositions of deuterolysis products. In addition to the yields *P* formally calculated as

$$P\ (\%) = (\text{number of product moles})\times 100\%\ /\ \text{number of Mg moles},$$

Table 1 gives the yields calculated with consideration for the reaction stoichiometry; that is, the fact that four rather than one metal atoms enter the composition of the product. In fact, it is likely that these yields are also underestimated because the elemental analysis and the preparation of a dideuterated deriva-

Table 1 Yields of deuterioanthracenes and deuterated 9,10-dihydroanthracene derivatives (mol/mol Mg) in the deuterolysis of magnesium co-condensates with anthracene at different temperatures.

T/K	Molar ratio anthracene/Mg	Yield (mol%) in terms of Mg				Yield in terms of Mg_4[a]
		3	**4**	**5**	Total products	Total products
80	50	0	0	0	0	0
80	470	0	0	0	0	0
100	50	3.5	2.8	0	6.3	25.2
100	118	4.8	3.5	0	8.3	33.2
298	50	3.6	3.4	3.3	10.3	41.2
298	130	4.3	3.5	3.2	10.1	40.4
298	490	3.7	2.8	2.0	8.5	34.0
298[b]	430	0	0	0	0	0

[a]Data on the yields corrected for the empirical formula $C_{14}H_{10}Mg_4$. [b]Mg and anthracene were condensed layer-by-layer.

[†] In the course of MVS, magnesium and anthracene vapours were condensed onto the surface of an evacuated reactor cooled with liquid nitrogen. The co-condensation surface area was 200 cm^2. Magnesium was resistively evaporated at a rate of 0.001–0.1 g h^{-1} for 1–12 h (the anthracene-to-magnesium ratio was 40–500). Note that magnesium vapour consists of magnesium atoms.[5] Next, the reaction mixtures were heated to 100–298 K, and water (H_2O or D_2O) or fluorobenzene was added. The composition of the deuterolysis products was determined by chromatography–mass spectrometry. The amount of magnesium in the samples was determined by chelatometric titration.

The elemental analysis of adducts prepared at RH/Mg > 200 free of finely dispersed metal was performed. The RH/Mg ratio at which finely dispersed magnesium was absent was determined from the data on the reaction with fluorobenzene. Finely dispersed magnesium does not react with fluorobenzene.[1] Therefore, samples with different RH/Mg values were treated with fluorobenzene and filtered. Next, the hydrolysis products of the organomagnesium compound in the filtrate and the magnesium content on the filter were analysed. For this purpose, after repeatedly washing the filter with fluorobenzene, it was treated with hydrochloric acid and the magnesium content was determined. It was found that at RH/Mg > 100 magnesium was absent from the filter. The filtrate was hydrolysed with the formation of benzene in the ratio $[Mg]/[C_6H_6] = 4$ and hydrogen in the ratio $[H_2]/[C_6H_6] = 3$ in accordance with the equation of phenyltetramagnesium fluoride hydrolysis.[1]

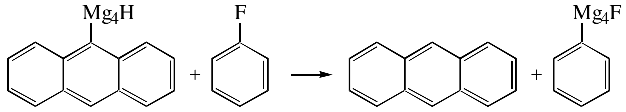
In the case of elemental analysis, the co-condensate after heating to room temperature was additionally heated to 80–100 °C on continuously pumping with a diffusion pump to remove an excess of the hydrocarbon. After evacuation, the reactor was filled with argon, and the sample was removed in a dry box and analysed by standard methods.

The products of the reaction with fluorobenzene were identified by MALDI-TOF mass spectrometry. For this purpose, after the removal of unreacted anthracene and dihydroanthracene by evacuation, a ten-fold excess of liquid fluorobenzene was added to the reaction product of magnesium and anthracene in a dry box at ambient temperature. The solution was held for 2 h and applied to a special target for MALDI-TOF MS. The target was placed in a mass spectrometer after evaporating an excess of the halobenzene. The spectra were measured on a VISION 2000 mass spectrometer. A portion of the product was simultaneously subjected to deuterolysis and examined as described above.

tive in the deuterolysis are indicative of the formation of product **2**, which likely contains eight magnesium atoms, in a detectable amount. If it is believed that the efficiency of formation of deuterated derivatives in the deuterolysis of organomagnesium MVS products is 100%, the yield of the latter in terms of magnesium can be estimated at ≥ 50%.

As can be seen in Table 1, if the sample was heated to room temperature before the addition of D_2O, a mixture of mono- and dideuterated 9,10-dihydroanthracene derivatives was formed along with **3**, **4**. 9,10-Dihydroanthracene **5** was also obtained in hydrolysis under the same conditions. It is well known that it also appears in the hydrolysis of a magnesium–anthracene adduct synthesised in a THF solution;[2] this adduct is a good donor of active magnesium.[3,4] It is likely that an adduct similar to that prepared previously[2] is formed in the course of transformations of MVS primary products on heating.

The cluster structure of the newly synthesised derivatives was supported by the composition of products of their reactions with organic bromides and chlorides. It is of importance that, in contrast to previously known magnesium–anthracene derivatives,[2] they also react with fluorobenzene. The reactions with aryl halides resulted in 'cluster Grignard reagents,' which are identical to those prepared earlier by the MVS method:[1]



6

Indeed, the hydrolysis of the reaction products of **1**, **2** with aryl halides, as well as the MVS products, was accompanied by the release of hydrogen. This is typical of cluster Grignard reagents **6**, which were prepared previously by MVS.[1] The cluster nature of the product was unambiguously established by MALDI-TOF mass spectrometry (Figure 1). The mass spectrum exhibits only the peaks of phenyltetramagnesium fluoride at *m*/*z* 50–400. The spectrum is identical to the previously measured spectrum of **6**:[1] only the peaks of quasi-molecular ions of the protonated molecules $[\mathrm{PhMg_4F + H}]^+$ appeared at *m*/*z* 193–196 Da. The formation of compound **6** with a Mg_4 nucleus is indicative of the presence of such cluster fragments in the products of a low-temperature reaction of magnesium with anthracene, and it supports the proposed formulae for **1**, **2**.

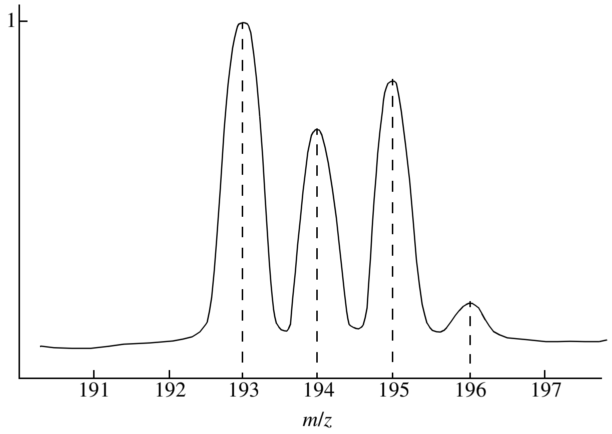


Figure 1 MALDI-TOF mass spectrum of phenyltetramagnesium fluoride prepared by the reaction of a magnesium–anthracene adduct with fluorobenzene (bars correspond to the theoretical isotope distribution).

Thus, compounds **1**, **2** can be used as magnesium cluster donors, which provide an opportunity to prepare cluster analogues of Grignard reagents. On the one hand, this fact is indicative of the sufficiently high stability of a cluster nucleus; on the other hand, it is indicative of its ability for changing organic substituents in the course of re-metallation without a decrease in the nuclearity. Note that cluster derivative **6** was prepared under ordinary conditions (in solution at room temperature).

In studies of the reactions of products **1**, **2**, we found another unusual phenomenon: compound **5** can be obtained in catalytic yields. The yields of **5** after heating the reaction mass up to 300 K, holding it at this temperature for a time (t) and hydrolysing were considerably higher than those in the cases when water was condensed onto a magnesium–anthracene co-condensate film at 80 or 130 K and then the samples were heated to room temperature. The yield of **5** with respect to magnesium increased with t and became catalytic at $t > 2$–3 h. At $t = 24$ h, the yield of **5** was as high as 4.7 molecule per magnesium atom (or 18.8 molecule per cluster on the assumption of tetranuclear magnesium aggregates). Consequently, in this case, the major portion of dihydroanthracene was formed in the course of anthracene autohydrogenation, which occurs with catalytic yields in the presence of organomagnesium clusters, rather than in the hydrolysis of organomagnesium compounds. Note that after heating condensates we also detected an insoluble solid polymer precipitate, which likely resulted from the consolidation of anthracene dehydrogenation products.

Thus, we inserted magnesium clusters into the C_{sp^2}–H bond and prepared organomagnesium cluster derivatives of anthracene. They can be magnesium donors and exhibit catalytic activity in the autohydrogenation of the parent hydrocarbon.

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