

EXAFS investigation of metal organic synthesis tools

Wolfgang Hörner, Helmut Bertagnolli *

Institut für Physikalische Chemie der Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

Received 17 March 1999; received in revised form 1 April 1999; accepted 11 November 2001

Abstract

An EXAFS spectroscopical study of three metal organic systems is presented. First, a series of differently concentrated Grignard compounds in solution were measured in order to obtain the degree of association and to find an eventual concentration dependence of the structure. No significant changes in the structure could be detected in the measured concentration range. The second investigated system $\text{Mg}(\text{CHBr}-\text{CH}_2\text{Ph})_2$, dissolved in THF, belongs to the relatively new class of carbenoids. A structural model of this compound, especially of the local environment of the α -carbon atom is deduced. Thirdly, Reformatsky compounds in solution with different ester groups, solvents and concentrations were studied. It is shown that the structure of these compounds depends on the polarity of the solvents. © 2002 Published by Elsevier Science B.V.

Keywords: EXAFS; Grignard compounds; Carbenoids; Reformatsky compounds

1. Introduction

Although the first metal organic compound was already found in 1760 by Cadet, the break-through of these reagents came in the late 19th century. A lot of compounds were found which turned out to be very useful in synthetic chemistry. Especially Grignard compounds [1,2], general formula $\text{R}-\text{Mg}-\text{X}$ (R = alkyl, X = Cl, Br, I), became an important synthesis tool which is still used in modern chemistry. The structure of Grignard compounds was the object of many investigations since the discovery of these species. A survey of

all methods, which were used for these investigations and a summary of the results are given in Ref. [3]. Nevertheless, the structure of Grignard compounds in solution is under debate up to the present stage. One of the fundamental questions in connection with the structure of Grignard compounds is the degree of association of the compounds in solution. Monomeric species as well as dimeric species are proposed, and the existence of an equilibrium between both components is suggested (Fig. 1). Our EXAFS spectroscopical investigations at the magnesium K-edge have confirmed the existence of dimers, as we found a magnesium–magnesium distance of about 330 pm [4], and of monomers in the investigated solutions. Now, we attempt to answer the question, whether an equilibrium exists. If yes, a change in the concentration of the Grignard compound must change the ratio monomer to dimer. Therefore we investigated differently concentrated Grignard systems, dissolved in diethylether. In detail, we investigated $\text{Me}-\text{Mg}-\text{Br}$ (Me = methyl) and $\text{Ph}-\text{Mg}-\text{Br}$ (Ph = phenyl) in concentrations of 0.25, 0.5 and 1.0 M.

While Grignard compounds exist for nearly 100 years, the carbenoid compounds were found in the last 20 years. Originally, the term ‘carbenoid’ was denoted for α -haloalkyl lithium compounds [5]. Later it was extended to all metal organic compounds with α -haloalkyl groups, general formula $\text{X}-\text{C}(\text{R}_1\text{R}_2)-\text{M}$ (X =

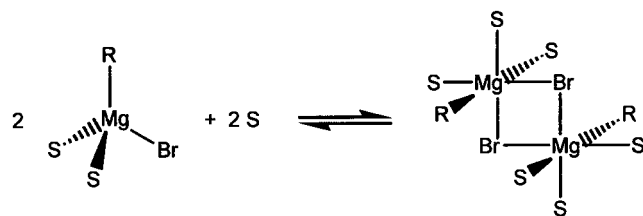


Fig. 1. Proposed equilibrium between monomer and dimer Grignard species. A tetrahedral coordination is suggested for both species in Ref. [4].

* Corresponding author. Tel.: +49-711-685-4450; fax: +49-711-685-4443.

E-mail address: h.bertagnolli@ipc.uni-stuttgart.de (H. Bertagnolli).

leaving group, e.g. Cl, Br, I, OR; R = organic group; M = metal, e.g. Li, Mg). Owing to their nucleophilic as well as electrophilic properties, which are similar to those of carbanions and carbeniumions, many interesting reactions can be performed with carbenoids [6–10], although these compounds are difficult to handle. Nearly all carbenoids decompose at temperatures higher than $-50\text{ }^{\circ}\text{C}$. As one can imagine in view of this behaviour, it is difficult to perform investigations of structure of carbenoid compounds. So it is not surprising that only little information about geometry and distances are available. From downfield shifts, obtained by ^{13}C -NMR spectroscopy, qualitative statements about the character of the species are possible [9–13] X-ray diffraction studies revealed some significant changes in bond length and bond angles compared with other metal halogen compounds [14–16]. But these information refer to samples in solid state and we are interested in the structure of carbenoids in solution. Therefore, we performed an EXAFS investigation of a 0.4 M solution of $\text{Mg}(\text{CHBr}-\text{CH}_2\text{Ph})_2$ dissolved THF.

An other important species of metal organic synthesis tools are the Reformatsky compounds [17,18], general formula $\text{E}-(\text{CH}_2)_n-\text{Zn}-\text{Br}$ (E = ester group). The main difference between Reformatsky and Grignard compounds is the use of zinc instead of magnesium, which leads to a different reaction behaviour, especially to a higher selectivity. Although Reformatsky compounds are known for more than 100 years and found their way into all text books of metal organic chemistry, not all questions concerning the structure of the species could be answered [19–22]. A first step of the elucidation of the structure happened in 1984, when it was possible to perform a X-ray diffraction of a Reformatsky compound with a large alkyl residue at the ester group [23]. It was shown that Reformatsky compounds form a cyclic dimer in the solid state with the zinc atom and the oxygen atom of the carbonyl group as bridging atoms. But there does not exist any reliable structure model for the species in solution. Therefore we performed EXAFS measurements of two different Reformatsky systems in solution. We used the Reformatsky compounds, corresponding to methyl bromoacetate and *tert*-butyl bromoacetate. From the use of two different alkyl residues it is possible to check whether the size of the ester group can influence the behaviour of Reformatsky compounds in solution. In order to examine whether the solvent (especially the polarity of the solvent) can exert any effect on the structure of the compounds in solution, we selected THF, pyridine and DMSO as solvents. Additionally, we investigated the influence of the concentration on the structure by measuring a 0.3, 0.8 M and saturated solutions.

2. Experimental

A review of the EXAFS spectroscopy is given in Refs. [24–26]. The EXAFS experiments were carried out mainly at CLRC Daresbury Laboratory (beamline 9.2), Warrington (GB), and additionally at HASYLAB (beamlines ROEMO2 and W1) at DESY, Hamburg (D). The Grignard compounds, the carbenoid and a part of the Reformatsky compounds were measured at the bromine K-edge at 13474.0 eV and all Reformatsky compounds at the zinc K-edge at 9659.0 eV. The ambient conditions were the same during all experiments at CLRC (temperature $18\text{ }^{\circ}\text{C}$, voltage 3.0 GeV, beam current 200 mA) and at HASYLAB (temperature $18\text{ }^{\circ}\text{C}$, voltage 6.0 GeV, beam current 50 mA). The experimental arrangement was typical of measurements in transmission mode with two ionization chambers. Both chambers were filled with a mixture of Ar and N_2 so that the calculated absorption of the beam was 10% in the first and 80% in the second chamber. The double crystal monochromator was fitted with two $\text{Si}\langle 220 \rangle$ (HASYLAB: $\text{Si}\langle 311 \rangle$) crystals. In order to reject higher harmonics the second crystal was detuned by about 30% from the maximum flux position. The energy was calibrated before and after the energy scans by measuring a $30\text{ }\mu\text{m}$ thick tablet of anhydrous KBr or a $5\text{ }\mu\text{m}$ thick zinc foil. The samples were filled in a cell for liquids under inert gas [27]. The thickness of the sample was adjusted to a change in the absorption coefficient of 1.5 at the absorption edge. All measurements were performed under inert gas atmosphere to avoid decomposition reactions. The investigation of the carbenoid requires some modifications. Since the compounds decompose at temperatures higher than $-50\text{ }^{\circ}\text{C}$, a solution of $\text{Mg}(\text{CHBr}-\text{CH}_2\text{Ph})_2$ in dry THF was prepared at $-78\text{ }^{\circ}\text{C}$ at the synchrotron laboratory [13] and the sample was analysed after the measurements. During the experiments the sample cell was kept at temperatures lower than $-50\text{ }^{\circ}\text{C}$.

The analysis of the EXAFS data was performed with our program package [28]. First, the pre-edge absorption is obtained by a Victoreen-type polynomial, which is extrapolated beyond the edge and subtracted from the measured absorption. Then, the background is determined with a smoothing-spline algorithm, subtracted and the resulting function is normalized to the background. The program EXCURV90 [29] was used for fitting the experimental EXAFS data.

3. Results

3.1. Grignard compounds

Fig. 2 shows the obtained EXAFS functions and the corresponding Fourier transforms for one of the six

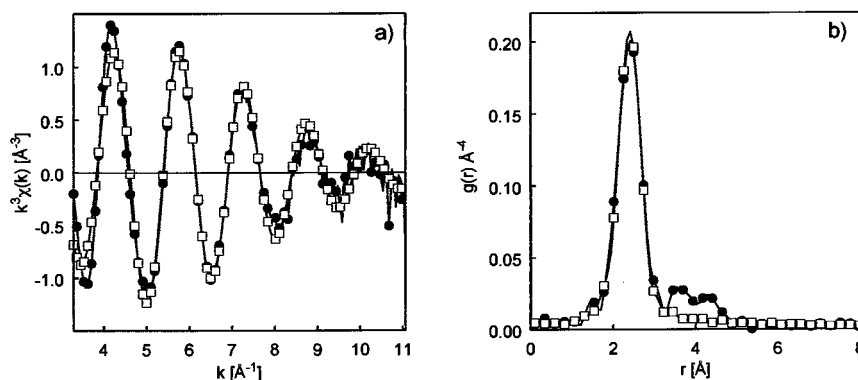


Fig. 2. Experimental (circles) and calculated (squares) EXAFS functions (a) and the corresponding Fourier transforms (b) of a 1.0 M solution of Me–Mg–Br in diethylether.

investigated Grignard systems. The other spectra look similar to this. All six Fourier transforms contain an isolated, well-pronounced peak in the range at about 240–250 pm. As expected, this peak can be described with magnesium as backscatterer. It was checked by fitting a Fourier filtered range (100–280 pm) that these symmetrical peaks contain no other atoms. While fitting the calculated EXAFS function on the experimental function it is problematic to iterate simultaneously the coordination number and the Debye–Waller factor. This method can produce wrong coordination numbers, as these values depend on the Debye–Waller factor and reverse. In order to obtain reliable values for the degree of association it was necessary to minimize the effect of the Debye–Waller factor on the coordination number. Therefore, the Debye–Waller factor was not iterated at all fits. But in this case, we had to find the basic value for the Debye–Waller factors of both chemical systems first. In a first step, the systems with the medium concentration were evaluated. The magnesium shell was fitted by iterating the distance, the coordination number and the Debye–Waller factor. In order to check the determined values one of the parameters was varied and the two other were fitted. The Debye–Waller factor of the best fit was

Table 1

Br–Mg distances, $r(\text{Br–Mg})$, and number of magnesium atoms, bonded or coordinated to the bromine atom, $N(\text{Mg})$ for the Grignard systems Me–Mg–Br and Ph–Mg–Br, dissolved in diethylether

Concentration (M)	Me–Mg–Br		Ph–Mg–Br	
	$r(\text{Br–Mg})$ (pm)	$N(\text{Mg})$	$r(\text{Br–Mg})$ (pm)	$N(\text{Mg})$
0.25	247 ± 2	1.54 ± 0.07	245 ± 2	1.57 ± 0.07
0.5	244 ± 2	1.54 ± 0.05	243 ± 2	1.62 ± 0.06
1.0	244 ± 2	1.54 ± 0.04	243 ± 2	1.63 ± 0.04

The Debye–Waller factors were fixed to 11.0 pm, the energy threshold to $\Delta E_0 = 16.2$ eV.

used for the data evaluation of the measurements with the other concentrations. In detail, the Debye–Waller factors of both systems amount 11.0 pm. This fit procedure seems to be permissible in the opinion of the authors. On the one hand, from the chemical view, the systems differ only in the concentration. On the other hand, the EXAFS measurements were performed in a short period under equal conditions, especially beam conditions. The distances and coordination numbers, obtained with the method described above, are shown in Table 1.

3.2. Carbenoid compounds

The Fourier transform of the carbenoid compound (Fig. 3) shows three well-pronounced peaks. This means that at least three backscatterers are necessary to describe the experimental EXAFS function. The distance at 200 pm fits exactly to one carbon atom, the distance at 304 pm can be described very well with a magnesium atom. It is obvious that the peak at 420 pm must be assigned to an atom with a large atom number, because only such atoms can generate remarkable scattering effects at those distances. Indeed, the shell can be described with a bromine atom. The addition of two further shells, a carbon atom at 281 pm and a bromine atom at 477 pm, leads, however, to a remarkable improvement of the agreement between experimental and calculated EXAFS function. The refined values of the parameters of all the shells are given in Table 2.

3.3. Reformatsky compounds

The zinc K-EXAFS functions and the corresponding Fourier transforms of three typical Reformatsky systems are shown in Figs. 4–6. The samples that only differ in the organic group R or in the concentration give nearly the same spectra. But systems with different solvents, exhibit significant differences in the EXAFS data as well as in the Fourier transforms. The spectra

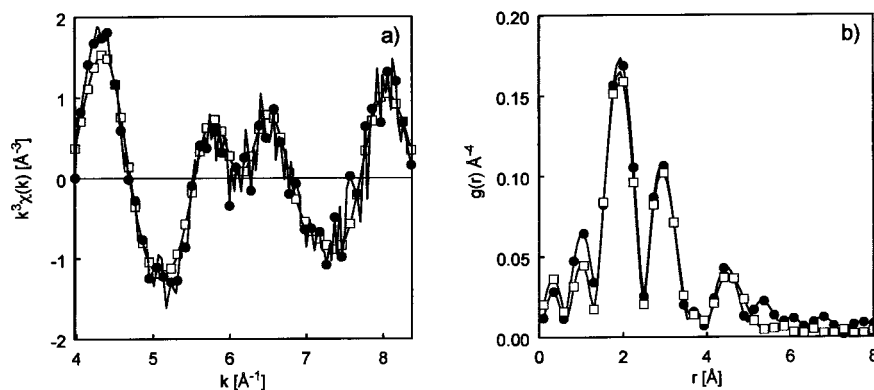


Fig. 3. Experimental (circles) and calculated (squares) EXAFS functions (a) and the corresponding Fourier transforms (b) of a 0.4 m solution of $\text{Mg}(\text{CHBr}-\text{CH}_2\text{Ph})_2$ in THF.

of the Reformatsky compounds, dissolved in THF, can be described with four backscatterers. In detail, we found a Zn–C ($N_{\text{C}} = 1$), a Zn–Br ($N_{\text{Br}} = 1$) and two different Zn–O distances ($N_{\text{O}1} = 1$, $N_{\text{O}2} = 1$). The EXAFS spectra of the systems, dissolved in pyridine, are similar. We found a Zn–C ($N_{\text{C}} = 1$), a Zn–Br ($N_{\text{Br}} = 1$), a Zn–O ($N_{\text{O}} = 1$) and a Zn–N ($N_{\text{N}} = 1$) distance. Completely different results were obtained for the samples with DMSO as solvent. Here we found a Zn–C ($N_{\text{C}} = 1$), a Zn–Br ($N_{\text{Br}} = 1$), a Zn–O ($N_{\text{O}} = 2$) and a Zn–S ($N_{\text{S}} = 1$) distance. We obtained only one Br–Zn ($N_{\text{Zn}} = 1$) distance from the data of the measurements at the bromine K-edge, independent of the investigated Reformatsky system. Of course, the distances were equal to those, which were obtained at the zinc K-edge. In Tables 3–5 data and results are listed.

4. Discussion

4.1. Grignard compounds

The coordination numbers obtained for the magnesium atom give an information about the degree of association of the investigated Grignard compounds and contributes to the answer of the question, whether an increasing concentration affects the equilibrium between monomer and dimer species, which is postulated in Refs. [3,4]. Coordination numbers with values of 1 and 2 mean the existence of pure monomers or pure dimers, respectively. Values between 1 and 2 mean a co-existence of both species. In case of $\text{Me}-\text{Mg}-\text{Br}$ the value is at 1.54, independent of the concentration, while the bromine–magnesium distance decreases slightly from 247 to 244 pm but is in the expected range [3,4,30–33]. Similar data were obtained for $\text{Ph}-\text{Mg}-\text{Br}$. The bromine–magnesium distances are in the range from 243 to 245 pm [3] and the coordination number increases slightly from 1.57 to 1.63 with increasing concentration.

In order to discuss the results we first had to check the error range of the values obtained. It is possible to calculate the ratio x of the monomeric species to the nominal concentration of Grignard compounds c_0 from the experimentally determined coordination number N according to:

$$x = 2 - N \quad (1)$$

Then, the total concentration of monomers and dimers c is given by:

$$c = xc_0 + (1 - x)c_0/2 = c_0/2(1 + x) \quad (2)$$

and the equilibrium constant K_c for the dimerization can be calculated according to:

$$K_c = (1 - x)/(2x^2c_0) \quad (3)$$

As x can be calculated from the experimentally determined coordination number according to Eq. (2), the equilibrium constant K_{c_0} can be determined. It follows for the different nominal concentration c_0 :

$$K_{0.25} = 5.32 \text{ kg mol}^{-1}; K_{0.5} = 2.66 \text{ kg mol}^{-1};$$

$$K_{1.0} = 1.33 \text{ kg mol}^{-1}$$

Now, it is possible to estimate the change in the concentration number from the lowest and largest value

Table 2

Type and number (N) of backscatterers, located at the distance r , relative to the bromine atom, and Debye–Waller factor σ of a 0.4 m solution of $\text{Mg}(\text{CHBr}-\text{CH}_2\text{Ph})_2$ in THF

Backscatterer	r (pm)	N	σ (pm)
Carbon	200	1	6.3
Carbon	281	1	12.0
Magnesium	304	1	11.4
Bromine	420	1	11.6
Bromine	477	1	11.6

The energy threshold amounts $\Delta E_0 = 16.7$ eV, the medium errors for the distance and the coordination number have values about $\Delta r = \pm 3$ pm and $\Delta N = \pm 0.05$.

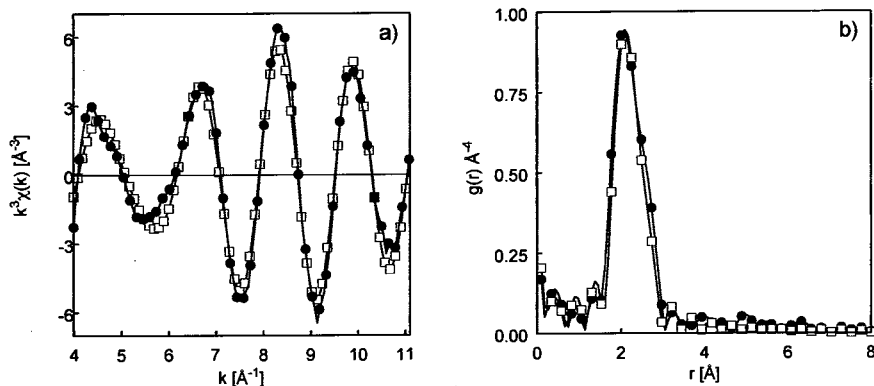


Fig. 4. Experimental (circles) and calculated (squares) EXAFS functions (a) and the corresponding Fourier transforms (b) of a Reformatsky compound soluted in THF (0.3 M, methyl ester).

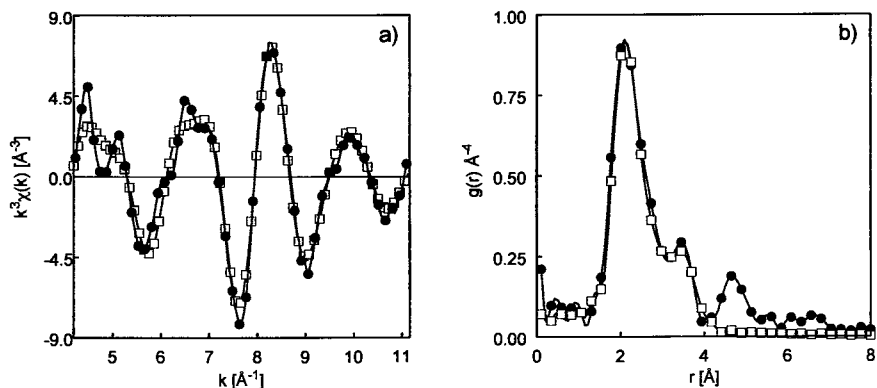


Fig. 5. Experimental (circles) and calculated (squares) EXAFS functions (a) and the corresponding Fourier transforms (b) of a Reformatsky compound soluted in pyridine (0.3 M, methyl ester).

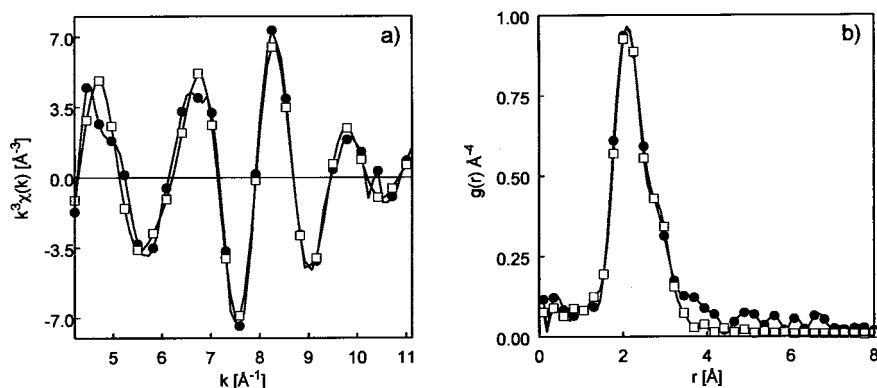


Fig. 6. Experimental (circles) and calculated (squares) EXAFS functions (a) and the corresponding Fourier transforms (b) of a Reformatsky compound soluted in DMSO (0.3 M, methyl ester).

of the equilibrium constant. It follows from these calculations that N ranges from 1.31 to 1.74. This range has to be compared with the experimental error in the determination of the coordination number. As it is not possible to give an exact experimental error, it is common practice to calculate the error range from the correlation matrix of all independent parameters, which are the distance, the coordination number, the Debye–

Waller factor and the energy threshold. This calculated error is between 0.04 ($c = 1.0 \text{ mol kg}^{-1}$) and 0.07 ($c = 0.25 \text{ mol kg}^{-1}$) and consequently significantly smaller than the observed effects.

Therefore, it can be seen from our data that the degree of association of the Grignard compounds do not change within the concentration range investigated. This result is in contrast to earlier studies, which were

obtained by the use of ebullioscopic and osmotic methods [34,35]. In these works a concentration dependence of the degree of association was postulated for alkyl and aryl Grignard compounds, dissolved in diethylether. An association of 1.5 was obtained in solutions up to 0.5 M. But with further increasing concentration the value rose to 2 for a 1.0 m solution and increased to 3 for a 1.5 m solution. We never

Table 3

Type and number (N) of backscatterers, located at the distance r , relative to the zinc atom, and Debye–Waller factor σ of a 0.3 M solution of Br–Zn–CH₂–COOMe in THF

Backscatterer	r (pm)	N	σ (pm)
Carbon	199	1	4.5
Oxygen	200	1	4.5
Oxygen	207	1	5.0
Bromine	231	1	8.6

The energy threshold amounts $\Delta E_0 = 17.4$ eV, the medium errors for the distance and the coordination number have values about $\Delta r = \pm 3$ pm and $\Delta N = \pm 0.05$.

Table 4

Type and number (N) of backscatterers, located at the distance r , relative to the zinc atom, and Debye–Waller factor σ of a 0.3 M solution of Br–Zn–CH₂–COOMe in pyridine

Backscatterer	r (pm)	N	σ (pm)
Carbon	197	1	5.0
Nitrogen	199	1	8.1
Oxygen	200	1	5.0
Bromine	231	1	5.0

The energy threshold amounts $\Delta E_0 = 24.1$ eV, the medium errors for the distance and the coordination number have values about $\Delta r = \pm 3$ pm and $\Delta N = \pm 0.05$.

Table 5

Type and number (N) of backscatterers, located at the distance r , relative to the zinc atom, and Debye–Waller factor σ of a 0.3 M solution of Br–Zn–CH₂–COOMe in DMSO

Backscatterer	r (pm)	N	σ (pm)
Carbon	193	1	5.5
Oxygen	198	2	4.5
Bromine	233	1	6.3
Sulphur	297	2	10.5

The energy threshold amounts $\Delta E_0 = 22.0$ eV, the medium errors for the distance and the coordination number have values about $\Delta r = \pm 3$ pm and $\Delta N = \pm 0.05$.

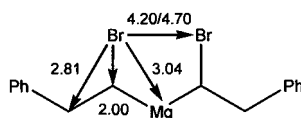


Fig. 7. The investigated carbenoids and the obtained distances.

obtained such high values, even in our earlier investigations of 3.0 M Grignard solutions [3].

4.2. Carbenoid compounds

At the first glance, the existence of two bromine distances, each one with the coordination number $N = 1$, is surprising. But we have to bear in mind that $\text{Mg}(\text{CHBr}-\text{CH}_2\text{Ph})_2$ can exist in four configurations (Fig. 7). The S/R -configuration is identical to the R/S -configuration and the S/S -configuration is identical to the R/R -configuration. The two Br–Br distances can be assigned to the remaining two different configurations. Since the carbenoid was synthesized without any stereochemical control, the frequency of both distances should be identical, which is indeed confirmed by our EXAFS results.

Interesting facts can already be obtained from the first two shells. The Br–C bond of 200 pm is longer than in the most cases (about 192 pm), but corresponds with data from X-ray diffraction of a magnesium–bromine carbenoid with a sp^2 -carbon atom [15] and lithium–chlorine carbenoids [14,16]. The elongation of the Br–C bond seems to be typical for carbenoids. The distance between bromine and magnesium of 304 pm is very short and has to be compared with the sum of the van der Waals radii, which amounts only to 301 pm. Other studies of carbenoids [15] also found a short Br–Mg distance, but not so short. It is obvious, however, that there must be an interaction between both atoms. In this context the term ‘coordinative bonding’ was used [6,7,15], which may describe the interaction between both atoms quite well. Of course our EXAFS investigation at the bromine K-edge could not obtain a carbon–magnesium distance. But in connection with two other carbenoid distances a reflection must be allowed. The sum of the van der Waals radii of carbon and magnesium amounts to 212 pm. X-ray diffraction studies of carbenoids yielded longer distances, for example, 219 pm [15]. From these values we estimated a distance of 215 pm. The angle between bromine, carbon and magnesium decrease from theoretical 109.48 to 94.1°. An estimated distance of 220 pm reduces the angle to 92.6°.

Both calculations indicate that the geometry round the carbenoid carbon atom is different from the structure, which is typical for a sp^3 hybridized carbon atom. It can be concluded from the long C–Br distance that this bond contains a higher p quota. The small angle of nearly 90° can be explained with a tendency of the carbon atom to form a pure p_z orbital. Both facts are a reference to the re-hybridization of the carbenoid carbon atom from sp^3 to sp^2 , which is also suggested from ^{13}C -NMR measurements by finding a strong downfield shift [13]. From these results a structure can be proposed which is a mixture of a tetrahedral, nucleophilic

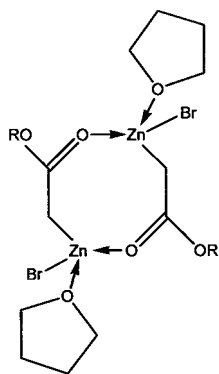


Fig. 8. Structure model of a Reformatsky compound soluted in THF (R = methyl, *tert*-butyl).

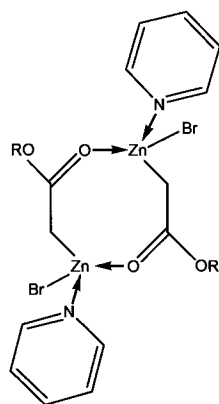


Fig. 9. Structure model of a Reformatsky compound soluted in pyridine (R = methyl, *tert*-butyl).

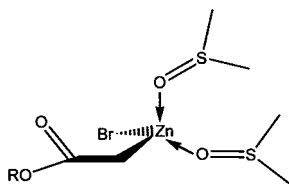


Fig. 10. Structure model of a Reformatsky compound soluted in DMSO (R = methyl, *tert*-butyl).

carbenoid and a trigonal pyramidal geometry, with the carbon atom as centre and the bromine atom on the top. The latter explains the electrophilic character of $\text{Mg}(\text{CHB}_1\text{CH}_2\text{Ph})_2$.

4.3. Reformatsky compounds

The data of the methyl and *tert*-butyl substituted compounds do not differ. Therefore, it can be concluded that the structure of Reformatsky compounds in solution is not influenced by the size of the ester group. Also the variation of the concentration in the range from 0.3 M up to saturated solutions has no effect on the structure of the species, but the change of the solvent. It can be concluded from the bromine K-edge

spectra that bromine atoms are not involved in the formation of dimers. The Zn–Br bond at about 230 pm is the most reliable one from all recorded spectra. Since only one zinc backscatterer is obtained from the EXAFS data, dimers, like proposed for Grignard compounds (Fig. 1), can be excluded.

The situation is more difficult at distances of about 200 pm, because the corresponding peak consists of more than one backscatterer. We found a Zn–C and a Zn–O distance for all the systems investigated in that range, but the coordination number of oxygen depends on the solvents. In our first calculations, we assumed the existence of only one Zn–O distance and the fit yields a coordination number $N_{\text{O}} = 2$ for the compounds, dissolved in THF. In the following refinement we tried to fit the EXAFS spectra with two different oxygen shells with $N_{\text{O}} = 1$ for each shell, and, indeed, a significant improvement of the fit index (about 25%) could be observed. This result can only be interpreted that two different oxygen atoms exist in the neighbourhood of the zinc atom. We also found a coordination number of $N_{\text{O}} = 2$ in case of the compounds, dissolved in DMSO. As we did in the evaluation of the THF spectra, we tried to split this shell into two, but the fit index increases. These findings indicate very clearly that local environment of the zinc atom is affected by the type of solvent. The spectra of the compounds, dissolved in pyridine, were fitted with different backscatterers. The fit to the peak at 200 pm could be achieved with one carbon, one oxygen and one nitrogen atom. In addition to the EXAFS experiments we performed some IR measurements. The spectra of the compounds dissolved in THF and pyridine do not exhibit carbonyl absorption band in the range at about 1700 cm^{-1} , while the IR spectra of the compounds in DMSO have an absorption band in this region.

Summarizing the results we propose a dimeric structure for Reformatsky compounds, dissolved in THF (Fig. 8), which is similar to those in solid state [23] and also when the Reformatsky reagents are dissolved in the more polar pyridine (Fig. 9). In both cases the zinc atoms are surrounded by four different or differently bonded backscatterers. The absence of the characteristic carbonyl band in the IR spectra can be explained with the coordination of the zinc atom by the carbonyl oxygen atom. In the third case, when DMSO as solvent was applied, we propose a monomeric structure for the Reformatsky compounds (Fig. 10). The zinc atom is coordinated by two equivalent oxygen atoms of DMSO-molecules. This result is confirmed by the existence of the corresponding sulphur atoms, which can be obtained from the EXAFS data at about 297 pm. A further confirmation is the detection of the IR-band of the free carbonyl bond.

The structure of Reformatsky compounds in solution depends very sensitively on the polarity of the solvents.

Low and medium polarities favour the formation of dimeric species. Only high polar solvents can stabilize monomeric Reformatsky compounds.

References

- [1] V. Grigard, *Compt. Rend.* 130 (1900) 1322.
- [2] E.C. Ashby, *Q. Rev.* 21 (1967) 259.
- [3] T.S. Ertel, H. Bertagnolli, *Polyhedron* 12 (1993) 2175.
- [4] I. Abraham, W. Hörner, T.S. Ertel, H. Bertagnolli, *Polyhedron* 15 (1996) 3993.
- [5] G.L. Closs, R.A. Moss, *J. Am. Chem. Soc.* 86 (1964) 4042.
- [6] G. Köbrich, *Angew. Chem.* 79 (1967) 15; *Angew. Chem. Int. Ed. Engl.* 6 (1967) 41.
- [7] R.W. Hoffmann, A. Kusche, *Chem. Ber.* 127 (1994) 1311.
- [8] M. Duraisamy, H.M. Walborsky, *J. Am. Chem. Soc.* 106 (1984) 5035.
- [9] M. Topolski, M. Duraisamy, J. Rachon, J. Gawronski, K. Gawronska, V. Goedken, H.M. Walborsky, *J. Org. Chem.* 58 (1993) 546.
- [10] A. Maercker, *Angew. Chem.* 105 (1993) 1072; *Angew. Chem. Int. Ed. Engl.* 32 (1993) 1032.
- [11] D. Seebach, H. Siegel, J. Gabriel, R. Hässig, *Helv. Chim. Acta* 63 (1980) 2046.
- [12] D. Seebach, R. Hässig, J. Gabriel, *Helv. Chim. Acta* 66 (1983) 308.
- [13] V. Schulze, R. Löwe, S. Fau, R.W. Hoffmann, *J. Chem. Soc. Perkin Trans. II* (1998) 463.
- [14] G. Boche, M. Marsch, A. Müller, K. Harms, *Angew. Chem.* 105 (1993) 1081; *Angew. Chem. Int. Ed. Engl.* 32 (1993) 1032.
- [15] G. Boche, K. Harms, M. Marsch, A. Müller, *J. Chem. Soc. Chem. Commun.* (1994) 1393.
- [16] A. Müller, M. Marsch, K. Harms, J.C.W. Lohrenz, G. Boche, *Angew. Chem.* 108 (1996) 1639; *Angew. Chem. Int. Ed. Engl.* 35 (1996) 1518.
- [17] S.N. Reformatsky, *Ber. Dtsch. Chem. Ges.* 20 (1887) 1210.
- [18] M.W. Rathke, *Org. React.* 22 (1975) 423.
- [19] F. Gaudemar-Bardone, M. Gaudemar, *Bull. Soc. Chim. Fr.* 6 (1969) 2088.
- [20] F. Orsini, F. Pellizzoni, G. Ricca, *Tetrahedron Lett.* 23 (1982) 3945.
- [21] W.R. Vaughan, S.C. Bernstein, M.E. Lorber, *J. Org. Chem.* 79 (1965) 1790.
- [22] W.R. Vaughan, H.P. Knoess, *J. Org. Chem.* 35 (1970) 2394.
- [23] J. Dekker, P.H.M. Budzelaar, J.B. Boersma, G.J.M. van der Kerk, *Organometallics* 3 (1984) 1403.
- [24] B.K. Teo, *EXAFS: Basic Principles and Data Analysis*, Springer, Berlin, 1973.
- [25] D.C. Koningsberger, R. Prins, *X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES*, Wiley, New York, 1988.
- [26] H. Bertagnolli, T.S. Ertel, *Angew. Chem.* 106 (1994) 15; *Angew. Chem. Int. Ed. Engl.* 33 (1994) 15.
- [27] T.S. Ertel, H. Bertagnolli, *Nucl. Instrum. Methods Phys. Res. Sect. B.* 73 (1993) 199.
- [28] T.S. Ertel, H. Bertagnolli, S. Hückmann, U. Kolb, D. Peter, *Appl. Spectrosc.* 46 (1992) 690.
- [29] H. Binsted, S.J. Gurman, J.W. Campbell, CLRC Daresbury Laboratory EXCURV90 Program, 1990.
- [30] G.D. Stucky, R.E. Rundle, *J. Am. Chem. Soc.* 86 (1964) 4825.
- [31] L.J. Guggenberger, R.E. Rundle, *J. Am. Chem. Soc.* 90 (1968) 5375.
- [32] F.A. Schröder, *Chem. Ber.* 102 (1969) 2035.
- [33] L.M. Engelhardt, S. Harvey, C.L. Raston, A.H. White, *J. Organomet. Chem.* 341 (1988) 39.
- [34] S. Hayes, *Bull. Soc. Chim. Fr.* (1963) 1404.
- [35] E.C. Ashby, M.B. Smith, *J. Am. Chem. Soc.* 86 (1964) 4363.