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INTRAMOLECULAR COORDINATION BETWEEN MAGNESIUM AND OXYGEN IN CYCLIC ORGANOMAGNESIUM COMPOUNDS

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Summary

Association measurements in THF solution reveal that cyclic organomagnesium compounds capable of intramolecular coordination between magnesium and a suitably located oxygen atom in the ring exist exclusively as monomers in THF solution, whereas their oxygen-free analogues have a high tendency to dimerize; 1-oxa-5-magnesacyclooctane (I), 1-oxa-6-magnesacyclodecane (II), its dibenzoanalogue III, and the corresponding di-Grignard reagents IIB and IIIB were investigated. A thermochemical investigation of I–III yielded more quantitative information: the intramolecular coordinative O–Mg bond has been found to be stronger than the intermolecular bond to THF. The ring strain in these compounds is discussed.

Introduction

We have reported that the cyclic dialkylmagnesium 1-oxa-5-magnesacyclooctane (I) in THF solution is present exclusively in the monomeric form [1]. This behaviour contrasts sharply with that of oxygen-free cyclic organomagnesium compounds which have a high tendency to adopt the dimeric structure; in particular, the closely related magnesacycloheptane and magnesacyclodecane exist as pure dimers in THF, presumably as 14- and 20-membered rings, respectively [2].

The abnormal behaviour of I has been explained in terms of intramolecular complexation between oxygen and magnesium. The driving force for adoption of this structure was obviously considerable. This was also evident from the observation that in THF the di-Grignard reagent related to I, 3,3′-bis(bromomagnesio)di-n-propyl ether (IB), was completely converted into I and $MgBr_2$, as determined by association measurements; normally, the Schlenk equilibrium for mono- and di-Grignard reagents in THF lies at an intermediate position [1].

In order to quantify the strength of the intramolecular coordinative bond the

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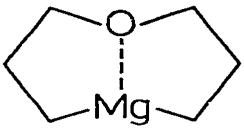
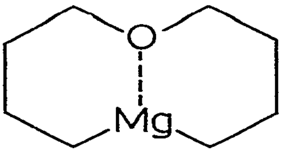
following compounds were investigated by association and thermochemical measurements:

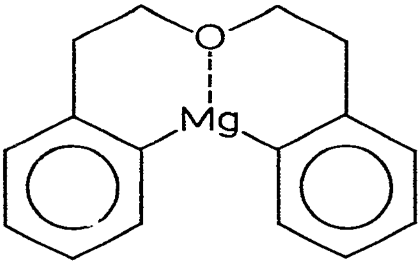
I, 1-oxa-5-magnesacyclooctane;
II, 1-oxa-6-magnesacyclodecane;
III, 5,6,8,9-tetrahydrodibenz[*d*,*g*][1,6]oxamagnesecin, the dibenzoanalogue of II.



I



II

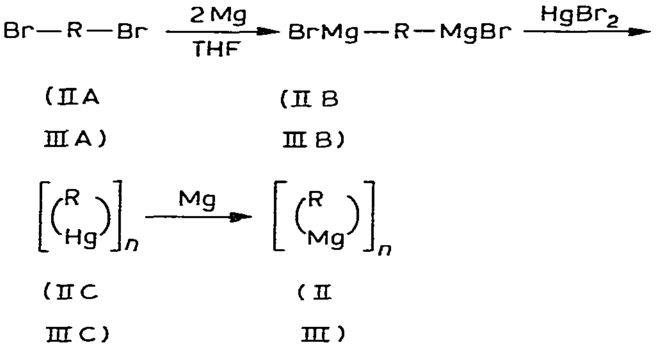


III

Results and discussion

Compounds II and III were synthesized by analogy to I [1] (Scheme 1). The appropriate dibromo compounds IIA and IIIA (see Experimental section) were converted into the corresponding di-Grignard reagents IIB and IIIb, respectively. Treatment of the latter with one molar equivalent of $HgBr_2$ gave the cyclic mercura-derivatives IIc and IIIc, which were transformed into II and III, respectively, by shaking in THF with magnesium metal.

The degree of association *i* of II, IIB, III and IIIB was determined by the method of stationary isothermal distillation developed by Van Vulpen [3]; its application to organomagnesium compounds has been previously described [2]. The results of the measurements are presented in Tables 1–4. They parallel those found for I and IB: the cyclic compounds II and III are completely monomeric ($i = 1$) in THF solution in the concentration range investigated, whereas the di-Grignard reagents IIB and



II : R = $(CH_2)_4O(CH_2)_4$

III : R = $o\text{-}C_6H_4CH_2CH_2OCH_2CH_2\text{-}o\text{-}C_6H_4$

SCHEME 1

IIIB are completely disproportionated to $MgBr_2$ and II and III, respectively; in other words the Schlenk equilibria:

$$\text{IIB} \rightleftarrows \text{II} + MgBr_2, \tag{1}$$

$$\text{IIIB} \rightleftarrows \text{III} + MgBr_2, \tag{2}$$

which furnish 2 particles (e.g. II and $MgBr_2$) for each particle of di-Grignard reagent (e.g. IIB), are completely shifted to the right ($i = 0.5$). Again, our interpretation is that intramolecular complexation between oxygen and magnesium strongly favours the cyclic compounds and stabilizes them in the monomeric form, because the inherently unstable [2] medium-sized rings are transformed into two 5-membered (I) or 6-membered (II, III) rings.

In order to obtain more quantitative information on the strength of the intramolecular coordination between oxygen and magnesium, the reaction enthalpies were measured for the protonation of I–III in THF, using 1 mol of acetic acid per C–Mg bond as a proton donor.

TABLE 1

ASSOCIATION OF 4,4′-BIS(BROMOMAGNESIO)DI-n-BUTYL ETHER (IIB) IN THF AT 28.50°C

$[\text{IIB}]_f$ [a]	S_a [b]	S_{th} [c]	i [d,e]
5.493	0.393	0.218	0.56
10.986	0.846	0.436	0.52
16.479	1.300	0.655	0.50
21.972	1.730	0.873	0.50
27.465	2.251	1.091	0.48
32.958	2.296	1.309	0.49

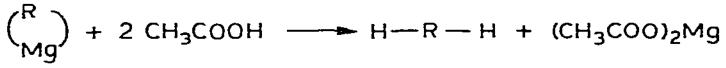
[a] $[\text{IIB}]_f$ = formal concentration of IIB (in mmol l^{-1}); i.e. concentration if all particles of IIB were monomeric containing two Mg atoms. [b] S_a = apparent rate of evaporation (in mm h^{-1}). [c] S_{th} = theoretical rate of evaporation (in mm h^{-1}) = $[\text{IIB}]_f\ S_s$, where S_s (in mm h^{-1} mmol^{-1} l) is the standard rate of evaporation found by calibration of the apparatus with triphenylmethane: $S_s = 0.04120$. [d] Degree of association $i = S_{th}/S_a$. [e] Mean value of $i = 0.51 \pm 0.02$ (standard deviation).

TABLE 2

ASSOCIATION OF 1-OXA-6-MAGNESACYCLODECANE (II) IN THF AT 28.50°C

$[II]_f$ [a]	S_a [b]	S_{th} [c]	i [d,e]
5.670	0.229	0.234	1.02
11.300	0.451	0.466	1.03
16.880	0.687	0.695	1.01
22.420	0.926	0.924	1.00
27.950	1.159	1.152	0.99
33.380	1.392	1.375	0.99

[a] $[II]_f$ = formal concentration of II (in mmol l^{-1}); i.e. concentration if all particles of II were monomeric containing one Mg atom. [b,c,d] See Table 1. [e] Mean value of $i = 1.01 \pm 0.02$ (standard deviation).



(3)

(I, II, III)

The thermochemical experiments were carried out with an improved version of the calorimeter system developed by Van der Wal [4] (see Experimental section). The results are presented in Table 5.

For evaluation, the reaction enthalpies of I–III must be compared with those of a suitable reference compound. In doing so, it is assumed that the partial structures of starting material and product which are not involved in the transformation make the same contribution to the respective enthalpies of formation, which is a justifiable assumption [2,4]. The ideal reference compounds for I and II would be strain-free, monomeric magnesacyclooctane and magnesacyclodecane, respectively.

The absence of strain in the model compound is important. Monomeric magnesacycloheptane and magnesacyclodecane do not exist as such, and the same undoubtedly holds for magnesacyclooctane (which has not been investigated); due to Baeyer, Pitzer and non-bonded strain, these compounds exist as macrocyclic dimers only [2]. On the other hand, it is well known that non-bonded interactions in medium sized rings are reduced by the introduction of a transannular bond. The

TABLE 3

ASSOCIATION OF 2,2'-BIS(2-BROMOMAGNESIOPHENYL)DIETHYL ETHER (IIIB) IN THF AT 28.50°C

$[IIIB]_f$ [a]	S_a [b]	S_{th} [c]	i [d,e]
4.907	0.411	0.201	0.49
9.814	0.821	0.402	0.49
14.721	1.212	0.603	0.50
19.630	1.679	0.804	0.48

[a] $[IIIB]_f$ = formal concentration of IIIB (in mmol l^{-1}; cf. Table 1, footnote [a]). [b,c,d] See Table 1; in this case $S_s = 0.04095$. [e] Mean value of $i = 0.49 \pm 0.01$ (standard deviation).

TABLE 4

ASSOCIATION OF 5,6,8,9-TETRAHYDRODIBENZ[*d*,*g*][1,6]OXAMAGNESECIN IN THF AT 28.50°C

$[III]_f$ [a]	S_a [b]	S_{th} [c]	i [d,e]
2.541	0.108	0.104	0.96
4.935	0.206	0.202	0.98
7.195	0.308	0.295	0.96
9.331	0.394	0.382	0.97
11.354	0.480	0.465	0.97

[a] $[III]_f$ = formal concentration of III (in mmol l^{-1}; cf. Table 1, footnote [a]). [b,c,d] See Table 1; in this case $S_s = 0.04095$. [e] Mean value of $i = 0.97 \pm 0.01$ (standard deviation).

strain in cyclodecane (50.2 kJ mol^{-1} [5]) is much greater than that in transdecalin (9.8 kJ mol^{-1} [6]); however, for the transition from cyclooctane (40.1 kJ mol^{-1} [7]) to *cis*-bicyclo[3.3.0]octane (55.2 kJ mol^{-1} [6]), the opposite is true. It was anticipated that I and II would not be strain-free in spite of the intramolecular coordinative bond, since their geometries are expected to deviate substantially from those of their carbon analogues. This is mainly caused by the structural requirements of the magnesium atom, with its rather long bonds and wide bond angles (e.g. in 1,6-dimagnesacyclodecane [8,9] and 1,7-dimagnesacyclodocedane [10], the C–Mg bond lengths range from 211–215 pm, the C–Mg–C bond angles from 128–141.5°): models of I and II constructed with such structural parameters suggest considerable (Baeyer) strain.

As the strain-free models magnesacyclooctane and magnesacyclodecane do not exist and thermochemical data are not available for these hypothetical substances, the data for 1,11-dimagnesacycloeicosane (IV) were used instead. The reaction enthalpy of IV with acetic acid per C–Mg bond ($\Delta H_{R,IV} = -221.9 \pm 1.6$ kJ mol^{-1} [2]) is, within the limits of the standard deviations, identical with that of diethylmagnesium (V; $\Delta H_{R,V} = -219.4 \pm 3.5$ kJ mol^{-1} [2]). Comparing the enthalpies per mol of I and II with that of the hypothetical reference compound $\frac{1}{2}$ IV we obtain from Table 5:

$$\Delta\Delta H_{R,I} = 2(\Delta H_{R,I} - \Delta H_{R,IV}) = 22.2 \pm 5.9 \text{ kJ mol}^{-1}; \tag{4}$$

$$\Delta\Delta H_{R,II} = 2(\Delta H_{R,II} - \Delta H_{R,IV}) = 18.6 \pm 4.0 \text{ kJ mol}^{-1}. \tag{5}$$

The interpretation of these results is based on the following considerations. In the first place we notice that $\Delta\Delta H_{R,I}$ and $\Delta\Delta H_{R,II}$ are positive. This indicates that I and II are more stable than IV; we may assume (vide supra) that this extra stability of I and II is largely due to the favourable intramolecular coordination which transforms the repulsive interactions in the medium-sized rings into strongly attractive interactions. With the exception of a few special cases, the magnesium atom in organomagnesium compounds is tetracoordinate. For diorganomagnesiums of the type discussed here, this means that two ether oxygen atoms are coordinated to Mg. In THF solution, this implies 2 molecules of THF for IV (and for V and diphenylmagnesium (VI); however, in I, II and III, 1 THF will be replaced by the stronger intramolecular bond.

TABLE 5

REACTION ENTHALPIES PER C–Mg BOND OF ORGANOMAGNESIUM COMPOUNDS WITH ACETIC ACID IN THF AT 25°C

Compound	CH_3COOH [a] (mmol)	ΔH_R (kJ mol^{-1})	Mean value ΔH_R [b] (kJ mol^{-1})
I	0.223	−211.9	−210.8 ± 3.8
	0.242	−211.1	
	0.242	−207.0	
	0.243	−211.7	
	0.264	−207.3	
	0.275	−214.1	
	0.297	−212.7	
II	0.184	−213.6	−212.6 ± 2.0
	0.281	−211.3	
	0.291	−214.7	
	0.305	−209.9	
	0.316	−213.6	
III	0.201	−195.6	−199.6 ± 3.9
	0.210	−203.5	
	0.228	−205.2	
	0.260	−198.2	
	0.263	−199.2	
	0.265	−196.0	
IV			−221.9 ± 1.6 [c]
V			−219.4 ± 3.5 [c]
VI			−190.3 ± 1.1 [c]

[a] Exactly 1 mol of acetic acid per C–Mg bond was used. [b] With standard deviation. [c] Ref. 2.

Thus, all other contributions being equal, $\Delta\Delta H_R$ will depend on the following parameters:

$$\Delta\Delta H_R = -(\Delta H_{INTRA} - \Delta H_{INTER}) - \Delta\Delta H_{STRAIN}, \tag{6}$$

where ΔH_{INTRA} = enthalpy change in the formation of the intramolecular O–Mg bond (exothermic), ΔH_{INTER} = enthalpy change in the formation of the intermolecular O–Mg bond with the second molecule of THF (exothermic; estimate of Van der Wal for $Et_2Mg \cdot 2\,THF$: $\Delta H_{INTER} = -68$ kJ mol^{-1} [4]) and $\Delta\Delta H_{STRAIN}$ = difference in strain between I (or II) and IV; as the strain in IV is assumed to be zero, $\Delta\Delta H_{STRAIN} = \Delta H_{STRAIN,\,I\text{ or }II}$ (endothermic). We thus obtain:

$$\Delta H_{INTRA} = -(\Delta\Delta H_R - \Delta H_{INTER}) - \Delta H_{STRAIN}\text{ kJ mol}^{-1} \tag{7}$$

$$\Delta H_{INTRA,I} = -(22.2 + 68) - \Delta H_{STRAIN,I}\text{ kJ mol}^{-1} \tag{8}$$

$$= -90.2 - \Delta H_{STRAIN,I}\text{ kJ mol}^{-1} \tag{9}$$

$$\Delta H_{INTRA,II} = -(18.6 + 68) - \Delta H_{STRAIN,II}\text{ kJ mol}^{-1} \tag{10}$$

$$= -86.6 - \Delta H_{STRAIN,II}\text{ kJ mol}^{-1} \tag{11}$$

As the ring strain in I and II cannot be determined, the absolute value of ΔH_{INTRA} remains unknown; however, as $\Delta H_{STRAIN} > 0$ (vide supra), the values of $\Delta H_{INTRA,I} = -90.2$ kJ mol^{-1} and $\Delta H_{INTRA,II} = -86.6$ kJ mol^{-1} must be considered as upper limits for the bond formation enthalpy of the intramolecular O–Mg bond. This means that the bond dissociation energies, D, of the intramolecular O–Mg bond for I and II are at least 90.2 and 86.6 kJ mol^{-1}, respectively. This conclusion is even more justified when the effect of the first coordinated oxygen on the second is considered. Up till now, it has been tacitly assumed that the strength of the THF–Mg bond in I · THF and II · THF is equal to that in $Et_2Mg \cdot 2$ THF (68 kJ per mol THF). It may, however, be expected that the stronger intramolecular bond somewhat weakens the intermolecular bond to THF, so that the real strength of the former must be increased by a corresponding amount. Thus, the intramolecular coordinative bond in I and II is considerably stronger than that towards the (relatively strong) Lewis base THF. Compared to the O–Mg bond energy of 250 kJ mol^{-1} in MgO or MgOH [12], the intramolecular O–Mg bond surpasses 35% of the strength of a "full" O–Mg bond (cf. $Et_2Mg \cdot 2$ THF: 27%).

In view of the uncertainties discussed above the observed differences in ΔH_{INTRA} between I and II must be treated with great reserve. The values suggest a slightly more stable chelate bond in I. The real difference is probably greater, as I possesses more strain than II, as is suggested by the inspection of models: incorporation of Mg (and oxygen) into the bicyclo[3.3.0]octane skeleton to yield I causes more strain than into the bicyclo[4.4.0]decane skeleton to yield II. This decreases the value of ΔH_{INTRA} for I relative to II, which is in line with the general experience [13] that 5-membered ring chelates are more stable than their 6-membered counterparts.

For compound III, the choice of suitable reference compounds is more limited. Again, with the assumption that the enthalpies of formation for the unaffected parts of the molecule are equal and thus cancel each other, diphenylmagnesium (VI) may be considered as a satisfactory reference for III. Thus

$$\Delta H_{INTRA,III} = -49.4 - \Delta H_{STRAIN,III} \text{ kJ mol}^{-1} \qquad (12)$$

is obtained, which means that the overall effect of intramolecular coordination is unfavourable compared to the enthalpy of coordination of a second molecule of THF in VI, if the latter is close to the value for V (−68 kJ mol^{-1}). It is very unlikely that this is caused by a weaker intramolecular O–Mg bond. On the contrary, it is likely that this bond is stronger in III than in II, because the Mg atom in III is expected to be a stronger Lewis acid, since it bears two phenyl groups which are more electronegative than the two alkyl groups on Mg in II. Therefore, the bond strength of the intramolecular O–Mg bond in II ($D = -\Delta H_{INTRA} = 86.6$ kJ mol^{-1}) may be taken as a lower limit for the intramolecular O–Mg bond strength in III. With this assumption, the ring strain in III can be derived from eq. 12; it is at least 37 kJ mol^{-1} larger than that in II. The reason for this increase in strain is not obvious. Models suggest that the increased rigidity in III enforces a more unfavourable conformation. In the oxygen-free cyclic organomagnesium compounds the effect of incorporation of benzene rings on strain was found to be strongly variable [2]; further investigations are needed to analyse this effect.

Experimental section

The preparation of II and III and the measurements were carried out in evacuated and fully sealed gas apparatus [14]. ^1H NMR spectra were recorded on a Bruker WH 90 spectrometer at 90 MHz.

1-Oxa-5-magnesacyclooctane (I)

Compound I was prepared as described previously [1].

4,4'-Dibromo-di-n-butyl ether (IIA)

Compound IIA was prepared according to Sieber [15] from THF, methanesulfurylbromide and $ZnCl_2$. The purification of the product mixture was achieved by a simple distillation followed by column chromatography on aluminum oxide "90", Merck, Darmstadt (70–230 mesh ASTM), with CCl_4/methanol (50/1) as eluent. The boiling point, refractive index and NMR spectrum were in accord with the literature. *The compound must be handled with care, because it is extremely vesicant.*

4,4'-Bis(bromomagnesio)di-n-butyl ether (IIB)

A solution of 3.6 g (12.5 mmol) of IIA in 20 ml THF was added with stirring over a period of 6 h to 4.0 g (165 mmol) magnesium in 200 ml THF. After the addition, stirring was continued for a further 24 h at room temperature. The yield of IIB was 98% as determined from acid/base and EDTA titration of the clear, decanted liquid. The compound was used without further purification for the association measurements.

1-Oxa-6-mercuracyclodecane (IIC)

A solution of 4.3 g (12.0 mmol) $HgBr_2$ dissolved in THF (30 ml) was slowly added to a stirred solution of IIB (12.0 mmol). Stirring was subsequently continued for 1 h. The THF was evaporated and the residue treated with 150 ml water and 100 ml benzene. The benzene layer was washed, dried over $MgSO_4$ and concentrated. The resulting colourless oil was dissolved in a small volume of benzene, from which IIC was isolated after cooling as colourless crystals (90% yield), m.p. 69.0–73.0°C. Anal. Found: C, 30.02; H, 5.09; Hg, 59.88; O, 5.05. $C_8H_{16}HgO$ calcd.: C, 29.22; H, 4.91: Hg, 61.00; O, 4.87%. ^1H NMR (C_6D_6), δ 1.06 (4H, t, J 7 Hz, CH_2–Hg), 1.30–2.20 (8H, m, CH_2–CH_2), 3.46 ppm (4H, t, J 6 Hz, CH_2–O).

1-Oxa-6-magnesacyclodecane (II)

A solution of 3.3 g (10.0 mmol) IIC in 140 ml THF was shaken in sealed glass apparatus for 50 h at room temperature with 4.2 g (172 mmol) magnesium. Titration of part of the decanted clear solution revealed a 100% conversion to II. ^1H NMR (THF-d_8), −0.54 (4H, t, J 7 Hz, CH_2–Mg), 1.51–2.20 (8H, m, CH_2–CH_2), 3.80 ppm (4H, t, J 6 Hz, CH_2–O).

2,2'-Bis(2-bromophenyl)diethyl ether (IIIA)

Compound IIIA was synthesized from 2-(2-bromophenyl)ethanol (prepared as described by Gilman and Marrs [16]) by the method described by Senderens for 2-phenylethanol [17]. A mixture of 20 g (100 mmol) 2-(2-bromophenyl)ethanol and 1.4 ml 64% H_2SO_4 was heated for 2 h at 160°C while stirring. The water formed in the reaction was distilled off. After cooling, the mixture was worked up in the usual way. Vacuum distillation (bp. 163°C/10^{-2} Torr) yielded IIIA as colourless crystals (73% yield), m.p. 57.5–59.0°C. Anal. Found: C, 50.09; H, 4.19; Br, 41.55; O, 4.20. $C_{16}H_{16}Br_2O$ calcd.: C, 50.06; H, 4.20; Br, 41.57; O, 4.27%. ^1H NMR ($CDCl_3$), δ 3.00 (4H, t, J 7 Hz, aryl-CH_2), 3.65 (4H, t, J 7 Hz, CH_2–O), 6.91–7.29 (6H, m, aryl-H), 7.42–7.58 ppm (2H, m, aryl-H).

2,2'-Bis(2-bromomagnesiophenyl)diethyl ether (IIIB)

Compound IIIB was prepared by adding a solution of 8.5 g (22.2 mmol) of IIIA in 20 ml THF dropwise to 3.9 g (160 mmol) magnesium in 200 ml THF during 7 h. After stirring for additional 24 h, the yield of IIIB was 96% (titration). The decanted, clear solution was used for association measurements and for preparative purposes.

5,6,8,9-Tetrahydrodibenz[d,g][1,6]oxamercurecin (IIIC)

To a solution of 21.7 mmol IIIB in 190 ml THF was added dropwise 7.82 g (21.7 mmol) $HgBr_2$ in 30 ml THF. After stirring for a further 1 h the THF was evaporated and the residue treated with a mixture of 150 ml water and 150 ml benzene. Washing of the benzene layer with water, followed by drying over $MgSO_4$ and evaporation yielded a solidifying colourless oil. Crystallization from benzene yielded white crystals of IIIC (5.6 g, 13.0 mmol, 60% yield), m.p. 133.5–135.0°C. Anal. Found: C, 45.20; H, 3.97; Hg, 47.12; O, 3.58. $C_{16}H_{16}HgO$ calcd.: C, 45.23; H, 3.80; Hg, 47.21; O, 3.77%. ^1H NMR ($CDCl_3$), δ 3.05 (4H, m, aryl-CH_2), 3.70–4.06 (4H, m, CH_2–O), 7.10–7.60 ppm (8H, m, aryl-H).

5,6,8,9-Tetrahydrodibenz[d,g][1,6]oxamagnesecin (III)

A solution of 4.5 g IIIC (10.6 mmol) in 135 ml THF was treated for 5 d in a sealed glass apparatus with 2.0 g (82 mmol) magnesium. The colourless solution was decanted from the magnesium amalgam. Titration of a part of the solution indicated a quantitative conversion into III. ^1H NMR (THF-d_8), δ 2.97 (4H, m, aryl-CH_2), 3.77–4.00 (4H, m, CH_2–O), 6.80–7.02 (6H, m, aryl-H), 7.68–7.88 ppm (2H, m, aryl-H).

Thermochemical measurements

The thermochemical measurements were carried out with the calorimeter system developed by Van der Wal [4]. Some improvements were introduced: the change in resistance through the temperature change accompanying the chemical reaction is now measured with a digital ohm-meter (Fluke, type number 8502 A) controlled by a microprocessor *. In a calibration or an enthalpy measurement, the microprocessor registers the time intervals for every 10 ohms change in resistance. After a total change of 100 ohms (the "initial period"), the microprocessor activates a device to break the ampoule containing a known amount of acetic acid; this ampoule being immersed in the solution of the organometallic compound under investigation. During the temperature/resistance jump accompanying the exothermic reaction, the microprocessor continues to register the time intervals every 10 ohms. As soon as the processor has detected the straight line of the "final period", the measurement is terminated after another 10 resistance measurements. Each enthalpy measurement is preceded and followed by electrical calibration. Afterwards, the microprocessor calculates the enthalpy in kJ mol^{-1} on the basis of the amount of heat of the calibration and the number of mmols acetic acid reacted; the amount of acetic acid was exactly equivalent to the amount of C–Mg bonds in the organomagnesium compound to be investigated. The calorimeter system was tested by measuring the enthalpy of solution of tris(hydroxymethyl)aminomethane (TRIS) in 0.1 *N* HCl at

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* For more experimental details of the calorimeter system contact O.S. Akkerman.

25°C. (Found $\Delta H(\mathrm{soln}) = -29.686 \pm 0.182$ kJ mol^{-1}, lit. value [18] $\Delta H(\mathrm{soln}) = -29.744 \pm 0.006$ kJ mol^{-1}).

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