Journal of Organometallic Chemistry, 240 (1982) 217–227
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE DIMERIZATION OF SOME MAGNESACYCLOALKANES AND BENZOMAGNESACYCLOALKENES; THE RELATION BETWEEN RING SIZE, RING STRAIN AND DEGREE OF ASSOCIATION

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(Received June 25th, 1982)

Summary

Magnesacycloalkanes and benzomagnesacycloalkenes have a high tendency to dimerize. To relate this tendency to the ring size of the compounds, the degree of association i of magnesacyclohexane (I) (monomer/dimer equilibrium) [1], its 2,3-benzo-derivative II (monomer/dimer equilibrium), magnesacycloheptane (III) ($i = 2$), its 4,5-benzo-derivative IV ($i = 1$) and magnesacyclodecane (V) ($i = 2$) was determined. The reaction enthalpies for interaction of the compounds with proton donors were measured and the dimerization enthalpy, apparently equal to the ring strain in the monomers, was evaluated. The relationship between ring size, ring strain, and the degree of association is discussed.

Introduction

In the course of our investigations of cyclic organomagnesium compounds, we considered the degree of association of magnesacyclopentane and magnesacyclohexane [1–4]. It was found that, whereas magnesacyclopentane exists in THF solution exclusively as a dimer [1,4], magnesacyclohexane is present in a monomer/dimer equilibrium in THF [2,3]. The equilibrium constants for this equilibrium, were determined at two temperatures ($K_1(28.25°C) = 609 \pm 35$ l mol^{-1}, $K_1(48.50°C) = 182 \pm 9$ l mol^{-1}), and the enthalpy and entropy for the dimerization reaction thus evaluated: $\Delta H = -48.0 \pm 3.0$ kJ mol^{-1} and $\Delta S = 106.0 \pm 10.0$ J mol^{-1} K^{-1}. An X-ray diffraction analysis of crystalline magnesacyclohexane revealed that the dimeric compound consisted of a twelve-membered ring, 1,7-dimagnesacyclododecane [3]. It was concluded that the dimeric form of magnesacyclopentane has an analogous ring structure: 1,6-dimagnesacyclodecane [4]. The high tendency of magnesacyclo-pentane and -hexane towards dimerization was apparently caused by the large C–Mg–C bond angle (128° in 1,6-dimagnesacyclodecane and 141.5° in 1,7-dimagnesacyclododecane) which causes Baeyer strain in the five- and six-membered ring systems.

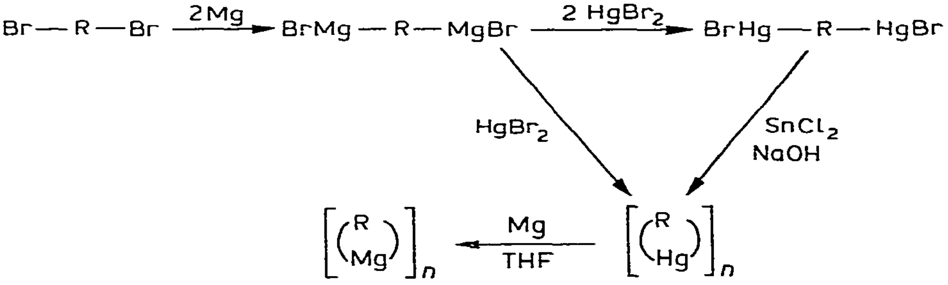
0022-328X/82/0000–0000/$02.75

In order to obtain more insight into the relationship between ring size, association number, and ring strain for magnesacyclic compounds, the present study was undertaken. To this end the following compounds were investigated: magnesacyclohexane (I), 3,4-dihydro-2H-1-magnesanaphthalene (II), magnesacycloheptane (III), 1,2,4,5-tetrahydro-3-benzomagnesepin (IV) and magnesacyclodecane (V). For comparison, diethylmagnesium (VI) and diphenylmagnesium (VII) were included in the study.

Results and discussion

The magnesacycloalkanes were synthesized essentially by the method of Holtkamp [1,2,4]. The α,ω-dibromoalkanes, 1,2-bis(2-bromoethyl)benzene and 3-(2-bromophenyl)bromopropane were converted into the corresponding di-Grignard reagents, from which the α,ω-bis(bromomercurio) derivative was prepared by reaction with 2 equivalents of $HgBr_2$; conversion of the bromomercurio derivatives to mercuracycloalkanes was achieved with $SnCl_2$ in a basic medium. In the case of the benzoderivatives, the mercuracycloalkane was obtained directly by addition of 1 equivalent of $HgBr_2$ to the di-Grignard reagent. Finally, the pure magnesacycloalkanes were obtained in a high vacuum system by shaking the mercuracycloalkanes in THF with metallic magnesium (Scheme 1).

SCHEME 1



The association measurements were performed in a sealed and evacuated system by the method of stationary isothermal distillation [2,5]. The degree of association i, determined from S_{th}/S_a, is the ratio of formal concentration of particles containing one magnesium atom and the actual concentration of particles; stated in a different way, i gives the average number of Mg atoms per particle. The results of the association measurements are given in Tables 1–4; they were evaluated by the method desribed by Holtkamp [3].

The dependance of the degree of association on the concentration for II can only be explained in terms of a monomer/dimer equilibrium $2IIA \rightleftarrows IIB$, favouring the dimer, with the equilibrium constant $K_{II} = 185.5 \pm 5.8\ l\ mol^{-1}$ at 28.50°C. Compound III and V are purely dimeric in THF, whereas compound IV is monomeric (Scheme 2).

The picture which emerges from Scheme 2 is rather puzzling. The fusing of an aromatic nucleus to I to form II does not greatly affect the associative behaviour; both compounds display a monomer/dimer equilibrium. However, if an aromatic nucleus is fused to III, yielding IV, the degree of association changes from 2 to 1. In the comparison of both pairs of compounds it should be kept in mind that II has a

TABLE 1

ASSOCIATION OF 3,4-DIHYDRO-2H-1-MAGNESANAPHTHALENE (II) IN THF AT 28.50°C[a]

[Mg][b]	S_a[c]	S_{th}[d]	i[e]	K[f]
3.133	0.102	0.128	1.258	184
6.040	0.182	0.247	1.359	194
8.742	0.254	0.358	1.410	189
11.262	0.319	0.461	1.446	186
13.716	0.379	0.558	1.471	183
15.822	0.435	0.648	1.489	177

[a] For details of the experimental technique and apparatus see refs. [2,5]. [b] $[Mg]_f$ = formal concentration of Mg in mmol l^{-1} (i.e. concentration if all particles were monomeric containing one Mg atom). [c] S_a = apparent rate of evaporation in mm h^{-1}. [d] S_{th} = theoretical rate of evaporation (in mm h^{-1}) = $[Mg]_f S_s$, where S_s (in mm h^{-1} mmol^{-1} l) is the standard rate of evaporation found by calibration of the apparatus with triphenylmethane; $S_s = 0.04095$. [e] Degree of association $i = S_{th}/S_a$. [f] Mean value $K = 185.5 \pm 5.8$ l mol^{-1}.

SCHEME 2

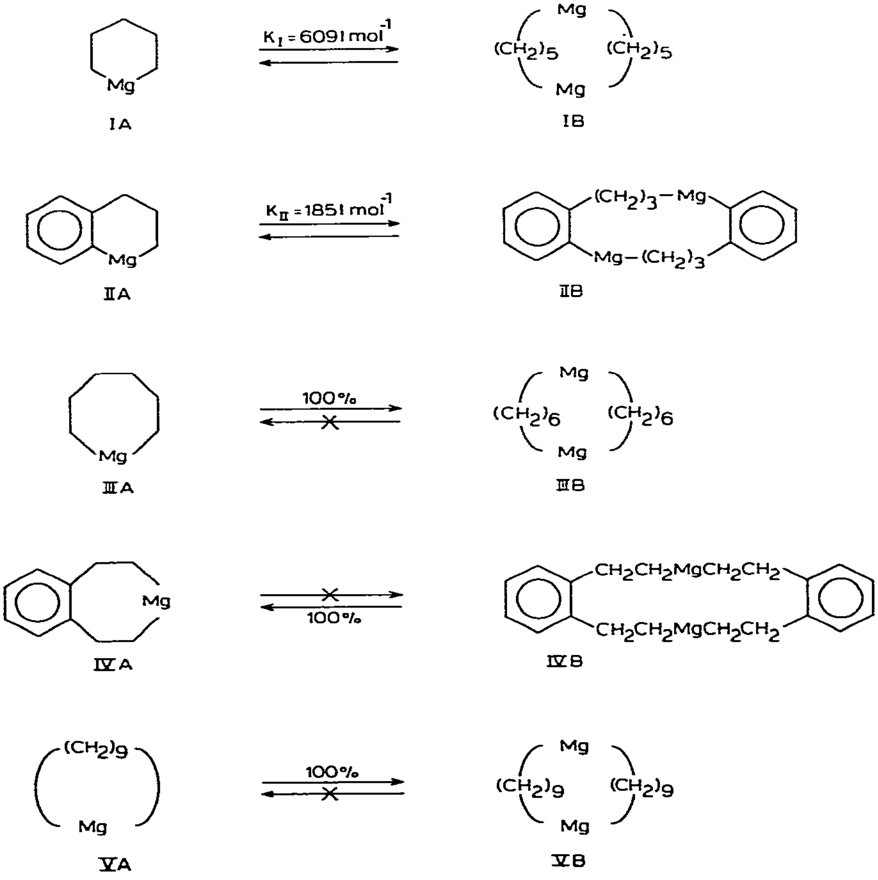


TABLE 2

ASSOCIATION OF MAGNESACYCLOHEPTANE (III) IN THF AT 28.50°C [a]

$[Mg]_f$ [b]	S_a [c]	S_{th} [d,g]	i [e,h]
3.059	0.056	0.127	2.26
5.909	0.120	0.246	2.05
8.572	0.183	0.357	1.95
11.065	0.234	0.462	1.97
13.403	0.285	0.559	1.96
15.602	0.331	0.652	1.96

[a] For notes see Table 1. [g] $S_s = 0.04171$. [h] Mean value $i = 2.02 \pm 0.08$.

TABLE 3

ASSOCIATION OF 1,2,4,5-TETRAHYDRO-3-BENZOMAGNESEPIN (IV) IN THF AT 28.50°C [a]

$[Mg]_f$ [b]	S_a [c]	S_{th} [d,g]	i [e,h]
2.989	0.111	0.126	1.14
5.978	0.249	0.253	1.02
8.967	0.383	0.380	0.99
11.956	0.514	0.507	0.99
14.945	0.644	0.634	0.98

[a] For notes see Table 1. [g] $S_s = 0.04240$. [h] Mean value $i = 1.02 \pm 0.08$.

TABLE 4

ASSOCIATION OF MAGNESACYCLODECANE (V) IN THF AT 28.50°C [a]

$[Mg]_f$ [b]	S_a [c]	S_{th} [d,g]	i [e,h]
4.557	0.082	0.187	2.28
9.090	0.175	0.375	2.14
13.599	0.269	0.560	2.08
18.084	0.362	0.745	2.06
22.426	0.449	0.934	2.06
26.841	0.549	1.106	2.01

[a] For notes see Table 1. [g] $S_s = 0.04120$. [h] Mean value $i = 2.07 \pm 0.08$.

magnesium bonded to a sp^2 and to a sp^3 hybridized carbon atom whereas in IV the magnesium is bonded to two sp^3 carbon atoms; but if this difference were of decisive influence, IV would be expected to behave similarly to its analogue III, since both have only aliphatic carbon–magnesium bonds. Also, the complete dimerization of the ten-membered VA to the twenty-membered 1,11-dimagnesaeicosane (VB) was unexpected, as the ten-membered ring of 1,6-dimagnesacyclodecane appears to be perfectly stable [4]. Clearly, additional information on the factors influencing the association of the cyclic magnesium compounds was desirable.

For this purpose the enthalpies of reaction of the compounds in THF solution with acetic acid were measured. Use was made of the calorimeter system developed by Van der Wal and Freijee [6,7,8]; this system allows the introduction of the compound to be investigated and the proton donor (contained in a separate ampoule) with complete exclusion of air and moisture. The measurements were performed at a mean temperature of 25°C; exactly 1 mol of acetic acid per C–Mg bond was used. At least 5 measurements were executed for each compound, except for V (3 measurements due to the limited amount of material). For comparison, diethylmagnesium (VI) and diphenylmagnesium (VII) were included, as both compounds may be considered as strain-free models for aliphatic and aromatic organomagnesiums, respectively, and are completely monomeric in THF [9,10]. The results of the thermochemical experiments are listed in Table 5.

Inspection of Table 5 shows that the values for III, V and diethylmagnesium are identical, thus confirming that the cyclic compounds have ring structures which are free of strain. In drawing this conclusion, the underlying supposition is that in solution the difference in standard enthalpy of formation of ethane and hexane or nonane is equal to the difference in standard enthalpy of formation of diethylmagnesium and half the standard enthalpy of formation of 1,8-dimagnesacyclotetradecane (IIIB) or 1,11-dimagnesacycloeicosane (VB); the correctness of this assumption has been extensively discussed by Van der Wal [6]. Put in a different way this means (other things such as reagent, bond type and ring strain being equal) that the enthalpy of reaction per C–Mg bond is independent of the structure of the unaffected organic part of the molecule.

The formal concentration of I in the THF solution used for the thermochemical experiments was 0.84 mmol l^{-1}. From the association measurements [2,3] it can be derived that at this concentration the association constant $\alpha = 0.40$, yielding a ratio of 3:1 for IA:IB. In IA there are two carbon–magnesium bonds against four in 1,7-dimagnesacyclododecane. As IB has no ring strain [3], its enthalpy of reaction per carbon–magnesium bond with acetic acid must be equal to that of diethylmagnesium (cf. IIIB and VB). The reaction enthalpy per C–Mg bond of IA, ΔH_x, is higher because of the ring strain in Ia. The experimental value of -233.0 kJ mol^{-1} must be equal to $(2a\,\Delta H_x + 4b\,\Delta H_{VI})/(2a + 4b)$, in which term a is the number of molecules of IA, b the number of molecules of IB, and ΔH_{VI} the reaction enthalpy for diethylmagnesium per mol acetic acid. This yields a value for $\Delta H_x = -242.1 \pm 7.1$ kJ mol^{-1}. Thus, conversion of one mol of IA into half a mol of strain-free IB is an exothermic reaction with $\Delta H_I = 2(\Delta H_x - \Delta H_{VI}) = -45.4 \pm 6.5$ kJ mol^{-1}. This value represents the ring strain in IA; it is in good agreement with the dimerization enthalpy as determined [2,3] from association measurements at two different temperatures (-48.0 ± 3 kJ mol^{-1}, vide supra). Analogous reasoning can be applied to the thermochemical values of the equilibrium mixture of IIA and IIB. From the equilibrium constant $K_{II} = 185.5 \pm 5.8$ l mol^{-1} the ratio 8:1 can be calculated for IIA:IIB at the concentration of the thermochemical measurement. The theoretical value for the reaction enthalpy for pure IIA can now be calculated as shown above, taking account of the presence of one aliphatic C–Mg bond (standard: Et_2Mg) and one aromatic C–Mg bond (standard: Ph_2Mg) in IIA; it is found to be -229.2 ± 2.7 kJ mol^{-1}. Thus, the enthalpy change in the conversion of one mol of IIA to half a mol of IIB is $\Delta H_{II} = -48.7 \pm 3.9$ kJ mol^{-1}, being equal to the strain in IIA. From the equilibrium constant K_{II}, $\Delta G_{II} = -13.0 \pm 0.2$ kJ mol^{-1} can be calculated, and further the entropy of dimerization $\Delta S_{II} = -118.0 \pm 12.0$ J mol^{-1} K^{-1} (at 28.50°C)

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})
IA ⇄ IB	0.242	−231.4	−233.0 ± 4.0
	0.264	−231.2	
	0.294	−233.9	
	0.307	−227.2	
	0.339	−239.1	
	0.365	−235.2	
IIA ⇄ IIB	0.235	−225.1	−224.3 ± 2.2
	0.277	−223.7	
	0.285	−224.3	
	0.287	−227.2	
	0.308	−221.2	
IIIB	0.250	−219.9	−220.9 ± 1.7
	0.267	−218.9	
	0.284	−223.5	
	0.310	−221.2	
	0.310	−221.1	
IVA	0.257	−223.5	−224.8 ± 3.5
	0.265	−223.3	
	0.267	−222.1	
	0.311	−222.2	
	0.316	−231.3	
	0.355	−226.1	
VB	0.192	−222.7	−221.9 ± 1.6
	0.206	−222.9	
	0.215	−220.1	
VI	0.150	−216.2	−219.4 ± 3.5
	0.279	−223.6	
	0.287	−216.3	
	0.290	−218.0	
	0.307	−222.7	
VII	0.214	−188.9	−190.3 ± 1.1
	0.244	−190.2	
	0.267	−190.8	
	0.285	−189.3	
	0.290	−190.6	
	0.309	−191.8	

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

(cf. $\Delta S_I = -106 \pm 10$ J mol^{-1} K^{-1} from association measurements [2,3] and $\Delta S_I = -98$ J mol^{-1} K^{-1} from this work).

Thus in spite of the differences in structure, I and II show great similarities. In both cases, dimerization is strongly favoured by ring strain in the monomer; in fact, the monomer can only be observed experimentally because the measurements are performed in dilute solutions (1–10 mmol l^{-1}) which shifts the equilibrium towards the monomeric form. In view of the experimental error, the differences in the thermodynamic parameters of the two equilibria may not be very significant;

however, it seems that the ring strain in the benzo-annelated six-membered ring of IIA is slightly larger than in IA. This may be a consequence of angle strain in IIA, with both magnesium and the benzene ring preferring large bond angles; this probably also increases the torsional strain by ring flattening, although this latter effect will be partially compensated by the absence of 4 C–H bonds in IIA. The enthalpic effect dominates the equilibrium; it is counteracted by the negative entropy of dimerization, which is larger for IA than for IIA. The net effect is a slightly stronger dissociation of IIB.

The reaction enthalpy per C–Mg bond of IVA with acetic acid is -224.8 ± 3.5 kJ mol^{-1}. Comparison with the value for $\mathrm{Et_2Mg}$ reveals that the energy content of IVA is 10.8 ± 6.3 kJ mol^{-1} higher than that of $\mathrm{Et_2Mg}$. If the (theoretical) dimer of IVA, IVB, is free of ring strain as suggested by the results for I and II, the enthalpy of dimerization of IVA $\Delta H(\mathrm{dim}) = -10.8 \pm 6.3$ kJ mol^{-1}.

The accuracy of the determination of the degrees of association is about 2–3%, indicating that the ratio of IVA to IVB will be larger than 30:1. At a formal concentration of 0.84 mmol l^{-1}, this leads to an association constant $\alpha < 0.06$, from which an equilibrium constant for the equilibrium 2IVA ⇄ IVB: $K_{\mathrm{IV}} < 40$ l mol^{-1} and $\Delta G > -9$ kJ mol^{-1} at 28.50°C can be derived. An analogous discussion applied to III gives an association constant $\alpha > 0.98$, implying an equilibrium constant $K_{\mathrm{III}} > 1.4 \times 10^6$ l mol^{-1}. Thus for the (theoretical)) dimerization of 2IIIA ⇄ IIIB, $\Delta G < -35$ kJ mol^{-1} at 28.50°C. The same holds for the equilibrium 2VA ⇄ VB. In Table 6 the measured and estimated values of the dimerization parameters for compounds I–V are given.

Assuming that the entropy of dimerization of III will be approximately the same as that for I or II (e.g. $\Delta S_{\mathrm{III}} =$ ca. -100 J mol^{-1} K^{-1}), the enthalpy of dimerization of III ΔH_{III} will be more negative than -65 kJ mol^{-1}. This value indicates that the ring strain in IIIA will be about 20 kJ mol^{-1} larger than in IA. Comparison with the difference in ring strain between cyclohexane and cycloheptane (25.7 kJ mol^{-1} [11]) yields a rather good agreement. The ring strain in cyclodecane is about 50 kJ mol^{-1} larger than that in cyclohexane [11], suggesting that the dimerization enthalpy for VA is even more negative than that for IIIA. As the dimerization entropy for V is probably negative just like that of I and II, complete dimerization of V results. Although this result appears to be consistent with the results for I, III and V, the

TABLE 6

MEASURED AND ESTIMATED DIMERIZATION PARAMETERS FOR THE COMPOUNDS I–V AT 28.50°C

Equilibrium	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	i
2IA ⇄ IB	-16.0[a]	-45.4[a]	-98.0[a]	1–2
2IIA ⇄ IIB	-13.0[a]	-48.7[a]	-118.0[a]	1–2
2IIIA ⇄ IIIB	< -35.0[c]	< -65.0[d]	-100.0[b]	2
2IVA ⇄ IVB	> -9.0[c]	-10.8[a]	$\ll 0.0$[d]	1
2VA ⇄ VB	< -35.0[c]	< -65.0[d]	$\ll 0.0$[d]	2

[a] Derived from measurements. [b] Estimated from I and II. [c] Estimated from detection limits of the association measurements. [d] Derived from [a], [b] or [c] (see Text).

strong tendency of VA to dimerize to VB was initially rather unexpected in view of the stability of the ten-membered ring compound 1,6-dimagnesacyclodecane (VIII), the dimer of magnesacyclopentane [4]. However, a satisfactory explanation can be derived from the crystal structure of VIII [12]. As discussed previously [3], VIII has a conformation in which two *transoid* butane units are separated by two magnesium atoms. Obviously, the long C–Mg bond lengths (214 pm) in combination with the rather large C–Mg–C valence angle (128°) sufficiently separate the two butane units to prevent any significant degree of the unfavourable transannular steric interaction which is well known in the all-carbon analogue cyclodecane. We assume that replacement of one Mg atom in VIII by a CH_2 group, leading to VB, brings the two butane units into unfavourable proximity (and otherwise changes the conformation of the ring) in such a way that the medium-sized ring strain is no longer sufficiently alleviated.

The situation with IV is less well understood. In comparison with VI, IVA shows a ring strain of $\Delta H_{IV} = 10.8 \pm 6.3$ kJ mol^{-1}. A value of $\Delta S_{IV} < -7$ J mol^{-1} K^{-1} would then be sufficient to fully counteract the enthalpy gain on dimerization, and make IVB undetectable ($< 2\%$) by the association measurement. In view of the strongly negative dimerization enthalpies observed for I and II, it is very likely that ΔS_{IV} fulfills this requirement. More surprising, however, is the low value of ΔH_{IV} as compared to ΔH_{II} and ΔH_{III}. Undoubtedly, relief of Pitzer strain by removal of 4 C–H bonds from III to IV must be favourable; also, Baeyer strain is expected to be less important in the seven-membered ring of IVA compared to the six-membered ring of IIA. Still, the magnitude of this effect is surprising, and cannot be explained satisfactorily.

In summary, we conclude that the combination of ring size and bonding characteristics of the heteroatom magnesium leads to interesting conformational behaviour which may differ considerably from that for the more common carbocyclic and heterocyclic systems. A particularly fascinating aspect of cyclic organomagnesium compounds is the rapid establishment of thermodynamic equilibrium between different ring sizes by C–Mg bond exchange [13] which allows the molecules to reach readily the energetic minima on the energy hyperface, and makes the investigation of such minima possible.

Experimental section

The magnesacycloalkanes were synthesized according to Scheme 1. The preparation and measurements on I–VII were carried out in fully sealed and evacuated glass apparatus [2,3,8,9]. The synthesis of I has been described by Holtkamp [2]. ^1H NMR spectra were measured on a Bruker WH 90 spectrometer at 90 MHz.

1,6-Bis(bromomercurio)hexane (IIII) [14]

1,6-Dibromohexane (5.5 ml; 36 mmol) in 20 ml THF was added at room temperature to 5 g (206 mmol) magnesium in 170 ml THF during 8 h. After another 20 h stirring the yield of 1,6-bis(bromomagnesio)hexane was 97% as determined by acid/base and complexometric titration. To the decanted, clear solution, 26.0 g (7. mmol) $HgBr_2$ in 50 ml THF was slowly added with stirring. The white precipitate was filtered off, extracted with 100 ml H_2O at 100°C, washed with H_2O, ethanol and diethyl ether, dried and crystallized from toluene to yield white crystals of IIII

(43%), m.p. 260°C with decomposition. Anal. Found: C, 13.68; H, 2.47; Hg, 59.43. $C_6H_{12}Hg_2Br_2$ calcd.: C, 11.47; H, 1.87; Hg, 62.16%. No spectroscopic data are available due to the insolubility of the compound.

Mercuracycloheptane (III2)

Compound III2 was synthesized as described by Sawatzky and Wright [15] by adding a solution of 7.5 g (33 mmol) of $SnCl_2 \cdot 2H_2O$ in 150 ml NaOH (20%) to a stirred suspension of III1 in 300 ml NaOH (10%). Stirring was then continued for another 15 h. The solid was filtered off and washed with H_2O, dried and extracted three times with 50 ml of xylene at 75°C. After evaporation of the xylene solution the remaining yellow solid was dissolved in $CHCl_3$ and slowly cooled to −75°C; white crystals of III2 separated (yield 66%), m.p. 75–76°; III2 slowly decomposed at room temperature with formation of metallic mercury. Anal. Found: C, 25.92; H, 4.38; Hg, 69.67; $C_6H_{12}Hg$ calcd.: C, 25.31; H, 4.25; Hg, 70.44%. ^1H NMR ($CDCl_3$), δ: 1.11 (4H, t, J 8 Hz, α-CH_2), 1.25–1.67 (4H, m, γ-CH_2), 1.70–2.20 ppm (4H, m, β-CH_2).

1,8-Dimagnesacyclotetradecane (IIIB)

A mixture of 3.13 g (11 mmol) of III2, 3.0 g (120 mmol) magnesium and 100 ml THF was shaken for 3 d at 80°C; a clear solution was obtained. After decantation of the supernatant liquid, acid/base and complexometric titration indicated a quantitative yield of IIIB. Cooling to −80°C yielded a semi-crystalline product which, after decantation of the mother liquor, was used for the association measurements and the thermochemical experiments. No elemental analysis could be performed due to the extreme oxygen and moisture sensitivity of IIIB. ^1H NMR (THF-d_8), δ: −0.56 (4H, t, J 8 Hz, α-CH_2), 1.20–1.80 ppm (8H, m, β- and γ-CH_2).

1,9-Bis(bromomercurio)nonane (V1)

Compound V1 was prepared in the same way as III1. After addition of the $HgBr_2$ solution to 1,9-bis(bromomagnesio)nonane, both the precipitate and the supernatant solution were used for isolation of V1 by the procedure of Hilpert and Grüttner [14], because V1 is quite soluble in THF (60% yield from 1,9-dibromononane). Crystallization from THF gave white crystals of V1, m.p. 166.5–167.5°C. Anal. Found: C, 15.87; H, 2.77; Hg, 58.69. $C_9H_{18}Hg_2Br_2$ calcd.: C, 15.73; H, 2.64; Hg, 58.38%.

Mercuracyclodecane (V2)

Mercuracyclodecane was obtained in the way described for III2. The yield was 42%. The white amorphous compound was crystallized from $CHCl_3$ by slowly cooling the solution from boiling to room temperature. V2 decomposed slowly at room temperature with formation of metallic mercury. The degree of association of V2 is not known. Anal. Found: C, 33.67; H, 5.79; Hg, 59.60. $C_9H_{18}Hg$ calcd.: C, 33.08; H, 5.55; Hg, 61.38%. ^1H NMR ($CDCl_3$), δ: 1.11 (4H, t, J 8 Hz, α-CH_2), 1.22–2.10 ppm (14H, m, β-ε-CH_2).

1,11-Dimagnesacycloeicosane (VB)

A mixture of 3.2 g (132 mmol) magnesium, 2.56 g (7.8 mmol) V2 and 70 ml THF was shaken for 3 d at 100°C to give a clear solution, which was decanted from the magnesium amalgam. Acid/base and complexometric titration revealed quantitative magnesium–mercury exchange. The solution was used as such for the association and thermochemical measurements. ^{1}H NMR (THF-d_8), δ: -0.60 (8H, t, J 8 Hz, α-CH$_2$), 1.13–1.84 ppm (28H, m, β-ϵ-CH$_2$).

3-Bromo-1-(2-bromophenyl)propane (II1)

This starting material for the synthesis of II was prepared according to the method of Gilman and Marrs [16]; b.p. 75–76°C/0.1 mmHg.

3,4-Dihydro-2H-1-mercuranaphthalene (II2)

The bis(bromomagnesio) compound from II1 was prepared by adding a solution of 12 g (43.2 mmol) II1 in 20 ml of THF to 4.0 g (164 mmol) magnesium in 200 ml THF during 8 h at room temperature. After the addition, stirring was continued for 24 h. The solution was decanted from the unreacted magnesium; acid/base and complexometric titration of an aliquot indicated a yield of 76% for the dibromomagnesio compound. To this di-Grignard solution a solution of 11.8 g (32.8 mmol) HgBr$_2$ in 30 ml THF was slowly added. After stirring for 1 h, the solution was filtered and the residue dried for 24 h on a high vacuum line and then extracted with water and 200 ml benzene. The benzene extract was washed with water, dried and concentrated. The residue was purified by crystallization from benzene and yielded white crystals of II2 (37.5%), m.p. 140.0–145.0°C. The degree of association of II2 is not known. Anal. Found: C, 33.81; H, 3.14; Hg, 63.14. $C_9H_{10}Hg$ calcd.: C, 33.91; H, 3.16; Hg, 62.93%. ^{1}H NMR (CDCl$_3$), δ: 1.53 (2H, t, J 6 Hz, α-CH$_2$), 2.22–2.60 (2H, m, β-CH$_2$), 2.72–3.06 (2H, m, γ-CH$_2$), 7.04–7.30 ppm (4H, m, aryl H).

3,4-Dihydro-2H-1-magnesanaphthalene (II)

3.9 g (12.2 mmol) II2 in 75 ml THF was shaken for 8 h with 4 g (163 mmol) magnesium. The resulting clear solution was separated from the magnesium amalgam. Titration indicated 100% conversion to II. ^{1}H NMR (THF-d_8), δ: -0.16 (2H, t, J 7 Hz, α-CH$_2$), 2.15–2.70 (2H, m, β-CH$_2$), 3.00 (2H, t, J 7 Hz, γ-CH$_2$), 7.00–7.40 ppm (4H, m, aryl H).

1,2-Bis(2-bromoethyl)benzene (IV1)

1,2-Bis(2-hydroxyethyl)benzene, prepared according to Halford and Weissmann [17] was converted into IV1 with 48% HBr solution, as described by Muth et al. [18].

1,2,4,5-Tetrahydro-3-benzomercurepin (IV2)

The bis(bromomagnesio) derivative of IV1 was obtained by adding a solution of 12.13 g (41.5 mmol) IV1 in 20 ml THF to 5.13 g (211 mmol) magnesium in 170 ml THF during 7 h at room temperature. After stirring for another 20 h, titration indicated the formation of 59% of the di-Grignard reagent from IV1. A solution of 6.5 g HgBr$_2$ in 50 ml THF was then added with stirring. After one h the solid formed was filtered off and purified as described for III2. No crystalline product was obtained. The yield of IV2 was 95% based on the di-Grignard reagent. The degree of association of IV2 is not known. ^{1}H NMR (CDCl$_3$), δ: 1.25 (4H, t, J 8 Hz, α-CH$_2$), 3.00 (4H, t, J 8 Hz, β-CH$_2$), 7.07 ppm (4H, bs, aryl H).

1,2,4,5-Tetrahydro-3-benzomagnesepin (IVA)

A solution of 2.5 g (7.5 mmol) IV2 in 75 ml THF was shaken with 3 g (123 mmol) magnesium for 8 h. After decantation of the solution from the magnesium amalgam the yield of IV was found to be 100% by titration. ^{1}H NMR (THF-d_8), δ: −0.14 (4H, t, *J* 7 Hz, α-CH_2), 3.13 (4H, t, *J* 7 Hz, β-CH_2), 7.08 ppm (4H, m, aryl H).

Acknowledgement

This investigation was supported by the Netherlands Foundation for Chemical Research (SON), with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO). We thank Dr. K.L. Loening, Chemical Abstracts Service, for advice on the nomenclature of IV.

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