Journal of Organometallic Chemistry, 224 (1982) 217—221
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE SYNTHESIS AND STRUCTURE OF ZINCACYCLOPENTANE, ZINCACYCLOHEXANE AND ZINCACYCLOHEPTANE

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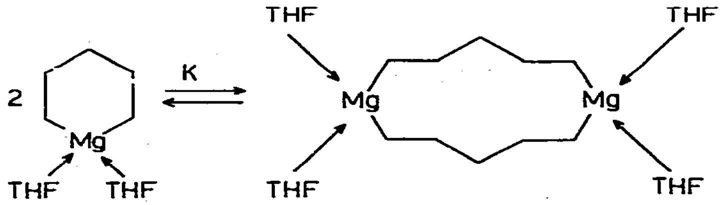
(Received August 13th, 1981)

Summary

The first bifunctional zinc compounds of 1,4-dibromobutane, 1,5-dibromopentane and 1,6-dibromohexane have been prepared by use of Rieke zinc; extraction of the salt mixture obtained after evaporation of the solvent THF with a diethyl ether/dioxane mixture yielded the title compounds. The new compounds are characterized by their ^{1}H and ^{13}C NMR spectra. Association measurements on THF solutions of the zincacycloalkanes at concentrations up to about 0.04 *M* at 28.50°C indicated a dimeric structure. Comparisons with the magnesium analogues are made.

Introduction

Some years ago we started an investigation on the structure of bifunctional and cyclic organomagnesium compounds in THF [1]. The results of this study were interpreted in terms of the existence of dimeric magnesacyclopentane and magnesacycloheptane [2]; magnesacyclohexane, however, exists in a monomer-dimer equilibrium [1,3]:

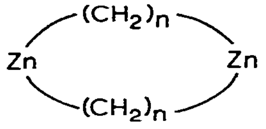


The thermodynamic parameters of magnesacyclohexane ($K(28.25°C) = 609$ l mol^{-1}, $K(48.50°C) = 182$ l mol^{-1}, $\Delta H = -48$ kJ mol^{-1}, $\Delta S = -106$ J mol^{-1} K^{-1}) indicate that the dimerization is exothermic; the unfavourable entropy of dimerization explains the absence of higher polymers. In order to obtain more insight into the relationship between the ring size and the degree of association, it seemed of interest to investigate whether a change of metal would also affect the association, and so the zincacycloalkanes having the same ring size as their magnesium analogues were studied, since zinc resembles magnesium in many aspects of its organometallic chemistry.

Results and discussion

Zincacyclopentane (I), zincacyclohexane (II) and zincacycloheptane (III) were prepared from the corresponding α,ω-dibromoalkanes and Rieke zinc as described in the Experimental section. Their structure in THF solution was determined by association measurements in the apparatus developed by Van Vulpen [4]. With this apparatus the rate of the quasi-isothermal distillation of pure solvent from an evaporator suspended on a spiral to the solution of the organozinc compound is measured. This rate is expressed as the "apparent rise" S_a of the evaporator in mm/h. The apparatus is calibrated for the solvent (THF) with triphenylmethane yielding the "standard rate" S_s in mm/h/mmol/l. The "theoretical rate" S_{th} in mm/h is found by multiplying S_s with the theoretical concentration c_f of monomeric particles containing one zinc. The association number i equals S_{th}/S_a. The formal concentration c_f of the organozinc compound was determined by acid base and complexon (EDTA) titration [5,6]. The result of the association measurements are given in Tables 1—3.

The i values in the Tables indicate that the investigated compounds I, II and III exist exclusively as dimers in THF solution and are in fact 1,6-dizincacyclodecane (Ia), 1,7-dizincacyclododecane (IIa) and 1,8-dizincacyclotetradecane (IIIa):



n = 4 : Ia
n = 5 : IIa
n = 6 : IIIa

The greater tendency towards dimerization of II compared with its magnesium analogue may be explained as follows. The coordinate bonds between the THF oxygens and the metal in the metallacycloalkanes will be stronger in the

TABLE 1

ASSOCIATION MEASUREMENTS OF ZINCACYCLOPENTANE (I) IN THF AT 28.50°C

c_f (mmol/l)	S_a (mm/h)	S_{th} (mm/h)	i
3.210	0.058	0.128	2.20
6.216	0.124	0.255	2.05
9.291	0.187	0.380	2.03
15.368	0.304	0.629	2.07
18.373	0.370	0.762	2.03

S_s = 0.04095 mm/h/mmol/l; i = 2.07 ± 0.07 (standard deviation 3.4%).

TABLE 2

ASSOCIATION MEASUREMENTS OF ZINCACYCLOHEXANE (II) IN THF AT 28.50°C

c_f (mmol/l)	S_a (mm/h)	S_{th} (mm/h)	i
5.741	0.112	0.236	2.10
11.482	0.240	0.471	1.96
17.223	0.362	0.707	1.95
22.964	0.486	0.943	1.94
28.705	0.609	1.179	1.94
34.499	0.740	1.417	1.92

S_s = 0.04106 mm/h/mmol/l; i = 1.97 ± 0.06 (standard deviation 3.4%).

TABLE 3

ASSOCIATION MEASUREMENTS OF ZINCACYCLOHEPTANE (III) IN THF AT 28.50°C

c_f (mmol/l)	S_a (mm/h)	S_{th} (mm/h)	i
6.158	0.125	0.257	2.05
12.268	0.250	0.512	2.05
18.331	0.373	0.785	2.05
24.347	0.498	1.016	2.04
30.371	0.600	1.264	2.11
36.241	0.722	1.512	2.09

S_s = 0.04711 mm/h/mmol/l; i = 2.06 ± 0.03 (standard deviation 1.4%).

case of magnesium since zinc is a weaker Lewis acid than magnesium [7]. Thus, the THF oxygens are bound to a less electronegative group in the case of zinc. According to Bent's rule [8] this will result in a decrease of the *p* character of the zinc orbitals involved in the carbon—zinc bonds as compared with the magnesium compounds, resulting in a larger carbon—metal—carbon bond angle in the zinc compounds. As the carbon—magnesium—carbon bond angle was found to be 141.5° in 1,7-dimagnesacyclododecaan [9], the corresponding angle in IIa is expected to be even larger. It can be assumed that such a larger bond angle will be general for dialkylzinc compounds and applies also to monomeric II. As a result the ring strain in II will increase considerably, leading to complete dimerization, yielding IIa. The same reasoning is probably also true for I and III, but since the corresponding magnesium compounds are completely dimeric, it cannot be checked experimentally.

Experimental section

The reaction of α,ω-dihaloalkanes with activated zinc does not give the corresponding bifunctional zinc compounds. 1,4-Diiodobutane and 1,5-diiodopentane react smoothly in refluxing diethyl ether producing the corresponding monofunctional iodoalkylzinc iodide [10]. 1,4-Dibromobutane and 1,5-dibromopentane do not react with Zn—Cu couple in diethyl ether. However, in di-n-butyl ether a violent reaction occurs at 90°C, yielding unsaturated hydrocarbons and zinc bromide [10]. In order to allow a lower reaction temperature, a more reactive form of zinc is needed. Therefore, the zinc powder prepared according to Rieke from the reaction of anhydrous zinc chloride with potassium in THF was used [11]. The zinc chloride used for the preparation of the Rieke-zinc was dried by heating at 350°C for 7 hours in vacuum.

Because of the extreme susceptibility of the organozinc compounds to oxygen and moisture, the purification of the starting materials and the solvents plus all the reactions were carried out in fully sealed and evacuated glass apparatus [12]. The analysis of the zinc compounds was performed through acid-base and complexon (EDTA) titration of a hydrolized aliquot of the ultimate THF solution of the zincacycloalkanes. The new zincaalkanes were characterized by their ^{1}H and ^{13}C NMR spectra measured on a Bruker WH-90 NMR spectrometer in perdeuterotetrahydrofuran as a solvent at 90 and 22.63 Mhz respectively (see (Table 4). The α,ω-dibromoalkanes were commercial products, obtained from E. Merck, Darmstadt.

Synthesis of 1,6-dizincacyclodecane (Ia)

To 70 mmol Rieke-zinc [11], prepared from 80 mmol $ZnCl_2$ and 140 mmol potassium in 110 ml THF, was added 25 mmol 1,4-dibromobutane. Stirring for 5 hours at 65°C yielded tetramethylenebis(zinc bromide) (92% based on 1,4-dibromobutane as revealed by titration). Next, the THF was removed by heating for 7 hours at 90°C on a vacuum line. Extraction of the remaining grey powder at 50°C with a mixture of 260 ml diethyl ether and 6.1 ml (72 mmol) dioxane gave 9.5 mmol of 1,6-dizincacylodecane, complexed with dioxane. The solution was concentrated to about 10 ml, after which 50 ml anhydrous pentane was added. The organozinc compound precipitated at once as a white powder. After standing overnight at —70°C the clear upper layer was decanted at room temperature. The dioxane was removed from the complex by heating the precipitate for 7 hours at 60°C on the vacuum line. The residue was dissolved in THF. For further purification the THF solution was concentrated to about 20 ml and kept overnight at —70°C. The 1,6-dizincacyclodecane, complexed

TABLE 4

THE NMR SPECTRA OF ZINCACYCLOALKANES MEASURED IN $THF\text{-}d_8$ AT 25°C (δ IN PPM RELATIVE TO INTERNAL TMS)

^{1}H NMR

Compound	α-CH_2	(β + γ)-CH_2
Ia	0.33, t, 4 H (^3J(H—H) = 7 Hz	1.57—1.79, m, 4 H
IIa	0.39, t, 4 H (^3J(H—H) = 7 Hz	1.32—1.93, m, 6 H
IIIa	0.31, t, 4 H (^3J(H—H) = 7 Hz	1.26—1.87, m, 8 H

^{13}C NMR

Compound	α-CH_2	β-CH_2	γ-CH_2
Ia	13.61	34.65	—
IIa	14.45	28.76	44.55
IIIa	13.94	28.63	37.69

with THF, separated slowly at this temperature as a micro-crystalline solid. After decantation of the clear supernatant liquid at about 30°C, the white precipitate was dissolved in pure THF for analysis. The yield was 9 mmol Ia (72%).

Synthesis of 1,7-dizincacyclododecane (IIa)

The same procedure for IIa with 157 mmol Rieke-zinc and 50 mmol 1,5-dibromopentane reacting at 70°C for 5 hours yielded 100% of pentamethylenebis-(zinc bromide). Evaporation, extraction with diethyl ether/dioxane mixture, evaporation of the dioxane, and dissolution in THF gave a solution containing 22.5 mmol of IIa (yield 90%).

Synthesis of 1,8-dizincacyclotetradecane (IIIa)

The same procedure with 135 mmol Rieke-zinc and 45 mmol 1,6-dibromohexane in 200 ml THF yielded 97% of hexamethylenebis(zinc bromide). Evaporation of the solvent, extraction, evaporation and dissolution in THF gave a solution containing 21 mmol of IIIa (yield 93%).

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). The authors are very grateful to Mr. G. Schat for performing the association measurements.

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