Journal of Organometallic Chemistry, 375 (1989) 11–20
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20123

The crystal and molecular structure of polymeric $[(\text{dineopentylmagnesium})_2 \cdot (\text{neopentylmagnesium bromide})_2]_n$: an unsolvated alkylmagnesium species

P.R. Markies, G. Schat, O.S. Akkerman, F. Bickelhaupt *,
Scheikundig Laboratorium, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam (The Netherlands)

W.J.J. Smeets, A.J.M. Duisenberg and A.L. Spek
Vakgroep Algemene Chemie, Afdeling Kristal- en Structuurchemie, Rijksuniversiteit Utrecht, Padualaan 8, 3584 CH Utrecht (The Netherlands)

(Received April 25th, 1989)

Abstract

The structure of an unsolvated adduct of dineopentylmagnesium and neopentylmagnesium bromide has been determined by a single crystal X-ray diffraction study. It consists of a polymeric chain of composition $[(Np_2Mg)_2 \cdot (NpMgBr)_2]_n$, involving an alternating pattern of two Np_2Mg and two NpMgBr fragments connected by bridging neopentyl and bromide groups, in which all Mg atoms are tetracoordinate. Crystals of $C_{15}H_{33}Mg_2Br$ are triclinic, space group $P1$, with unit cell dimensions a 9.654(1) Å, b 9.876(1) Å, c 11.334(2) Å, α 85.35(1)°, β 67.93(1)°, γ 74.59(1)°, $Z = 2$, V 965.3 (2) Å^3, $R = 0.0819$ for 2447 reflections with $I > 3.0\sigma(I)$.

Introduction

Owing to the limited accessibility of organomagnesium species in apolar solvents, they are usually studied in coordinating solvents such as diethyl ether or tetrahydrofuran. Such solvents are usually needed for the synthesis of organomagnesium compounds, and decomplexation is very difficult: only by prolonged heating in high vacuum can all the solvent be removed. The amorphous product obtained in this way cannot normally be used for structure determination. The characterization of unsolvated Grignard reagents is further complicated by the Schlenk equilibrium; disproportionation may occur, yielding a mixture of a diorganylmagnesium and magnesium halide [1].

As a result, very little is known about the structure of unsolvated organomagnesium species. Recently, the crystal structure of bis(tris(trimethylsilyl)-methyl)magnesium was reported [2]. Owing to steric repulsion between the bulky

0022-328X/89/$03.50

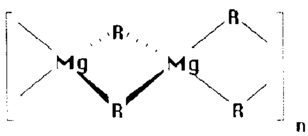

Fig. 1. Schematic representation of the R_2Mg crystal structure (R = Me or Et), obtained by powder diffraction [3].

alkyl groups this crystallizes as an unsolvated monomeric species, having a linear C–Mg–C angle and a Mg–C bond length of 2.126(6) Å. Two simple dialkylmagnesium species, $(Me_2Mg)_n$ and $(Et_2Mg)_n$, have been characterized by X-ray powder studies [3] and shown to consist of polymeric chains in which the tetracoordinated magnesium atoms are connected by pairs of symmetrically-bridging alkyl groups (see Fig. 1). The very low solubility of these polymers in apolar solvents is probably related to the relative stability of the Mg–C bonds (bond lengths 2.24(3) Å in dimethylmagnesium and 2.26(5) Å in diethylmagnesium), which prevents breakdown into smaller oligomers.

Dialkylmagnesium compounds having larger and/or branched alkyl groups behave quite differently [2,4]. In these compounds, association in the solid state is less favourable owing to steric hindrance. The larger alkyl group will be better solvated upon dissolution. In addition, electronic factors may play a role: substitution of the bridging carbon atom with a bulky alkyl group lowers its bridging ability by distributing the negative charge [5]. This results in a good solubility in hydrocarbons, as found for compounds such as bis(tris(trimethylsilyl)-methyl)magnesium, dineopentylmagnesium, and di-sec-butylmagnesium, and even high vacuum distillation/sublimation becomes possible. Dineopentylmagnesium, investigated by Anderson and Wilkinson [6] is a solid, but quite soluble in pentane or benzene; it can be sublimed with only slight decomposition in high vacuum. Cryoscopy in benzene indicates the presence of a trimeric species in solution. Di-sec-butylmagnesium [7] is a light yellow mobile liquid, miscible in all proportions with alkanes or benzene. In solution, dimeric species are present (osmometry in cyclopentane). High vacuum distillation is not possible, owing to ready decomposition involving elimination of magnesium hydride.

The special properties of dineopentylmagnesium make this compound attractive for further studies. Its volatility has been utilized in gas phase diffraction studies, which yielded the molecular structure of monomeric dineopentylmagnesium [8]. The molecule has a linear C–Mg–C unit, with C–Mg distances of 2.126(6) Å. In our laboratory the heat of sublimation, an essential parameter for calculating the heat of formation in the gas phase, has been measured using a Knudsen cell connected to a mass spectrometer, and this enabled determination of the mean dissociation energy of the C–Mg bond in dineopentylmagnesium. This was found to be 134(5) kJ mol^{-1} for the monomeric compound, whereas for the bridging neopentyl group in dimeric dineopentylmagnesium, the value was 205(3) kJ mol^{-1} [9].

In the present investigation, use has been made of the relatively high solubility of dineopentylmagnesium in non-coordinating solvents to grow crystals suitable for X-ray diffraction studies, which yield the structure of an unsolvated alkylmagnesium species. It was expected, that the different behaviour of the higher alkylmagnesium species compared with that of the simple species $(Me_2Mg)_n$ and $(Et_2Mg)_n$ (vide infra) would be reflected in the structure.

Experimental

Because of the high reactivity of organomagnesium compounds towards water and oxygen, all experiments were performed in sealed and evacuated glass apparatus. Dineopentylmagnesium (Np_2Mg) was synthesized from 1-bromo-2,2-dimethylpropane (25 mmol, dried on 4Å molecular sieve), which was stirred with magnesium (100 mmol, triply sublimed) in Et_2O (180 ml, distilled from sodium-potassium alloy). There was an initiation period of 1 day. When the reaction was complete (as indicated by titration of 'total base' and Mg^{2+}), 1,4-dioxane (1.05 equiv.) was added to precipitate $MgBr_2$. The clear supernatant solution was decanted and the solvent distilled off. The solid residue was kept under vacuum (2×10^{-6} mbar, 24 h) to remove the coordinated solvent and the resulting powder dissolved in n-pentane. Crystallization from this solution could be induced by slowly cooling to −20 °C, but the crystals obtained were too small to be used for diffraction studies. Crystallization from a 1/1 mixture of toluene/n-heptane gave better results. Heating (water bath) of the solid with this solvent mixture gave a concentrated solution, which yielded crystals on slow cooling to room temperature.

The crystals were isolated and transferred to a glove-box (Braun, Garsching, Germany, with built-in microscope, and filled with nitrogen containing less than 1 ppm H_2O and oxygen). A ^1H NMR spectrum in C_6D_6 was recorded at 400 MHz (Bruker MSL 400, $C_6D_5H = 7.17$): δ 0.327 (s, 4H, CH_2), 0.918 (s, trace of NpH), 1.222 (s, 18H, CH_3), and showed no ether signals. Crystals were selected and mounted in a Lindemann capillary. The remaining solid was hydrolyzed. Titration showed the presence of base (0.420 mmol) and Mg^{2+} (0.266 mmol) in a ratio indicating incomplete removal of the magnesium bromide in the treatment with dioxane. Apparently, upon crystallization we had obtained a mixed Grignard/dialkylmagnesium species. According to the titration-data (base: $Mg^{2+} = 1.58/1$, whereas pure Np_2Mg should give a ratio of 2/1), the species appeared to be an adduct with 1/1 stoichiometry of NpMgBr and Np_2Mg. Titration of some of the mother liquor after hydrolysis indicated that bromide was practically absent from the solution, and so the crystals obtained had apparently completely taken up the minute residual amount of NpMgBr originally present in the Np_2Mg solution.

The exact nature of the crystallized sample was elucidated by an X-ray crystal structure determination, which revealed that it was indeed a 1/1 adduct of NpMgBr and Np_2Mg. The residue from the crystallization experiment was evaporated to dryness and kept under high vacuum (2×10^{-6} mbar). After sealing of the ampoule, crystals of pure dineopentylmagnesium were obtained by sublimation (50–100 °C). The structure of this species is being investigated.

Structure determination and refinement of $[C_{15}H_{33}Mg_2Br]_n$

A colourless plate shaped crystal suitable for an X-ray structure determination was mounted under nitrogen in a Lindemann-glass capillary, and mounted on an Enraf–Nonius CAD-4F diffractometer for data collection. Unit cell parameters were determined from a least squares treatment of the SET4 setting angles of 25 reflections in the range $8.0 < \theta < 13.2°$. Reflection profiles were relatively broad. The unit cell parameters were checked for the presence of higher lattice symmetry [10]. Data were corrected for Lp and for a linear decay of 2.4% during the 82 h of

X-ray exposure time but not for absorption. Standard deviations as obtained by counting statistics were increased according to an analysis of the excess variance of the two reference reflections: $\sigma_{cs}^2(I) = \sigma^2\ (I) + (0.0291)^2$ [11]. The structure was solved with direct methods (SHELXS86, [12]) and subsequent difference Fourier analyses. Refinement on F was carried out by full matrix least squares techniques. One of the neopentyl moieties which was found to be disordered over two positions in a 54/46 ratio was refined with a disorder model using geometrical restraints. All non-hydrogen atoms, except the disordered atoms, were refined with anisotropic thermal parameters. Methyl H-atoms were introduced in calculated positions (C–H 0.98 Å) and included in the refinement riding on their carrier atoms. The methyl groups are probably disordered about their C–C bond, as can be seen from the high values of the overall isotropic temperature factors of the methyl H-atoms ($U = 0.9(1)$; 1.0(1); 0.32(6) Å^2, respectively). Methylene H-atoms could not be located from a difference Fourier map and were therefore introduced at calculated positions and

Table 1

Crystal data and details of the structure determination

(a) Crystal data	
Formula	$C_{15}H_{33}Mg_2Br$
Molecular weight	341.94
Crystal system	triclinic
Space group	$P1$(Nr.2)
a, b, c (Å)	9.654(1), 9.876(1), 11.334(2)
α, β, γ (°)	85.35(1), 67.93(1), 74.59(1)
V (Å^3)	965.3(2)
Z	2
D_{calc} (g cm^{-3})	1.176
$F(000)$	364
μ(cm^{-1})	21.6
Crystal size (mm)	0.38 × 0.25 × 0.08
(b) Data collection	
Temperature (K)	294
θ_{min}, θ_{max} (°)	1.94, 27.5
Radiation	Mo-K_α (Zr-filtered), 0.71073 Å
Scan type	$\omega/2\theta$
$\Delta\omega$ (°)	$1.33 + 0.35 \tan\theta$
Horizontal and vertical aperture (mm)	4.0, 6.0
Distance crystal to detector (mm)	173
Reference reflections	334, 411
Data set	h −12:12; k −12:12; l −14:10
Total data	4706
Total unique data	4445
Observed data	2447[$I > 3.0\sigma(I)$]
(c) Refinement	
No. of refined parameters	209
Weighting	$w = 1$
Final R, R_w, S	0.082, 0.103, 2.11
$(\Delta/\sigma)_{av}$ in final cycle	0.053
Minimum and maximum residual density e/Å^3	−0.95, 1.09

Table 2

Fractional atomic coordinates and equivalent isotropic thermal parameters with esd's in parentheses for $[C_{15}H_{33}Mg_2Br]_n$

	x	y	z	U_{eq}^a or U_{iso} ($Å^2$)
Br	0.0586(2)	0.5918(2)	0.1243(1)	0.0492(4)
Mg(1)	0.1719(6)	0.5415(6)	−0.1397(4)	0.083(2)
Mg(2)	0.4290(7)	0.5140(6)	−0.3661(5)	0.091(2)
C(1)	0.094(2)	0.847(2)	−0.239(2)	0.087(6)
C(2)	0.188(2)	0.695(2)	−0.293(2)	0.092(6)
C(3)	0.082(3)	0.948(2)	−0.352(2)	0.13(1)
C(4)	0.173(2)	0.904(2)	−0.162(2)	0.13(1)
C(5)	−0.074(2)	0.841(2)	−0.149(2)	0.124(9)
C(6)	0.349(2)	0.432(2)	−0.518(1)	0.108(8)
C(7)	0.326(2)	0.305(2)	−0.575(2)	0.098(7)
C(8)	0.393(3)	0.301(2)	−0.724(2)	0.14(1)
C(9)	0.412(3)	0.164(2)	−0.528(2)	0.13(1)
C(10)	0.151(2)	0.308(3)	−0.534(2)	0.16(1)
C(11)	0.504(2)	0.258(2)	−0.179(2)	0.090(7)
#C(12) [b]	0.426(2)	0.418(2)	−0.175(2)	0.070(8)
C(13)	0.651(2)	0.222(2)	−0.307(2)	0.21(1)
#C(14)	0.559(3)	0.214(4)	−0.066(2)	0.12(1)
#C(15)	0.394(3)	0.166(4)	−0.175(3)	0.12(1)
Minor disorder positions [s.o.f. = 0.46(3)]				
C(121)	0.366(2)	0.350(4)	−0.213(3)	0.12(2)
C(141)	0.539(5)	0.341(9)	−0.088(4)	0.31(5)
C(151)	0.479(7)	0.118(3)	−0.112(5)	0.28(5)

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i \times a_j \times a_i a_j$. [b] # indicates major disorder position [s.o.f. = 0.54(3)].

included in the refinement, together with their carrier atoms, as rigid CH_2 groups. The refinement of the structure converged at $R = 0.0819$. A final difference Fourier synthesis showed some features of approximately 1 e/$Å^3$ around Br, which were interpreted as absorption artefacts. The relatively high R-factor is ascribed to the disorder and the poor quality of the crystal.

Crystal data and numerical details of the structure determination are given in Table 1. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 2; data on the geometry are given in Table 3. Neutral atom scattering factors were taken from ref. 13 and corrected for anomalous dispersion [14]. All calculations were performed with SHELX76 [15] and the EUCLID package [16] (geometrical calculations and illustrations) on a MicroVAX-II computer.

Supplementary data (anisotropic thermal parameters, all H-atom parameters, lists of bond lengths, bond angles, torsion angles and a lists of observed and calculated structure factor amplitudes) are available from A.L.S.

Description of the structure

From the toluene/heptane solution of dineopentylmagnesium containing a small amount of neopentylmagnesium bromide, the adduct crystallizes in the preferred stoichiometry of 1/1 free from solvent. The crystal structure consists of polymeric chains, having an alternating pattern of Np_2Mg and NpMgBr fragments. The

Table 3

Bond distances (Å) and angles (°) for the non-hydrogen atoms of $[C_{15}H_{33}Mg_2Br]_n$

Br–Mg(1)	2.808(4)	C(1)–C(4)	1.57(3)
Br–Mg(1)′ [a]	2.818(6)	C(1)–C(5)	1.57(3)
Mg(1)–C(2)	2.20(2)	C(6)–C(7)	1.55(3)
Mg(1)–C(12)	2.33(2)	C(7)–C(8)	1.57(2)
Mg(2)–C(2)	2.42(2)	C(7)–C(9)	1.58(3)
Mg(2)–C(6)	2.41(2)	C(7)–C(10)	1.57(3)
Mg(2)–C(6)″	2.23(2)	C(11)–C(12)	1.55(2)
Mg(2)–C(12)	2.29(2)	C(11)–C(13)	1.58(2)
C(1)–C(2)	1.57(2)	C(11)–C(14)	1.56(3)
C(1)–C(3)	1.58(3)	C(11)–C(15)	1.56(4)
Mg(1)–Br–Mg(1)′	86.4(2)	Mg(1)–C(2)–C(1)	111(1)
Br–Mg(1)–Br′	93.6(2)	Mg(2)–C(6)–Mg(2)″	74.9(6)
Br–Mg(1)–C(2)	128.6(5)	Mg(2)–C(2)–C(1)	151(1)
Br–Mg(1)–C(12)	100.6(5)	Mg(2)–C(6)–C(7)	147(1)
Br′–Mg(1)–C(2)	108.1(6)	Mg(2)″–C(6)–C(7)	113(1)
Br′–Mg(1)–C(12)	122.6(5)	C(6)–C(7)–C(8)	113(2)
C(2)–Mg(2)–C(6)	89.7(7)	C(6)–C(7)–C(9)	109(2)
C(2)–Mg(2)–C(6)″	120.8(6)	C(6)–C(7)–C(10)	112(2)
C(2)–Mg(2)–C(12)	99.6(6)	C(8)–C(7)–C(9)	108(2)
C(2)–Mg(1)–C(12)	105.1(7)	C(8)–C(7)–C(10)	106(2)
C(6)–Mg(2)–C(6)″	105.1(6)	C(9)–C(7)–C(10)	109(2)
C(6)–Mg(2)–C(12)	127.7(7)	C(12)–C(11)–C(13)	109(1)
C(6)″–Mg(2)–C(12)	113.1(8)	C(12)–C(11)–C(14)	112(2)
C(2)–C(1)–C(3)	110(1)	C(12)–C(11)–C(15)	113(2)
C(2)–C(1)–C(4)	111(2)	C(13)–C(11)–C(14)	108(2)
C(2)–C(1)–C(5)	108(1)	C(13)–C(11)–C(15)	109(2)
C(3)–C(1)–C(4)	110(2)	C(14)–C(11)–C(15)	107(2)
C(3)–C(1)–C(5)	108(2)	Mg(1)–C(12)–Mg(2)	74.4(6)
C(4)–C(1)–C(5)	110(1)	Mg(1)–C(12)–C(11)	132(1)
Mg(1)–C(2)–Mg(2)	74.1(5)	Mg(2)–C(12)–C(11)	116(1)

[a] One prime indicates symmetry operation: $-x, 1-y, -z$, two primes indicates symmetry operation: $1-x, 1-y, -1-z$.

repeating sequence in these chains is the centrosymmetric unit μ-BrMg-μ-Np$_2$Mg-μ-Np$_2$Mg-μ-Np$_2$Mg-μ-Br (crystallographic unique part: μ-BrMg-μ-Np$_2$Mg-μ-Np) (Fig. 2).

The tetrahedrally coordinated spiro magnesium atoms in this unit are connected by sets of two bridging neopentyl or bromide groups. This results in two different Np$_2$Mg$_2$ four-membered rings in a 2/1 ratio, and one Br$_2$Mg$_2$ four-membered ring, with every ring perpendicular to its neighbour. Rings with one neopentyl and one bromide bridge are not present, presumably because of their markedly different geometric requirements. The Mg–Np–Mg bridges are remarkably asymmetric, having a short (2.20(2)–2.23(2) Å) and a long (2.41(2)–2.42(2) Å) Mg–C bond, while in $(Me_2Mg)_n$ (2.24 Å) and $(Et_2Mg)_n$ (2.26 Å) the Mg–C–Mg bridges are completely symmetrical. These data can be understood in terms of an incipient dissociation of the polymeric chain into separate Np$_2$Mg units under the influence of the bulk of the neopentyl group. This is particularly evident in the central Np$_2$Mg$_2$ ring, which is centrosymmetric, having two long (2.41(2) Å) and two normal (2.23(2) Å) bridging Mg–C bonds. Probably, this arrangement would be formed in crystalline,

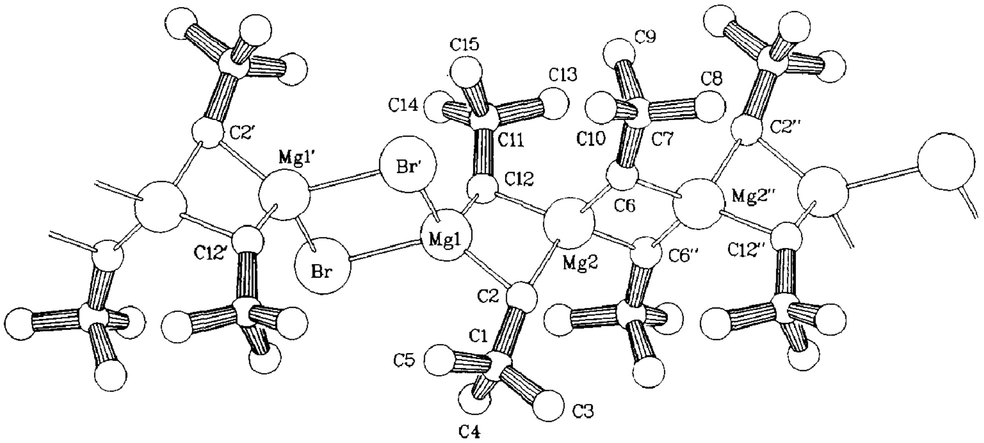

Fig. 2. PLUTON drawing of polymeric $C_{15}H_{33}Mg_2Br$ showing the adopted atom numbering; H-atoms were left out for clarity. Only the major disorder component is shown.

halogen-free Np_2Mg, which may consist of chains of weakly associated Np_2Mg molecules. The Br_2Mg_2 rings are also centrosymmetric, but have very long Br–Mg distances (2.808(4) and 2.818(6), vs. 2.58 Å in dimeric ethylmagnesium bromide [17]). This bond length probably indicates a partial charge separation in the polymeric chain, with negative charge on Br and positive charge on the Np_6Mg_4 unit. The Mg–Np–Mg bridges in the latter fragment are possibly stabilized by a partial positive charge on the $Mg_{1/1a}$ atoms (Tab. 4).

Another interesting feature involves the positions of the magnesium atoms in the polymeric chain. As can be seen in Fig. 3, pairs of magnesium atoms are arranged on two parallel lines (mutual distance 1.10(2) Å). In polymeric Me_2Mg and Et_2Mg, the magnesium atoms are arranged in a straight line, corresponding to a higher degree of symmetry.

The positions of the methylene hydrogen atoms could not be located owing to disorder, but estimation is possible using the geometries of the bridging neopentyl groups. The tetrahedral environment of the CH_2 carbon atoms shows little distortion as a consequence of the association of a second magnesium, as can be seen from the Mg–CH_2–t-Bu angles along the short C–Mg bond, which lie between 111 and 116 degrees (Fig. 4 and Table 4). The dihedral angle t-Bu–CH_2–Mg–Mg′ reveals the rotation of the t-butyl groups out of the CMg_2 plane, ranging from 27 to 34 degrees. This torsion will diminish the steric repulsion between adjacent t-butyl

Table 4

The geometry of the bridging neopentyl groups in the Mg_2Np_2 four-membered ring (angles and dihedral angles, in deg.), see Fig. 4

	Mg–CH_2–t-Bu	Mg′–CH_2–t-Bu	Mg′–Mg–CH_2–t-Bu
CH_2(2)	111(1)	151	31
CH_2(6)	113(1)	147	34
CH_2(12) [b]	116(1)	132	50

[b] Disordered CH_2-group.

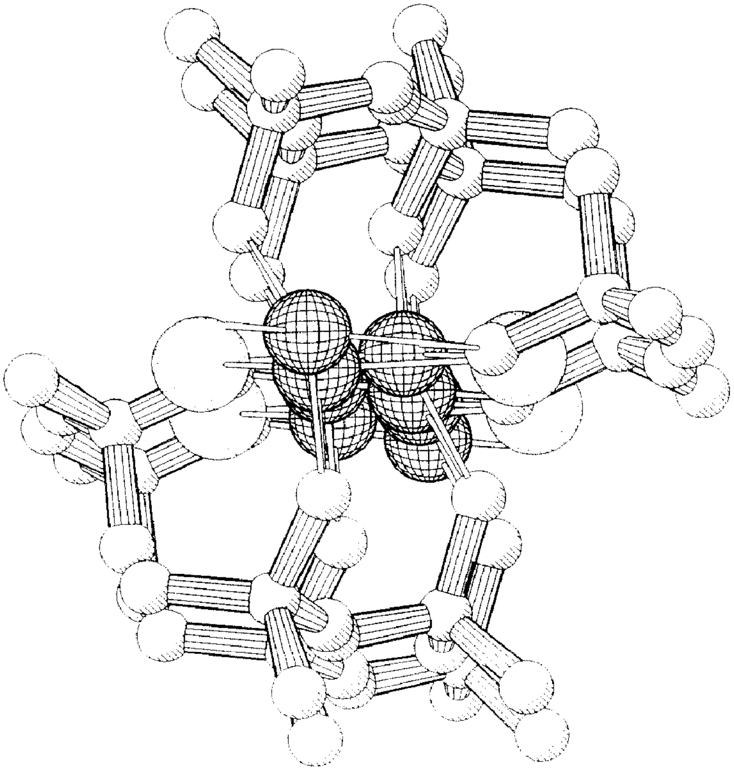

Fig. 3. PLUTON drawing of polymeric $C_{15}H_{33}Mg_2Br$ showing a perspective view along the polymer chain axis; H-atoms were left out for clarity. Only the major disorder component is shown.

groups, but also brings one of the CH_2-hydrogens in the Mg_2Np_2 plane into the vicinity of one of the magnesium atoms (Fig. 4).

Discussion

We were rather surprised that a halogen-containing organomagnesium species could be isolated from an ether-free solution. Intuitively, one would expect that a small amount of donor solvent would be needed for dissolution of a MgBr-contain-

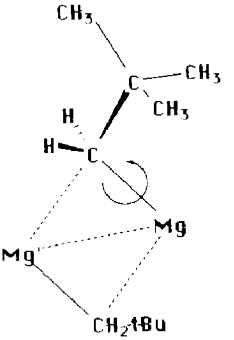

Fig. 4. The geometry of a bridging neopentyl group in a Mg_2Np_2 four membered ring.

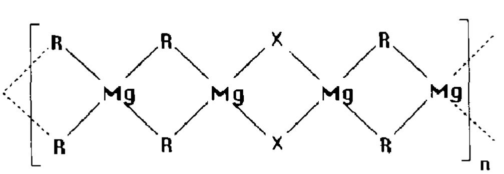

Fig. 5. Suggested structural fragment [19] for a $(R_3Mg_2Br)_n$ polymeric chain (R = alkyl, X = halogen).

ing species in an apolar medium. However, there is a precedent: crystalline Ph_3Mg_2Cl having been isolated from a tetralin solution [18]. Generally, solutions of Grignard compounds prepared in apolar media show a tendency to deposit MgX_2 (X = halogen); in many cases, the formation of an R_3Mg_2X stoichiometry in solution was observed but no explanation was given [19]. A solid state structure (Fig. 5) similar to that revealed by our crystal structure study was suggested, but has never previously been confirmed.

It would be of interest to know how our polymeric species breaks down upon dissolution in apolar (non-etherial) solvents. Two different modes can be suggested, leading to the fragments $NpMg\text{-}\mu\text{-}Np_2Mg\text{-}\mu\text{-}Br_2Mg\text{-}\mu\text{-}Np_2MgNp$ and $BrMg\text{-}\mu\text{-}Np_2Mg\text{-}\mu\text{-}Np_2Mg\text{-}\mu\text{-}Np_2MgBr$ in solution. While halogen bridges are normally stronger than alkyl bridges, the situation may be reversed under crowded conditions [20]. Such oligomers of $[R_3Mg_2X]$ may have a special stability, which prevents disproportionation into MgX_2 and R_2Mg and subsequent precipitation of MgX_2 from the non-etherial solution.

Conclusion

In this article we present the first crystal structural investigation of a polymeric $[R_3Mg_2X]_n$ species. The crystal structure of $[Np_3Mg_2Br]_n$ is largely in accordance with a previous suggestion for species of this general type [19]. The crystal structure suggests that the polymeric chain can be recorded as divided into $Np_6Mg_4Br_2$ units associated through the (weak) Mg–Br bonds. The different behaviour of the larger neopentyl group compared to that of the small methyl or ethyl groups is evident: because of steric hindrance, association of organomagnesium species by the formation of Mg–Np–Mg bridges is disfavoured.

Acknowledgement

The investigation was supported in part (P.R.M, W.J.J.S. and A.L.S.) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

References

1 E. Weiss, Chem. Ber., 98 (1965) 2805.
2 S.S. Al-Juaid, C. Eaborn, P.B. Hitchcock, C.A. McGeary, J.D. Smith, J. Chem. Soc., Chem. Commun., (1989) 273.
3 E. Weiss, J. Organomet. Chem., 2 (1964); ibid., 4 (1965) 101.
4 C.W. Kamienski, J.F. Eastham, J. Organomet. Chem., 8 (1967) 542.
5 O.T. Beachley, Jr., L. Victoriano, Organometallics, 7 (1988) 63.
6 R.A. Andersen, G. Wilkinson, J. Chem. S. Dalton, (1977) 809.

7 C.W. Kamienski, J.F. Eastham, J. Org. Chem., 34 (1969) 1116.
8 E.C. Ashby, L. Femholt, A. Haaland, R. Seip, R. Scott Smith, Acta Chem. Scand. A, 34 (1980) 213.
9 O.S. Akkerman, G. Schat, E.A.I.M. Evers, F. Bickelhaupt, Recl. Trac. Chim. Pays-Bas, 102 (1983) 109.
10 A.L. Spek, J. Appl. Cryst., 21 (1988) 578.
11 L.E. McCandlish, G.H. Stout, L.C. Andrews, Acta Cryst. A, 31 (1975) 245.
12 G.M. Sheldrick, SHELXS86. Program for crystal structure determination. University of Göttingen, Federal Republic of Germany, 1986.
13 D.T. Cromer, J.B. Mann, Acta Cryst. A, 24 (1968) 321.
14 D.T. Cromer, D. Liberman, J. Chem. Phys., 53 (1970) 1891.
15 G.M. Sheldrick, SHELX76. Crystal structure analysis package. University of Cambridge, England, 1976.
16 A.L. Spek, The EUCLID Package in D. Sayre (Ed.), Computational Crystallography, p. 528, Clarendon Press, Oxford, 1982.
17 A.L. Spek, P. Voorbergen, G. Schat, C. Blomberg, F. Bickelhaupt, J. Organomet. Chem., 77 (1974) 147.
18 D. Bryce-Smith, G.F. Cox, J. Chem. Soc. (1961) 1175.
19 B.J. Wakefield, Organomet. Chem. Rev. 1 (1966) 131.
20 P. Voorbergen, Thesis Vrije Universiteit, Amsterdam (1980).