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Synthesis of Cyclic Bifunctional Organomagnesium Compounds. X-ray Crystal Structures of Tetrameric Organomagnesium Clusters[†,‡]

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Abstract: Three cyclic bifunctional organomagnesium compounds were prepared by three different routes. Reaction of 1,8-dibromo- or 1,8-diiodonaphthalene with metallic magnesium gave the corresponding di-Grignard reagents **3**, from which the halide-free 1,8-naphthalenediylmagnesium (**4**) was isolated. *o*-Phenylenemagnesium (**10**) was prepared by transmetalation from *o*-phenylenemercury with magnesium. The reaction of freshly sublimed magnesium with diphenylacetylene gave a mixture of *cis*- and *trans*-diphenylvinylenemagnesium; *cis*-diphenylvinylenemagnesium (**15**) was isolated by crystallization from THF. The X-ray crystal structures of **4**, **10**, and **15** showed these compounds to be tetrameric in the solid state. Crystal data are as follow: **4**, $C_{56}H_{56}Mg_4O_4{\cdot}5C_4H_8O$, tetragonal, space group $I4_1/a$, with cell dimensions $a = 14.429(2)$ and $c = 34.927(4)$ Å, final $R = 0.068$, $R_w = 0.083$; **10**, $C_{40}H_{48}Mg_4O_4$, monoclinic, space group $I2/a$, with cell dimensions $a = 17.071(3)$, $b = 11.877(1)$, and $c = 18.809(1)$ Å, $\beta = 99.97(1)°$, final $R = 0.066$, $R_w = 0.092$; **15**, $C_{72}H_{72}Mg_4O_4{\cdot}2C_4H_8O$, tetragonal, space group $P\bar{4}2_1c$, with cell parameters $a = 17.464(1)$ and $c = 11.911(2)$ Å, final $R = 0.067$, $R_w = 0.089$. Their cores consist of distorted tetrahedrons of magnesium atoms. Each organic fragment is positioned above the face of such a tetrahedron and is bonded to three magnesium atoms via two carbon atoms. One carbon is single-bonded to a magnesium, and the other bridges two magnesiums by a 3-center, 2-electron bond. Each magnesium atom in the three structures has a pseudotetrahedral coordination; it is coordinated to one single-bonded and two bridging carbon atoms and a THF molecule. The arrangement of four organic groups over the four faces of a magnesium tetrahedron can be of either C_2 or of S_4 symmetry. Compounds **4** and **15** were found to have S_4 symmetry, whereas **10** has C_2 symmetry.

Introduction

For some time we have been engaged in an investigation of bifunctional organomagnesium compounds. The results of this work and that of other groups in this field have been reviewed.[1] Investigations on the structure of bifunctional organomagnesium compounds have been hampered by several factors. First of all, the extreme sensitivity of these compounds toward air necessitates the use of special equipment and techniques. A second problem is posed by the Schlenk equilibrium, which, schematically and in its simplest form, is represented for bifunctional organomagnesium compounds in Scheme I, as it relates di-Grignard reagents **A** to cyclic bifunctional organomagnesium compounds **B**. The Schlenk equilibria of di-Grignards have been evaluated in several cases.[2]

In solution, many additional equilibria involving association and/or exchange of the substituents at magnesium (organic rest, halogen) are operative. All these equilibria are generally very fast at room temperature. This leads to a complicated dynamic situation.

The situation is much simpler with cyclic organomagnesium compounds. Of the equilibria mentioned for Grignard reagents, only association is relevant, and as the exchange of the carbon anion (i.e., the organic rest) is usually rapid, the system will always adopt the thermodynamically favored degree of association. Some cyclic bifunctional organomagnesium compounds have been isolated and investigated by X-ray crystal structure determinations. Their structures were found to be monomeric,[2d,3] dimeric,[4] or trimeric.[5] In all these compounds, the number of carbon atoms separating two magnesium atoms is four or higher. Cyclic bifunctional organomagnesium compounds with less than four carbon atoms separating both magnesiums are virtually insoluble in THF and are therefore assumed to be polymeric.[6] Their poor solubility prevented structural characterization.

We now present the synthesis and structure of three cyclic bifunctional organomagnesium compounds in which the number of carbon atoms separating both magnesium atoms is two or

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[†] Dedicated to Prof. Dr. U. Schöllkopf on the occasion of his 65th birthday.

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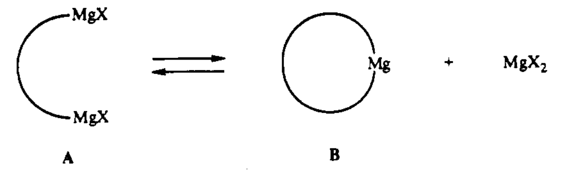
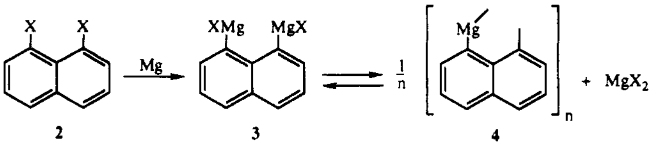
Scheme I



Scheme II



a : X = Br ; b : X = I

three. All magnesium-bonded carbon atoms in these compounds are sp^2 hybridized.

Results and Discussion

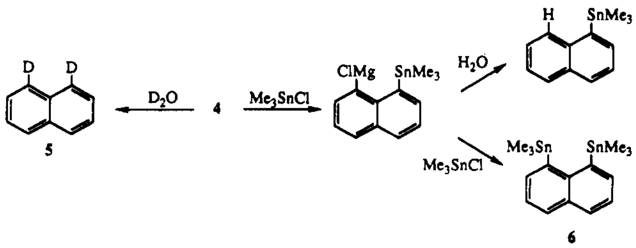
Several methods of preparing bifunctional organomagnesium compounds are available. The most important of these is the reaction of an organic dihalide with magnesium (direct synthesis); it results in the formation of a di-Grignard reagent or, more exactly, a solution having the formal composition of a di-Grignard reagent. Cyclic organomagnesium compounds can be obtained by three general methods: (A) conversion of a di-Grignard reagent into a cyclic organomagnesium compound by manipulation of the Schlenk equilibrium; (B) transmetalation of a cyclic organomercury compound with metallic magnesium; and (C) reaction of metallic magnesium with unsaturated molecules.

Synthesis of 1,8-Naphthalenediylmagnesium. Research on 1,8-dimetalated naphthalenes has been confined essentially to 1,8-dilithionaphthalene (**1**). It was first described by Letsinger et al. in 1962[7] and can be prepared in two ways: treatment of 1,8-dihalonaphthalenes **2** with *n*-butyllithium[7] or reaction of 1-bromonaphthalene with *n*-butyllithium, followed by a regioselective metalation using *n*-BuLi–TMEDA.[8] Reagent **1** has proved to be useful for the synthesis of 1,8-disubstituted naphthalenes; both organic[7,9] and organometallic[10] derivatives have been obtained.

In contrast, little attention has been paid to the corresponding organomagnesium compounds: the di-Grignard reagent **3** or the corresponding diarylmagnesium 1,8-naphthalenediylmagnesium (**4**), which are related by the Schlenk equilibrium (Scheme II). To our knowledge, there is only one brief mention by Schechter et al. of **3b** (X = I) as an alternative to **1** in the synthesis of 1*H*-cyclobuta[*de*]naphthalene.[9]

Compound **4** was obtained by the general method A (vide supra). Reaction of 1,8-dibromonaphthalene (**2a**) with magnesium in THF solution overnight at room temperature led to the formation of **3a**. The yield, 90%, was determined by hydrolysis followed by titration of the liberated base with HCl and of Mg^{2+} with ethylenediaminetetraacetic acid (EDTA);[11] the observed 1:1 ratio of $[OH^-]$ and $[Mg^{2+}]$ is usually a good indication of a Grignard reagent (RMgX). This analysis, however, does not give any information on the occurrence and position of the Schlenk equilibrium. Its establishment follows from the isolation of crystals of **4** upon cooling of the THF solution of **3a**. Hydrolysis of these crystals and titration with HCl and EDTA gave a ratio of 2:1 for $[OH^-]$:$[Mg^{2+}]$ as required for a diarylmagnesium species.

Scheme III



When 1,8-diiodonaphthalene (**2b**) was reacted with magnesium in THF at room temperature, a colorless precipitate formed immediately. The precipitate, which was isolated and shown to be magnesium iodide by titration, covered the magnesium surface and thus hindered the progress of the reaction. The THF solution contained **4**, as shown by titration, and unreacted **2b**; in order to drive the reaction to completion, it was necessary to add fresh magnesium and continue stirring. A better way of preparing **4** from **2b** and magnesium is to perform the reaction in 2-methyltetrahydrofuran (2-MeTHF). Under these conditions, a precipitate was *not* formed and the di-Grignard **3b** was obtained in 90% yield. Evaporation of the solvent gave an oily residue, which on addition of THF gave a precipitate of magnesium iodide; it was separated from the solution of **4** by filtration. Recrystallization of **4** from THF gave the pure compound.

In addition to hydrolysis and titration, **4** was chemically characterized by reaction with deuterium oxide, which gave [1,8-$^2H_2$]naphthalene (**5**) in quantitative yield, and with chlorotrimethylstannane, which gave 1,8-bis(trimethylstannyl)naphthalene (**6**)[10c] in low yield (22%) (Scheme III). The main product in this latter reaction after hydrolytic workup is 1-(trimethylstannyl)naphthalene, suggesting that the incorporation of a second trimethylstannyl group at a peri position is difficult, probably due to steric congestion. The ^1H and ^{13}C NMR spectra of **4** (vide infra) were in accord with the assigned structure.

The synthesis of **4** described above is a good illustration of general method A; differences in the solubilities of the three species involved in the Schlenk equilibrium are used to obtain **4** in a pure form.

Synthesis of *o*-Phenylenemagnesium. The direct synthesis of 1,2-di-Grignard reagents of benzene by reacting dihalobenzenes with magnesium is feasible, although the formation of benzyne is always a more or less prominent side reaction.[12] Under certain circumstances, such di-Grignards have been obtained in 20–40% yields.[13,14]

Transmetalation reactions were found to give better results. The synthesis of 1,2-bis(bromomagnesio)benzene (**9**), the di-Grignard analogue of *o*-phenylenemagnesium (**10**), has been reported by Wittig and Bickelhaupt; *o*-phenylenemercury (**7**) was converted by transmetalation to 1,2-dilithiobenzene (**8**), which, upon reaction with magnesium bromide, gave **9** (Scheme IV).[15]

In analogy to the transformation **7** → **8**, we have prepared *o*-phenylenemagnesium (**10**) by reacting **7** with metallic magnesium in THF (Scheme V); this is an illustration of the general method B (vide supra). The progress of this reaction was monitored by the disappearance of the sparingly soluble **7**. After

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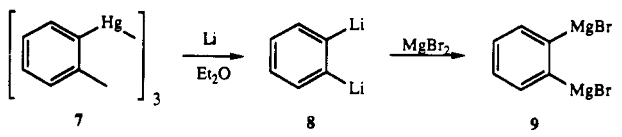
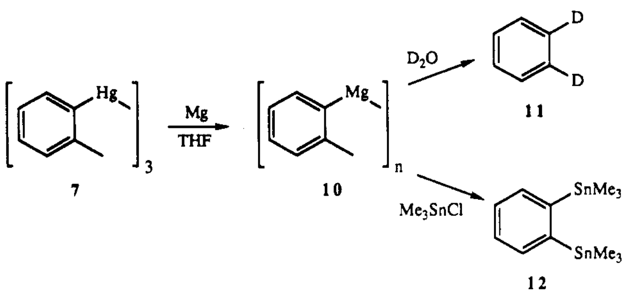
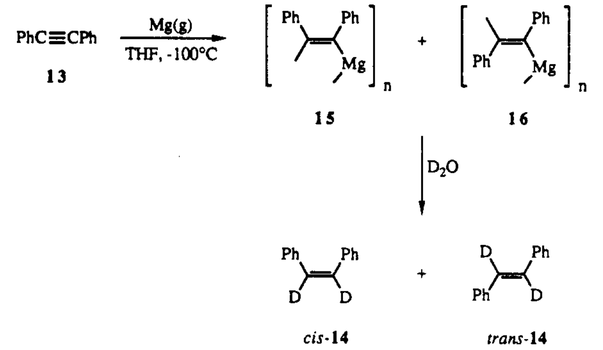
Scheme IV



Scheme V



Scheme VI



2 weeks of being stirred at room temperature, the resulting clear, brownish solution was carefully decanted from the finely divided amalgam to give **10** in 85% yield; crystallization from THF gave **10** in 68% isolated yield.

The compound was identified by its ^1H and ^{13}C NMR spectra (vide infra), which were in accordance with the assigned structure. Chemical derivatization with deuterium oxide or chlorotrimethylstannane yielded [1,2-$^2H_2$]benzene (**11**) or 1,2-bis(trimethylstannyl)benzene (**12**),[16] respectively.

Synthesis of Diphenylvinylenemagnesium. An example of the addition of magnesium to unsaturated organic compounds (general method C) is the reaction of magnesium with diphenylacetylene (**13**). The analogous reaction of lithium with **13** has been described by Szwarc et al., who observed that at −78 °C in THF, the dilithium adduct of **13** is formed.[17]

In our experience, unactivated sublimed magnesium in THF does not react with **13**, neither at room temperature nor under reflux. Activation with 1,2-dibromoethane or iodine did not result in the formation of the desired organomagnesium compound either. When magnesium was sublimed into a solution of **13** in THF at −100 °C in an apparatus designed after Kündig and Perret,[18] a reaction did occur. After the reaction mixture had been allowed to warm to room temperature, a dark brown solution containing a yellow precipitate was obtained. Reaction of an aliquot of the total reaction mixture with deuterium oxide yielded both *cis*-**14** and *trans*-**14** in a 3:2 ratio, indicating the formation of both *cis*-(**15**) and *trans*-diphenylvinylenemagnesium (**16**) (Scheme VI). The solution was decanted from the precipitate. Apparently, it contained mainly the better soluble **15**, because on cooling, pure **15** crystallized as bright yellow needles which, on reaction with deuterium oxide, gave *cis*-**14** exclusively.

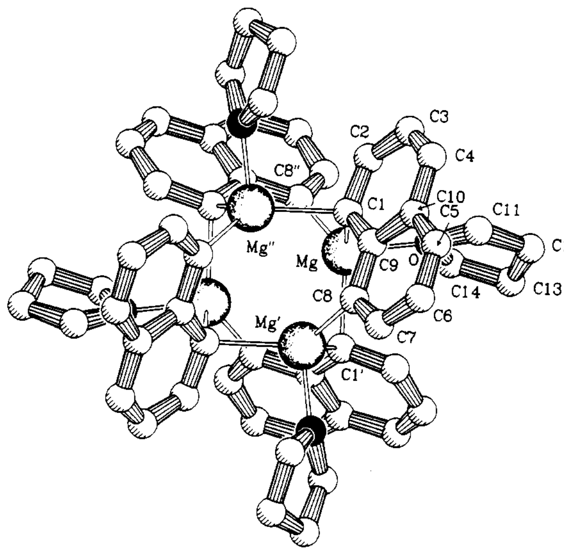


Figure 1. Pluton drawing of the molecular structure of **4**, with the adopted atom labeling. Hydrogen atoms were omitted for clarity.

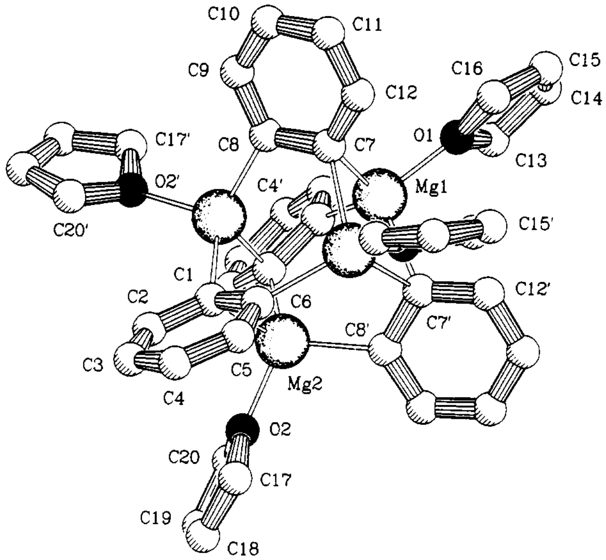


Figure 2. Pluton drawing of the molecular structure of **10**, with the adopted atom labeling. Hydrogen atoms were omitted for clarity.

X-ray Crystal Structures. Surprisingly, the X-ray crystal determinations of compounds **4**, **10**, and **15** revealed all three of them to be tetrameric clusters; their structures are depicted in Figures 1–3, respectively; bond lengths and angles are given in Tables I–III.

In organomagnesium chemistry, only one X-ray crystal structure of a tetrameric cluster is known: (η^5-cyclopentadienyl)-magnesium ethoxide (**17**) (Figure 4). This structure consists of a cubane skeleton with magnesium and oxygen occupying the corners.[19] It can, however, also be described as four magnesium atoms arranged as a tetrahedron, on each face (formed by three magnesiums) of which a μ^3-bridging ethoxide group is positioned. In this way the resemblance with the structures of **4**, **10**, and **15** becomes obvious; they can, likewise, best be described as consisting of a (distorted) tetrahedron of four magnesium atoms with one organic group attached to each of its faces. An important difference resides in the nature of the bridging group. In **17**, it

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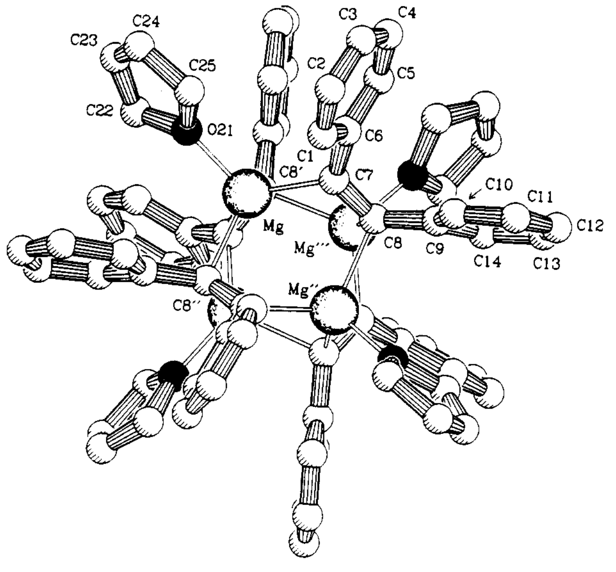

Figure 3. Pluton drawing of the molecular structure of **15**, with the adopted atom labeling. Hydrogen atoms were omitted for clarity.

Table I. Selected Bond Distances and Bond Angles for **4**

distance (Å)		angles (deg)	
Mg–O	2.060(3)	O–Mg–C(8)^b	105.05(19)
Mg–C(8)^b	2.142(5)	O–Mg–C(1)	99.96(16)
Mg–C(1)	2.271(5)	O–Mg–C(1)^a	98.3(2)
Mg–C(1)^a	2.267(5)	C(1)–Mg–C(8)^b	112.06(19)
C(1)–C(2)	1.367(8)	C(1)–Mg–C(1)^a	113.4(2)
C(1)–C(9)	1.455(7)	C(8)^b–Mg–C(1′)	123.55(19)
C(2)–C(3)	1.419(8)	Mg–C(1)–Mg^b	89.80(18)
C(3)–C(4)	1.302(9)	C(2)–C(1)–C(9)	117.2(5)
C(4)–C(10)	1.418(10)	C(1)–C(2)–C(3)	123.6(5)
C(5)–C(6)	1.334(12)	C(2)–C(3)–C(4)	121.0(6)
C(5)–C(10)	1.443(9)	C(3)–C(4)–C(10)	119.8(6)
C(6)–C(7)	1.418(10)	C(6)–C(5)–C(10)	122.5(6)
C(7)–C(8)	1.382(8)	C(5)–C(6)–C(7)	118.1(6)
C(8)–C(9)	1.400(8)	C(6)–C(7)–C(8)	125.2(6)
C(9)–C(10)	1.446(8)	C(1)–C(9)–C(8)	120.0(4)
Mg–Mg^a	3.203(2)	C(4)–C(10)–C(9)	121.4(5)
Mg–Mg^b	3.430(2)	C(4)–C(10)–C(5)	122.7(6)

[a] Indicates symmetry operation $y - {}^1/_4, {}^5/_4 - x, {}^1/_4 - z$. [b] Indicates symmetry operation ${}^5/_4 - y, {}^1/_4 + x, {}^1/_4 - z$.

Table II. Selected Bond Distances and Bond Angles for **10**

distances (Å)		angles (deg)	
Mg(1)–O(1)	2.041(4)	O(1)–Mg(1)–C(6)	112.5(2)
Mg(1)–C(6)	2.171(5)	O(1)–Mg(1)–C(7)	108.4(4)
Mg(1)–C(7)	2.273(6)	O(1)–Mg(1)–C(7)^a	106.3(2)
Mg(1)–C(7)^a	2.291(5)	C(6)–Mg(1)–C(7)	109.8(2)
Mg(2)–O(2)	2.031(4)	C(6)–Mg(1)–C(7)^a	116.3(2)
Mg(2)–C(1)	2.314(6)	C(7)–Mg(1)–C(7)^a	102.9(2)
Mg(2)–C(1)^a	2.237(6)	O(2)–Mg(2)–C(1)	102.3(2)
Mg(2)–C(8)^a	2.139(5)	O(2)–Mg(2)–C(1)^a	113.1(2)
C(1)–C(6)	1.418(8)	O(2)–Mg(2)–C(8)^a	111.0(2)
Mg(1)–Mg(1)^a	2.804(2)	C(1)–Mg(2)–C(1)^a	101.2(2)
Mg(1)–Mg(2)	3.305(3)	C(1)–Mg(2)–C(8)^a	120.0(2)
Mg(1)–Mg(2)^a	3.548(3)	C(1)^a–Mg(2)–C(8)^a	108.9(2)
Mg(2)–Mg(2)^a	2.841(2)	C(2)–C(1)–C(6)	118.4(5)
		C(1)–C(6)–C(5)	116.5(5)
		Mg(1)–C(7)–Mg(1)^a	75.8(2)
		Mg(2)–C(1)–Mg(2)^a	77.2(2)

[a] Indicates symmetry operation ${}^1/_2 - x, y, -z$.

is an alkoxide; alkoxides are well known for their tendency to form clusters and similar types of associated species.[19a] In **4**, **10**, and **15**, bridging is achieved by (formal) dicarbanions. To our knowledge, this type of purely carbon-bonded, tetrameric organomagnesium clusters has not been encountered previously.

Table III. Selected Bond Distances and Bond Angles for **15**

distances (Å)		angles (deg)	
Mg–O(21)	2.027(8)	O(21)–Mg–C(7)	113.7(4)
Mg–C(7)	2.178(10)	O(21)–Mg–C(8)^a	106.4(4)
Mg–C(8)^a	2.265(9)	O(21)–Mg–C(8)^b	106.8(4)
Mg–C(8)^b	2.261(11)	C(7)–Mg–C(8)^a	106.3(4)
C(6)–C(7)	1.519(14)	C(7)–Mg–C(8)^b	111.6(4)
C(7)–C(8)	1.354(14)	C(8)^a–Mg–C(8)^b	111.9(4)
C(8)–C(9)	1.480(15)	Mg^b–C(8)–Mg^c	84.6(3)
Mg–Mg^a	3.045(5)	C(6)–C(7)–Mg	123.0(7)
Mg–Mg^b	3.338(5)	C(8)–C(7)–Mg	111.0(6)
		C(6)–C(7)–C(8)	126.0(9)
		C(7)–C(8)–C(9)	122.4(9)

[a] Indicates symmetry operation $y, 1 - x, 1 - z$. [b] Indicates symmetry operation $1 - x, 1 - y, z$. [c] Indicates symmetry operation $1 - y, x, 1 - z$.

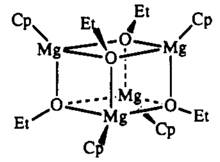

Figure 4. Structure of $(CpMgOEt)_4$ (Cp = η^5-cyclopentadienyl).[19a]

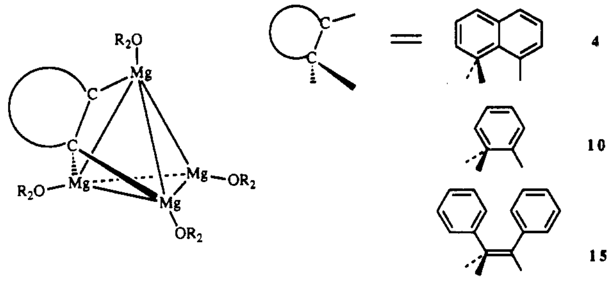

Figure 5. General bonding scheme of **4**, **10**, and **15** (only one organic group shown).

The structures of **4**, **10**, and **15** can also be looked upon as consisting of two dimeric units, connected by μ^2-bridging carbon atoms. In this description, two eight-membered rings in **4** and two six-membered rings in **10** and **15** are thus connected. The connection of two dimers may well be the genesis of the tetramers, and this is confirmed by several aspects of the structures, such as the different magnesium–magnesium distances; however, for the sake of simplicity, we choose to describe these structures as being derived from magnesium tetrahedrons.

The structure of a tetrameric cluster is schematically represented for one organic group in Figure 5. The organic group is bonded to the three magnesium atoms of one tetrahedral plane via two carbon atoms; one carbon atom is bonded via a magnesium–carbon single bond and the other is bridging in a μ^2 fashion over two magnesium atoms by a 3-center, 2-electron bond (cf. the μ^3-bridging of ethoxide groups in **17**). In the following, the shorthand notation η^2-(σ,μ^2) will be used to describe this type of bonding of the dicarbanionic ligand.

The magnesium–carbon bonding distances in **4**, **10**, and **15** are in reasonable agreement with similar ones reported for normal, monovalent organomagnesium compounds. Our Mg–C single bonds vary from 2.14 to 2.18 Å; values of 2.13 to 2.19 Å have been reported for diarylmagnesium compounds.[20] A few diarylmagnesium compounds containing bridging aryl groups are also known.[21] The values found for the Mg–C μ-bond distances in these compounds correspond to those found in **4**, **10**, and **15** (2.24–2.31 Å). The Mg–C_μ–Mg angles are slightly different for the three complexes **4**, 89.8(2)°; **10**, 77.2(2)/75.8(2)°; and **15**, 84.6(3)°.

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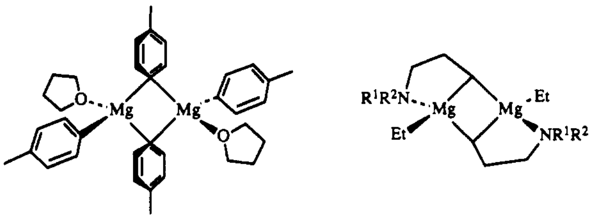
(20) Markies, P. R.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Adv. Organomet. Chem.* **1991**, *32*, 147 and references cited therein.

(21) (a) Markies, P. R.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; van der Sluis, P.; Spek, A. L. *J. Organomet. Chem.* **1990**, *393*, 315. (b) Thoennes, D.; Weiss, E. *Chem. Ber.* **1978**, *111*, 3726.



(a) (b)

Figure 6. Structures of dimeric organomagnesium aggregates. (a) (p-tolyl$_2$Mg)$_2$ (**18**). (b) R^1, R^2 = methyl; R^1 = methyl, R^2 = cyclohexyl.

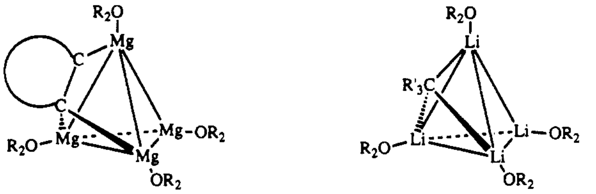


Figure 7. Comparison of tetrameric organomagnesium clusters with tetrameric organolithium clusters.

An important feature of the structures of **4**, **10**, and **15** is the coordination of the magnesium atoms, which is essentially the same for all magnesiums in the three structures. They have a pseudotetrahedral coordination to three carbons—one of which is single bonded and two are bridging—and only *one* THF molecule, while in simple organomagnesium compounds, tetracoordinate magnesium is coordinated to two ether molecules. To simplify the discussion of this coordination mode, the following notation will be used in which the ligating atoms are listed, and for the carbon atoms, the nature of the bond to magnesium is indicated $OC_\sigma(C_\mu)_2$. In this notation, the normal coordination mode of $R_2Mg{\cdot}(OR_2)_2$ is represented as $O_2(C_\sigma)_2$.

Only one similar $OC_\sigma(C_\mu)_2$ coordination has been reported, the dimeric [(p-tolyl)$_2$Mg·THF]$_2$ (**18**) (Figure 6a). This complex cocrystallized in a 1:1 ratio with the monomeric form (p-tolyl)$_2$Mg·THF$_2$ (which has the normal coordination mode $O_2(C_\sigma)_2$).[21a] Furthermore, two structures with a $NC_\sigma(C_\mu)_2$ coordination mode have been published[22] (Figure 6b).

These complexes, together with **17**, are the only examples of structurally identified organomagnesium compounds containing no metals other than magnesium which show aggregate formation in combination with coordination of ethers. Higher aggregates are typically formed only in the absence of Lewis bases, for instance $(Me_2Mg)_n$,[23] and $(Ph_2Mg)_n$,[21a] both of which have the coordination mode $(C_\mu)_4$. The reluctance of organomagnesium compounds to form aggregates is in sharp contrast with the behavior of organolithium compounds, where tetrameric and higher aggregates are common, whereas smaller ones are an exception.[24a]

There is an interesting resemblance between the structures of tetrameric alkyllithium compounds and those of **4**, **10**, and **15**. The alkyllithium compounds consist of a tetrahedron of lithium atoms with an alkyl group μ^3-bridging three lithiums,[24a] roughly similar to the structures of our organomagnesium clusters (Figure 7). In the lithium case, a monocarbanion bridges a $(Li^+)_3$ triangle in a μ^3 fashion, where in **4**, **10**, and **15**, a dicarbanion bridges a $(Mg^{2+})_3$ triangle in the η^2-(σ,μ^2) mode.

This stoichiometric correspondence of $(Li^+R^-)_4$ versus $(Mg^{2+}R^{2-})_4$ must be one of the factors governing the cluster formation of **4**, **10**, and **15**, but other electronic and steric factors are of importance as well. Aggregate formation of organometallic compounds is generally caused by the polarity of these compounds.[24a,b] Since organomagnesium compounds are less polar than organolithiums, they have an inherently lower tendency to form aggregates. Furthermore, magnesium is a stronger Lewis acid than lithium and therefore has a greater preference for hard Lewis bases, such as THF molecules. This explains why in organomagnesium chemistry, $O_2(C_\sigma)_2$ coordination is, in general, more stable than $OC_\sigma(C_\mu)_2$ and $(C_\mu)_4$ coordination; monomers will therefore be more stable than dimers such as **18**. In solution, however, monomer–dimer equilibria exist, as is for example illustrated by the case of (p-tolyl)$_2$Mg (vide supra).[21a]

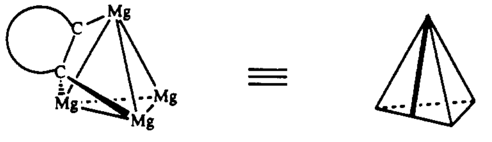


Figure 8. Schematic representation of a divalent organic group on top of one face of a tetrahedron of magnesium atoms.

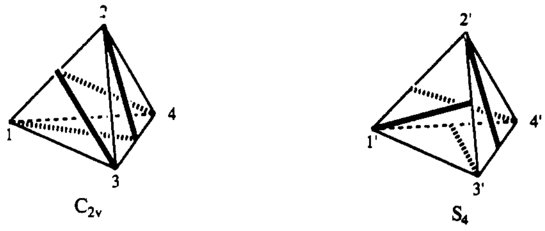


Figure 9. Two possible arrangements of four divalent organic groups bridging a tetrahedron of magnesium atoms.

Only in special cases, higher aggregates are formed. Thus in **17**, the ethoxide anions, combining μ_3-bridging ability[19] with hard Lewis base character, lead to tetramerization. We feel that in **4**, **10**, and **15**, other factors are decisive. With the exception of dimeric **4**, monomeric or dimeric species are unlikely to be formed because the small C–Mg–C bond angles in such species would cause excessive strain.[20] For higher aggregates and for dimeric **4**, models show that the $O_2(C_\sigma)_2$ coordination of the two magnesiums bonded to the same organic group (1,8-naphthalenediyl, o-phenylene, or *cis*-diphenylvinylene) would result in overcrowding, due to the proximity of the magnesiums with their two ether ligands. Aggregate formation, on the contrary, yields species that are less crowded, because only one THF molecule per magnesium is necessary to achieve tetracoordination. Finally, it should be emphasized that the specific geometric features of the three dicarbianions are also important. Their rigidity as well as the short distance between the two carbanionic carbon atoms in **4**, **10**, and **15** are prerequisite for the η^2-(σ,μ^2)-bridging mode, as they provide a good "fit" of the dianion on top of the Mg_3 triangle.

Not directly evident from the PLUTON drawings (Figures 1–3) is the relation between the four organic groups spanning the tetrahedron of magnesium atoms. Therefore, the schematic representation of Figure 8 is introduced. The organic groups are represented by their projection (bold line) on the face of the magnesium tetrahedron over which they are positioned. When the bold line ends at the corner of a triangle, it indicates a Mg–C σ-bond; when it ends in the center of an edge of the tetrahedron, it indicates a μ carbon atom bridging between the two magnesium atoms connected by that edge.

Taking into account that each magnesium has a $OC_\sigma(C_\mu)_2$ coordination mode, two arrangements are possible when four groups are introduced (Figure 9). They differ in symmetry, one possessing C_{2v} and the other S_4 symmetry. Differences between the two arrangements are particularly important for the Mg–Mg relationships. The C_{2v} arrangement has two pairs of magnesiums (Mg(1)–Mg(2) and Mg(3)–Mg(4)), each pair being μ-bridged by *two* carbon atoms; this results in two four-membered Mg_2C_2 rings. The other four pairs of magnesiums (Mg(1)–Mg(3), Mg-

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(22) Bogdanovic, B.; Koppetsch, G.; Krüger, C.; Mynott, R. *Z. Naturforsch.* **1986**, *41b*, 617.

(23) Weiss, E. *J. Organomet. Chem.* **1965**, *4*, 101.

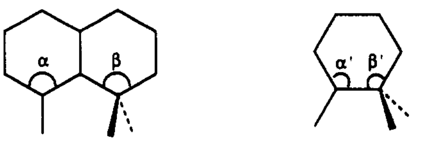
(24) (a) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353 and references cited therein. (b) Schade, C.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1987**, *26*, 169.

(1)–Mg(4), Mg(2)–Mg(3), and Mg(2)–Mg(4)) do not share a μ-bridging carbon atom. In the S_4 arrangement, there are four pairs of magnesiums that share one μ-bridging carbon, (Mg(1′)–Mg(2′), Mg(1′)–Mg(4′), Mg(2′)–Mg(3′), and Mg(3′)–Mg(4′)) and two pairs that share none (Mg(1′)–Mg(3′) and (Mg(2′)–Mg(4′)); there are no four-membered Mg_2C_2 rings.

Actually, both arrangements are realized: **4** and **15** have the S_4-like and **10** has the C_{2v}-like arrangement. The structure of **10** possesses only approximate C_{2v} symmetry. It has, in fact, C_2 symmetry, because the bridging of the phenylenes is unsymmetrical, i.e., the μ^2-bridging carbon atom is closer to one magnesium than to the other (2.237(6) vs 2.314(6) and 2.273(6) vs 2.291(5) Å, respectively, for the two independent phenylenes). In the structure of **10**, two four-membered Mg_2C_2 rings are present (Mg(1)–Mg(1′) and Mg(2)–Mg(2′), see Figure 2). The Mg–Mg distance in these rings is very short (2.804(2) and 2.841(2) Å, respectively) when compared to the other Mg–Mg distances in **10** (3.305(2)–3.548(2) Å). It is evident that this leads to a considerable distortion of the tetrahedron. Such a distortion is also present in the structures with S_4 symmetry. In **4**, the Mg–Mg distances are 3.203(2) Å (*one* bridging 1,8-naphthalenediyl) and 3.430(2) Å (unbridged). In **15**, the corresponding values are 3.046(5) and 3.338(4) Å, respectively. The tetrahedron of magnesiums in **4** is larger than that in **15**, which is obviously a reflection of the two different carbon skeletons, in particular of the larger distance between the two carbanionic centers in **4**.

The preference of a particular compound for one of the two arrangements is not obvious. In solution, there probably is a fast equilibrium between both arrangements, as evidenced by the equivalence of the σ- and μ-bridging carbon atoms in the ^{13}C NMR spectra (vide infra), indicating that both arrangements are very close in energy. A priori, a conceivable factor might have been the number of carbon atoms separating both magnesium functionalities in one organic group. However, this can be easily dismissed, as in **10** and **15** the magnesium atoms are bonded to adjacent carbon atoms, whereas in **4** they are separated by three carbon atoms, while the arrangements adopted by **10** and **15** are different (C_{2v} and S_4, respectively), whereas those of **4** and **15** are not. Possibly, the bulkiness of the organic group may play a role: **4** and **15**, containing larger organic groups, have the S_4 arrangement, while **10**, with the smaller *o*-phenylene group, has the C_{2v} arrangement.

Two metal substituents in close vicinity are obviously causing considerable steric hindrance to each other. Thus, while **10** is easily derivatized with chlorotrimethylstannane to give the di- and monosubstitution products in a ratio of 80:20, **4**, under the same conditions, yields a ratio of di-, mono-, and unsubstituted products of 22:67:11. Similarly, **6** and related compounds reveal serious distortions due to steric hindrance.[10] Obviously, 1,3-disubstitution with (more or less) parallel orientation of the 1,3-bonds as in **4** causes more crowding than 1,2-disubstitution with angles of approximately 120°; for this reason, **4** is more crowded than **10**. The higher degree of congestion in **15** as compared to **10** can be ascribed to the two phenyl substituents at the central double bond in the former. The observation that the less crowded situation as in **10** goes along with the C_{2v} arrangement suggests that its doubly μ-bridged, four-membered Mg_2C_2 rings are inherently more stable than the "open", alternating singly μ-bridged rings in the S_4 arrangement; on the other hand, the Mg_2C_2 rings entail closer proximity of the bridging groups and will be unfavorable when the bulk of these bridging groups increases. In view of the slight energy differences between the two different arrangements, crystal packing effects may be another important factor. In this regard, it may be relevant that a large amount of free, disordered THF molecules is present in the crystals of the S_4 arranged **4** and **15**. These molecules seem to be necessary for the stability of the crystal; this certainly holds for crystals of **4**, as they collapse in a THF-free environment, either in vacuum or under a nitrogen atmosphere. In contrast, the crystals of **10** are completely free of nonbonded THF molecules; apparently, the crystal packing is quite different. It is at present unclear which of these factors is dominant.



4 : α = 115.2(5)
β = 117.2(5)

10 : α′ = 116.5(5)/117.0(5)
β′ = 118.4(5)/118.2(5)

Figure 10. Effect of magnesium substitution on endocyclic angles.

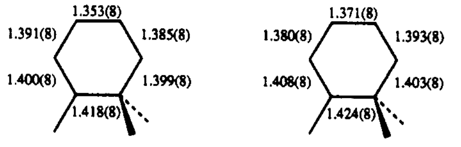


Figure 11. Bond distances (Å) in the two independent *o*-phenylene fragments of (**10**·THF)$_4$.

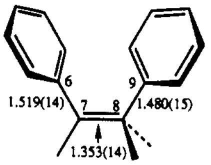


Figure 12. Bond distances (Å) in the *cis*-diphenylene fragment of (**15**·THF)$_4$.

The organic fragments in the crystalline complexes show some interesting features. The endocyclic C–C(Mg)–C bond angles α and β (see Figure 10) are distinctly smaller than the 120° usually found in the unsubstituted aromatics. This is a common feature for metalated aromatic compounds.[25] The angles at bridging carbon atoms (β and β') are slightly larger than those involving σ-bonds to carbon (α and α').

The carbon–carbon bond distances within the *o*-phenylene fragments of **10** are influenced by the substitution (Figure 11). The C(1)–C(2) bond distance is noticeably longer (about 1.42 Å) than the other C–C bond distances; the latter are close to that in benzene itself (1.397 Å[26]) with the exception of the bonds opposite to C(1)–C(2), which are remarkably short (average 1.36 Å). Two factors may be responsible, and both are a consequence of the fact that carbon atoms bonded to magnesium atoms bear a considerable negative charge: the charge as such will lead directly to electrostatic repulsion and indirectly to rehybridization of the carbon atoms such that the C–Mg bond will have more s-character and the intraannular C–C bonds more p-character; this is also in line with the small intraannular angles (vide supra).

The carbon–carbon distances in the benzene rings of **10** do not support the concept that C(2) is tetracoordinate in the sense that they resemble those in the Wheland complex of aromatic electrophilic substitution; rather, like in other bridging alkyl or aryl groups, the Mg–C(2)–Mg bond is of the 3-center, 2-electron type involving only the carbanionic σ-orbital of C(2).

An interesting detail of the structure of **15** involves the C(6)–C(7) and the C(8)–C(9) bond distances, which differ considerably: the bond of C(9) to the bridging C(8) is shorter (Figure 12). Also, the angles between the planes of the phenyl groups at C(7) and C(8) and the central double bond plane C(6)–C(7)–C(8)–C(9) are 73 and 41°, respectively. Both features suggest that a more efficient benzylic type π-overlap exists between the

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(25) (a) Thoennes, D.; Weiss, E. *Chem. Ber.* **1978**, *111*, 3726 and references cited therein. (b) Harder, S. Thesis, Rijksuniversiteit Utrecht, 1990.

(26) Ermer, O. *Angew. Chem.* **1987**, *99*, 791 and references cited therein.

(27) (a) van Vulpen, A.; Coops, J. *Rec. Trav. Chim. Pays-Bas* **1967**, *85*, 203. (b) van Vulpen, A. Thesis, Vrije Universiteit, Amsterdam, 1967. (c) Freijee, F. J. M. Thesis, Vrije Universiteit, Amsterdam, 1981.

Table IV. Degree of Association of **4** and **10**

4				**10**			
$[\mathrm{Mg}]_f$[a]	S_a[b]	S_{th}[c]	i[d]	$[\mathrm{Mg}]_f$[a]	S_a[b]	S_{th}[f]	i[d]
5.21	0.044	0.229	5.20[e]	7.12	0.079	0.318	4.02
10.42	0.113	0.459	4.06	13.69	0.152	0.611	4.02
15.63	0.172	0.688	4.00	19.77	0.228	0.882	3.87
20.84	0.229	0.917	4.00	25.41	0.296	1.133	3.82
26.05	0.291	1.146	3.94	30.65	0.345	1.367	3.96
31.26	0.350	1.375	3.93				

[a] $[\mathrm{Mg}]_f$ = formal concentration of magnesium in mmol L^{-1} (i.e., concentration if all particles were monomeric, containing one Mg atom). [b] S_a = apparent rate of the evaporation in mm h^{-1}. [c] S_{th} = theoretical rate of evaporation (in mm h^{-1}) = $[\mathrm{Mg}]_f S_s$, where S_s (in mm h^{-1} mmol^{-1} L^{-1}) is the standard rate of evaporation found by calibration of the apparatus with triphenylmethane, S_s (296 K) = 0.0440 mm h^{-1} mmol^{-1} L^{-1}. [d] Association number $i = S_{th}/S_a$. [e] The first value is often unreliable due to the low concentration (ref 27). [f] As in ref c, the standard rate of evaporation found by calibration of the apparatus with triphenylmethane just before the experiment: S_s (296 K) = 0.0446 mm h^{-1} mmol^{-1} L^{-1}.

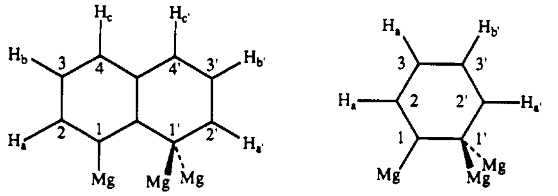

Figure 13. Numbering adopted for the discussion of the NMR spectra.

phenyl group at C(8) and the olefinic bond C(7)–C(8), resulting in a slight lengthening of this bond and shortening of the C(8)–C(9) bond.

Structure in Solution and NMR Spectroscopy. The novel type of crystal structure found for **4**, **10**, and **15** immediately raised questions about their structure in solution. The appreciable solubility of both **4** and **10** in THF (ca. 0.1 M at room temperature) allowed the investigation of their structure in THF solution by association measurements and by NMR spectroscopy. The degrees of association of **4** and **10** in THF were measured by the method of stationary isothermal distillation. Both compounds were found to be tetrameric in THF solution at room temperature (**4**, association number i = 3.98; **10**, i = 3.92). The data for the measurements are collected in Table IV.

Assuming that the tetrameric structures of **4** and **10** are the same in solution as in the crystalline state, this should have certain consequences for their NMR spectra. In the crystal, the organic groups are unsymmetric due to the fact that one carbon atom (C(1) in Figure 13) is single bonded to magnesium and the other one (C(1′)) is μ-bridging between two magnesiums (note the different numbering adopted for this part of the discussion).

As a consequence, C(1) and C(1′), but also the carbon atoms C(n) and C(n'), as well as the protons they carry, should experience different chemical surroundings, and therefore, in principal, they should have different chemical shifts. However, such differences were not observed (see Experimental Section); the compounds gave spectra as expected for a symmetrically 1,8-disubstituted naphthalene and a symmetrically 1,2-disubstituted benzene, respectively. In the ^{1}H broad-band decoupled ^{13}C NMR spectrum, signals assignable to C(1) and C(1′) are sharp singlets; line broadening relative to other signals was not observed. Measurements at low temperatures (as far as −80 °C) for **10** did not result in any decoalescence phenomena; such measurements were impossible for **4** because it precipitated on lowering the temperature.

We conclude that in THF solution there must be a mechanism leading to exchange of C(1) and C(1′) (or C(n) and C(n'), etc.) at a rate which is fast on the NMR time scale. An intermolecular exchange, which is usually rapid for monovalent organomagnesium compounds, is not likely for the divalent species at hand because of their stable tetrameric aggregation. An intramolecular exchange reaction may seem complex at first sight, since the conversion of a Mg–C σ-bond to a Mg–C μ-bond must result in complex changes throughout the cluster. The most simple way of C(1)–C(1′) exchange in one organic group involves rotation of this group relative to the face of the tetrahedron above which it is positioned (Figure 14); by this operation, a σ-bonded carbon (C_a) becomes μ-bridging, while the μ-bridging C_b becomes σ-bonded. From the representation of the structure by use of the projection of the organic group (cf. Figures 8 and 9), it is obvious that a rotation by only 60° is sufficient to achieve this exchange. A distinction between a concerted process and a mechanism in which these changes of the Mg–C bonds occur stepwise, e.g., first exchange of one of the bridging bonds of C_a, is not a priori possible. Both processes involve only a minor movement of atoms, as the nonbonding distances C(1)–Mg(2), C(1)–Mg(3), and C(1′)–Mg(1) are rather small.

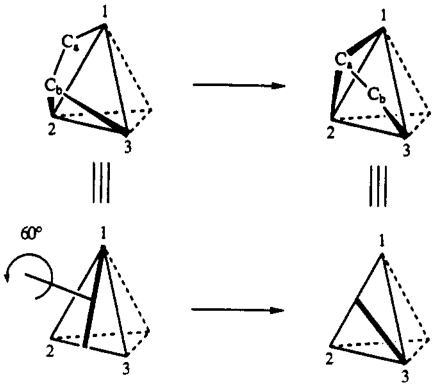

Figure 14. Rotation of an organic group.

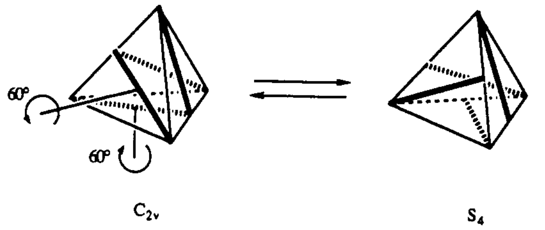

Figure 15. Interconversion of the arrangements by two rotations.

If one considers the tetrameric cluster as a whole, it is obvious that the rotation of one of the organic groups cannot occur without simultaneous rotations of other groups in the same cluster in order to maintain tetracoordination ($OC_\sigma(C_\mu)_2$) for each magnesium. The conversion of a C_{2v} arranged cluster into another one of C_{2v} symmetry requires rotation of all *four* organic groups. The same holds for an S_4–S_4 conversion. A conversion of a C_{2v} arranged cluster into one of S_4 symmetry requires only *two* of the organic groups to rotate (Figure 15). This interconversion between both arrangements results in the C(1)–C(1′) exchange for two of the four groups. At present, we feel that the intramolecular process is the one which is actually occurring; it is simple and can explain the observed phenomena in a satisfactory fashion.

Experimental Section

Apart from the synthesis of diphenylvinylenemagnesium, all reactions were carried out in fully sealed and evacuated glass apparatus. Solvents were dried on a sodium potassium alloy before use. Magnesium was sublimed twice before use. 1,8-Dibromonaphthalene,[10c] 1,8-diiodonaphthalene,[28] and o-phnylenemercury[15] were prepared according to published procedures. NMR spectra were recorded on Bruker WM 250 or AC 200 NMR spectrometers. GCMS analyses were performed on a Hewlett-

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[28] House, H. O.; Koepsell, D. G.; Campbell, W. J. *J. Org. Chem.* **1972**, *37*, 1003.

Packard 5970 Mass Selective Detector, equipped with a Hewlett-Packard 5890 gas chromatograph.

Synthesis of 1,8-Naphthalenediylmagnesium (4). (a) From 1,8-Dibromonaphthalene and Magnesium. 1,8-Dibromonaphthalene (1.56 g, 5.46 mmol) was stirred with magnesium (2.50 g, 103 mmol) in THF (80 mL) for 24 h. After the excess of magnesium was removed by filtration, an aliquot of known volume was hydrolyzed. Titration (HCl, EDTA) showed the presence of 9.75 mmol of base and 9.95 mmol of Mg^{2+} (90% yield of **3a**). Cooling of a solution of **3a** (0.6 mmol) in THF (10 mL) gave pale yellow crystals, which were crystallized twice from THF. Hydrolysis and titration of the resulting colorless crystals showed that $[OH^-]:[Mg^{2+}] = 2.0:1$, indicating their identity as **4**.

4·(THF)*n*: ^1H NMR (200 MHz, $[^2H_8]$THF, ref $[^2H_7]$THF = 1.75 ppm) δ 7.75 (dd, $^3J(HH) = 6.2$ Hz, $^4J(HH) = 1.4$ Hz, 2 H, H(2,7)), 7.54 (dd, $^3J(HH) = 8.0$ Hz, $^4J(HH) = 1.4$ Hz, 2 H, H(4,5)), 7.06 (dd, $^3J(HH) = 8.0$ Hz, 6.2 Hz, 2 H, H(3,6)); ^{13}C NMR (50.32 MHz, $[^2H_8]$-THF, ref $[^2H_8]$THF = 67.4 ppm) δ 176.2 (bs), 159.2 (bs), 141.4 (dd $^1J(CH) = 153$ Hz, $^3J(CH) = 8$ Hz), 133.3 (bs), 128.8 (bd $^1J(CH) = 154$ Hz, $^3J(CH) < 5$ Hz), 124.3 (bd, $^1J(CH) = 153$ Hz); ^{13}C NMR (62.9 MHz, $[^2H_8]$toluene, ref $[^2H_8]$toluene = 20.5 ppm) δ 176.1 (bs), 159.0 (bs), 141.4 (dd $^1J(CH) = 153$ Hz, $^3J(CH) = 8$ Hz), 133.2 (bs), 124.4 (d, $^1J(CH) = 157$ Hz), 68.4 (t, $^1J(CH) = 148$ Hz, THF C_α), 25.2 (t, $^1J(CH) = 134$ Hz, THF C_β).

(b) From 1,8-Diiodonaphthalene and Magnesium. 1,8-Diiodonaphthalene (**2b**) (3.80 g, 10.0 mmol) and magnesium (2.50 g, 103 mmol) were stirred in 2-MeTHF (100 mL) for 12 h. The excess of magnesium was removed by filtration. Titration of an aliquot of known volume showed that 17.7 mmol of base and 17.7 mmol of Mg^{2+} were present (89% of **3b**). Removal of 2-MeTHF by distillation yielded a thick, yellowish-brown oil. Addition of THF (180 mL) resulted in the immediate formation of a precipitate; filtration gave a brown solution. Crystallization by cooling of a saturated THF solution gave **6** (6.9 mmol, 69% based upon **2b**; determined by titration).

Reaction of 4 with Deuterium Oxide. A solution of **4** (0.017 mmol) in THF (7 mL) was reacted with ca. 0.5 mL of deuterium oxide. Water and diethyl ether were added and the layers separated. The aqueous layer was extracted with diethyl ether. The combined organic phases were washed with water and dried over $MgSO_4$. The solvent was removed in vacuo, leaving 0.0217 g of 1,8-dideuterionaphthalene (**5**) (98%).

5: ^1H NMR ($CDCl_3$, 200 MHz, ref $CHCl_3$ = 7.26 ppm) δ 7.8–7.9 (m, 2 H, H(4,5)), 7.47 (bd $^1J = 5.6$ Hz, 4H, H(2,3,6,7)). This second-order spectrum was simulated; best results were obtained using the coupling constants $^3J(D(1)H(2)) = 1.5$ Hz, $^4J(D(1)H(3)) = 0.2$ Hz, $^5J(D(1)H(4)) = 0.0$ Hz, $^3J(H(2)H(3)) = 6.0$ Hz, $^4J(H(2)H(4)) = 1.4$ Hz, and $^3J(H_3H_4) = 8.6$ Hz and a $\Delta\nu(H(4,5)–H(2,3,6,7)) = 75$ Hz (0.38 ppm). GCMS, *m/z* (rel intensity) 131 (10), 130 (M^+; 100), 129 (42), 128 (18), 127 (6).

Reaction of 4 with Chlorotrimethylstannane. An excess of chlorotrimethylstannane was added to a solution of **4** (0.17 mmol) in THF (5 mL). The reaction mixture was allowed to stand for 12 h at room temperature. The mixture was poured into water and extracted with diethyl ether. The combined ethereal layers were dried ($MgSO_4$) and evaporated. The residue was examined by GCMS. Products were naphthalene (11%), 1-(trimethylstannyl)naphthalene (67%), and **6** (22%; relative yields). GCMS: naphthalene, *m/z* (rel intensity), 129 (11), 128 ($M^{\bullet+}$, 100), 127 (44), 126 (19), 125 (5); 1-(trimethylstannyl)naphthalene, *m/z* (rel intensity), 292 ($M^{\bullet+}$, 9), 277 (M – 15, 100), 247 (55); **6**, *m/z* (rel intensity), 441 ($(M - 15)^+$, 34), 261 (41), 165 (Me_3Sn^+, 100). All tin-containing ions showed the expected isotope clusters.

Structure Determination and Refinement of 4. A yellow, block-shaped crystal was mounted under nitrogen in a Lindemann glass capillary and transferred to an Enraf–Nonius CAD-4 diffractometer for data collection. Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections with $9.1 < \theta < 14.4°$. The unit cell parameters were checked for the presence of higher lattice symmetry.[29] Data were corrected for *Lp* for a small linear decay (1%) of the intensity control reflections during the 112 h of X-ray exposure time but not for absorption. The structure was solved with direct methods (SHELXS86[30]) and a series of subsequent difference Fourier analyses. Refinement on *F* was carried out by full matrix least squares techniques. H atoms were introduced on calculated positions [C–H = 0.98 Å] and included in the refinement riding on their carrier atoms. All non-H atoms were refined with anisotropic thermal parameters, and H-atoms were refined with one common isotropic thermal parameter [$U = 0.135(7)$ Å^2]. At this stage ($R = 0.155$), a difference Fourier map showed various features of about 1 eÅ^{-3} located in four symmetry-related channels: parallel to the *a*-axis [at $y = 1/4$, $z = 1/4$ and $y = 3/4$, $z = 3/4$] and to the *b*-axis [at $x = 0$; $z = 0$ and $x = 1/2$; $z = 1/2$]. No discrete THF solvent model could be fitted in the electron density within these channels. The BYPASS procedure[31] was used to take the electron density in the channels into account in the subsequent structure factor and Fourier calculations. A total electron count of 814 was found for the four channels with a volume of 2978 Å^3, which is indicative of a total of 20 THF molecules in the unit cell (five molecules of THF in each channel). The average volume of one THF molecule in the channels is 149 Å^3, this is in reasonable accordance with the volume of one THF molecule in the liquid phase at 293 K (136 Å^3). Weights were introduced in the final refinement cycles, convergence was reached at $R = 0.068$, $R_w = 0.083$. Crystal data and numerical details of the structure determination are given in Table V. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table VI. Neutral atom scattering factors were taken from[32] and corrected for anomalous dispersion.[33] All calculations were performed with SHELX76[34] and the EUCLID package[35] (geometrical calculations and illustrations) on a Micro VAX cluster.

Table V. Crystal Data and Details of the Structure Determination for **4**

Crystal Data	
formula	$C_{56}H_{56}Mg_4O_4 \cdot 5C_4H_8O$
mol wt	1250.82
crystal system	tetragonal
space group	$I4_1/a$ (No. 88)
a,*c* (Å)	14.429(2), 34.927(4)
V (Å^3)	7272(2)
Z	4
d_{calc} (g cm^{-3})	1.142
F(000)	2688
μ(Mo Kα) (cm^{-1})	1.1
crystal size (mm)	0.65 × 0.50 × 0.42
Data Collection	
T (K)	294
radiation	Mo Kα (Zr-filtered), 0.710 73 Å
$\theta_{min}, \theta_{max}$ (deg)	1.17, 24.20
scan type	$\omega/2\theta$
$\Delta\omega$ (deg)	$0.60 + 0.35 \tan\theta$
hor and vert aperture (mm)	3.00, 6.00
d crystal to detector (mm)	173
reference reflections	–4 0 4, 0 –3 1, 0 4 4
data set	*h*: –16:0; *k*: –16:0; *l* 0:40
total data	6481
total unique data	2921 ($R_{int} = 0.0301$)
observed data	1556 [$I > 2.5\sigma(I)$]
Refinement	
no. refined parameters	146
weighting scheme	$w = 1.0/[\sigma^2(F) + 0.000\,201F^2]$
final *R*, R_w, *S*	0.068, 0.083, 2.86
$(\Delta/\sigma)_{av}$ in final cycle	0.0287
min and max resd *d* (e/Å^3)	–0.18, 0.19

Synthesis of *o*-Phenylenemagnesium (10). *o*-Phenylenemercury (**7**, 4.46 g, 16.1 mmol) and magnesium (3.65 g, 150 mmol) in THF (180 mL) were stirred for 2 weeks at room temperature and for 10 h at 70 °C. A pale yellow solution with a fine black precipitate was obtained. The solution was separated from the excess magnesium and the black precipitate by careful decantation. Titration of an aliquot (HCl, EDTA) indicated formation of **10** in a yield of 85%. Crystallization by slowly cooling this solution afforded colorless crystals (11.0 mmol, 68% isolated yield; yields determined by titration).

10·(THF)*n*: ^1H NMR ($[^2H_8]$toluene, 250 MHz, ref $[^2H_7]$toluene = 2.03) δ 8.12 (dd, $^3J = 5.0$ Hz, $^4J = 3.2$ Hz, 2 H), 7.23 (dd, $^3J = 5.0$ Hz, $^4J = 3.3$ Hz, 2 H), 3.24 (bs, 8 H), 1.2 (bs, 8 H); ^1H NMR (200 MHz, $[^2H_8]$THF, ref $[^2H_7]$THF = 1.75 ppm) δ 7.67 (dd, $^3J = 5.0$ Hz, $^4J = 3.2$

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Table VI. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for **4**

atom	x	y	z	$U(\mathrm{eq})^a$ [Å^2]
Mg	0.553 81(11)	0.644 03(11)	0.095 04(4)	0.0640(6)
O	0.5837(3)	0.5095(2)	0.079 66(10)	0.0813(16)
C(1)	0.6171(4)	0.6471(3)	0.154 57(14)	0.069(2)
C(2)	0.7076(4)	0.6244(4)	0.147 79(15)	0.079(2)
C(3)	0.7592(4)	0.5623(4)	0.170 97(19)	0.094(3)
C(4)	0.7216(5)	0.5222(4)	0.200 54(19)	0.095(3)
C(5)	0.5818(6)	0.4990(4)	0.242 27(19)	0.109(3)
C(6)	0.4929(6)	0.5148(5)	0.250 43(19)	0.113(3)
C(7)	0.4426(4)	0.5758(4)	0.226 30(18)	0.094(3)
C(8)	0.4783(4)	0.6206(3)	0.194 59(14)	0.069(2)
C(9)	0.5718(4)	0.6025(3)	0.186 89(14)	0.0653(19)
C(10)	0.6273(5)	0.5395(4)	0.209 51(17)	0.087(3)
C(11)	0.6114(5)	0.4335(5)	0.1034(2)	0.135(4)
C(12)	0.5923(6)	0.3473(4)	0.0818(2)	0.151(4)
C(13)	0.5352(5)	0.3732(5)	0.048 45(18)	0.109(3)
C(14)	0.5542(5)	0.4719(4)	0.044 06(17)	0.099(3)

[a] $U(\mathrm{eq})$ = $^1/_3$ of the trace of the orthogonalized U matrix.

Table VII. Crystal Data and Details of the Structure Determination for **10**

Crystal Data	
formula	$C_{40}H_{48}Mg_4O_4$
mol wt	690.04
crystal system	monoclinic
space group	$I2/a$ (No. 15)
a, b, c (Å)	17.071(3), 11.877(1), 18.809(1)
β (deg)	99.97(1)
V (Å^3)	3756.0(6)
Z	4
d_{calc} (g cm^{-3})	1.220
$F(000)$	1472
μ(Mo Kα) (cm^{-1})	1.3
crystal size (mm)	0.20 × 0.50 × 0.50
Data Collection	
T (K)	294
radiation	Mo Kα (Zr-filtered), 0.710 73 Å
$\theta_{min}, \theta_{max}$ (deg)	1.4, 26.5
scan type	$\omega/2\theta$
scan (deg)	$0.90 + 0.35 \tan\theta$
hor and vert aperture (mm)	4.00, 6.00
reference reflections	−1 2 −1, −2 −1 −3
data set	h: −21:0; k: 0:14; l: −23:23
total unique data	3921, 3591
observed data	1990 [$I > 2.5\sigma(I)$]
Refinement	
no. of refined parameters	220
weighting scheme	$w = 2.3950/[\sigma^2(F) + 0.001\,304F^2]$
final R, R_w, S	0.0663, 0.0916, 2.24
max and av shift/error	0.09, 0.01
min and max resd d (e/Å^3)	−0.18, 0.19

Table VIII. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for **10**

atom	x	y	z	$U(\mathrm{eq})$ [Å^2]
Mg(1)	0.686 37(9)	−0.0301(1)	0.038 16(8)	0.0437(5)
Mg(2)	0.7101(1)	−0.2648(1)	−0.072 85(8)	0.0479(6)
O(1)	0.6313(2)	0.1050(3)	0.0750(2)	0.069(1)
O(2)	0.6885(2)	−0.3967(3)	−0.1422(2)	0.076(2)
C(1)	0.8439(3)	−0.2866(5)	−0.0265(3)	0.056(2)
C(2)	0.8821(4)	−0.3884(5)	−0.0359(3)	0.065(2)
C(3)	0.9436(3)	−0.3983(5)	−0.0748(3)	0.062(2)
C(4)	0.9654(3)	−0.3054(5)	−0.1082(3)	0.065(2)
C(5)	0.9276(3)	−0.2030(5)	−0.1019(3)	0.060(2)
C(6)	0.8675(3)	−0.1889(4)	−0.0606(3)	0.049(2)
C(7)	0.6807(3)	−0.0103(5)	−0.0829(3)	0.053(2)
C(8)	0.6679(3)	−0.1107(4)	−0.1246(3)	0.052(2)
C(9)	0.6221(3)	−0.1012(5)	−0.1942(3)	0.065(2)
C(10)	0.5911(3)	−0.0006(5)	−0.2232(3)	0.066(2)
C(11)	0.6012(3)	0.0954(5)	−0.1822(3)	0.065(2)
C(12)	0.6464(3)	0.0899(5)	−0.1131(3)	0.062(2)
C(13)	0.5468(3)	0.1131(5)	0.0767(4)	0.076(3)
C(14)	0.5354(4)	0.2267(6)	0.1075(5)	0.095(3)
C(15)	0.6087(5)	0.2865(7)	0.1077(7)	0.142(5)
C(16)	0.6673(5)	0.2151(6)	0.0890(6)	0.122(4)
C(17)	0.7339(6)	−0.4052(8)	−0.2012(5)	0.130(4)
C(18)	0.7065(6)	−0.5100(8)	−0.2387(5)	0.138(4)
C(19)	0.6436(7)	−0.5525(9)	−0.2097(6)	0.171(6)
C(20)	0.6308(8)	−0.474(1)	−0.1525(7)	0.236(8)

Table IX. Crystal Data and Details of the Structure Determination for **15**

Crystal Data	
formula	$C_{72}H_{72}Mg_4O_4{\cdot}2C_4H_8O$
mol wt	1242.83
crystal system	tetragonal
space group	$P\bar{4}2_1c$ (No. 114)
a, c (Å)	17.464(1), 11.911(2)
V (Å^3)	3632.8(8)
Z	2
d_{calc} (g cm^{-3})	1.136
$F(000)$	1328
μ(Mo Kα) (cm^{-1})	1.1
crystal size (mm)	0.90 × 0.30 × 0.20
Data Collection	
T (K)	295
radiation	Mo Kα (Zr-filtered), 0.710 73 Å
$\theta_{min}, \theta_{max}$ (deg)	1.17, 24.20
scan type	$\omega/2\theta$
$\Delta\omega$ (deg)	$0.86 + 0.35 \tan\theta$
hor and vert aperture (mm)	3.00, 6.00
d crystal to detector (mm)	173
reference reflections	2 4 1, 4 2 −1, −4 0 2
data set	h −21:0; k 0:21; l 0:14
total data	3890
total unique data	1928 (R_{int} = 0.048)
observed data	869 [$I > 2.5\sigma(I)$]
Refinement	
no. of refined parameters	183
weighting scheme	$w = 1.0/[\sigma^2(F) + 0.002\,88F^2]$
final R, R_w S	0.067, 0.089, 1.55
$(\Delta/\sigma)_{av}$ in final cycle	0.044
min and max resd d (e/Å^3)	−0.20, 0.24

Hz, 2 H), 6.74 (dd, ^3J = 5.0 Hz, ^4J = 3.3 Hz, 2 H); ^{13}C NMR ([$^2H_8$]-THF, 62.9 MHz, ref [$^2H_7$]THF = 67.4 ppm) δ 189.1 (bs, C(1,2), 140.6 (dd ^1J(CH) = 150 Hz, ^3J(CH) = 5 Hz, C(3,6)), 124.3 (d, ^1J(CH) = 150 Hz, C(4,5)), 66.2 (bt, ^1J(CH) = 140 Hz, THF C_α)) 15.6 (bt, ^1J(CH) = 125 Hz, THF C_β).

Reaction of 10 with Deuterium Oxide. To an NMR sample of **10** in [$^2H_8$]THF was added 10 μL of D_2O. The resulting solution was examined by ^{1}H and ^{13}C NMR spectroscopy, without workup: apart from signals from partially deuterated solvents and THF, only signals in the aromatic region were observed, which were ascribed to [1,2-$^2H_2$]benzene (**11**). Water and Et_2O were added; the ether layer was separated, dried over $MgSO_4$, and examined by mass spectroscopy (direct inlet).

11: ^{1}H NMR ([$^2H_8$]THF, 200 MHz), δ 7.24 (bs); ^{13}C[^{1}H] NMR ([$^2H_8$]THF, 50.32 MHz), δ 128.9 (m); MS **11**, m/z (rel intensity) 81 (7), 80 ($M^{\bullet+}$, 100), 79 (21), 78 (13), 77 (5).

Reaction of 10 with Chlorotrimethylstannane. An excess of chlorotrimethylstannane was added to a solution of **10** (0.15 mmol) in THF. After standing for 24 h at room temperature, the reaction mixture was poured into water. Extraction with diethyl ether, drying of the combined ethereal layers ($MgSO_4$), and evaporation of the solvent gave a residue which was examined by GCMS. It was found to contain (trimethylstannyl)benzene (20%) and 1,2-bis(trimethylstannyl)benzene (**12**) (80%; relative yields). GCMS: (trimethylstannyl)benzene, m/z (rel intensity) 227 (100) $(M - Me)^+$, 212 (6) $(M - 2Me)^{\bullet+}$, 197 (42) $(M - 3Me)^+$; **12**, 391 (100) $(M - Me)^+$, 241 (52) $(M - Me_3Sn)^+$, 211 (41), 165 (77) $(Me_3Sn)^+$, 135 (44), 120 (33), 91 (39). All tin-containing ions showed the expected isotope clusters.

Structure Determination and Refinement of 10. This structure has been published as part of a communication to this journal. Crystal data and numerical details are given in Table VII. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table VIII.

Synthesis of Diphenylvinylenemagnesium. In an evacuated apparatus based on a design by Kündig and Perret,[18] 0.24 g (10 mmol) of magnesium was sublimed during several hours into a solution of 1.40 g (8 mmol) of diphenylacetylene (**13**) in THF (30 mL), which was kept at −100 °C in

Table X. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogens Atoms for **15**

atom	*x*	*y*	*z*	*U*(eq)[a] [Å^2]
Mg	0.416 61(17)	0.453 32(16)	0.4192(3)	0.0498(10)
O(21)	0.3153(4)	0.4165(4)	0.3562(7)	0.074(3)
C(1)	0.4925(8)	0.3760(7)	0.1341(10)	0.084(5)
C(2)	0.4830(10)	0.3300(9)	0.0433(11)	0.112(7)
C(3)	0.4917(8)	0.2543(11)	0.0544(12)	0.100(7)
C(4)	0.5114(7)	0.2202(7)	0.1578(13)	0.090(5)
C(5)	0.5192(6)	0.2666(7)	0.2521(10)	0.069(5)
C(6)	0.5103(5)	0.3464(7)	0.2413(8)	0.052(4)
C(7)	0.5160(6)	0.3992(5)	0.3423(7)	0.049(3)
C(8)	0.5811(6)	0.4181(6)	0.3975(7)	0.051(3)
C(9)	0.6575(6)	0.3913(5)	0.3608(9)	0.052(4)
C(10)	0.6821(7)	0.3870(7)	0.2499(10)	0.077(5)
C(11)	0.7576(7)	0.3628(8)	0.2216(12)	0.089(6)
C(12)	0.8055(7)	0.3429(8)	0.2983(17)	0.105(7)
C(13)	0.7858(7)	0.3453(9)	0.4099(17)	0.113(7)
C(14)	0.7133(7)	0.3726(7)	0.4379(10)	0.089(5)
C(22)	0.2414(8)	0.4160(11)	0.4081(15)	0.137(8)
C(23)	0.1928(10)	0.3715(18)	0.340(3)	0.245(17)
C(24)	0.2215(11)	0.3577(15)	0.237(2)	0.166(11)
C(25)	0.3047(8)	0.3825(10)	0.2454(14)	0.122(8)

[a] *U*(eq) = $^1/_3$ of the trace of the orthogonalized *U*.

a liquid nitrogen/pentane cooling bath. During this process, the reaction mixture gradually turned dark. When all of the magnesium had been sublimed, the apparatus was filled with argon, and the solution was allowed to warm to room temperature. At this stage, reaction of a sample with water gave *cis*- and *trans*-stilbene in a 3:2 ratio (based on the vinylic signals in the ^{1}H NMR spectrum); reaction with deuterium oxide gave the dideuterated stilbenes *cis*-**14** and *trans*-**14**, based on GCMS analysis. The dark brown solution, which contained a fine yellow precipitate, was transferred into a high-vacuum glass system in which the additional experiments were performed. After addition of 180 mL of THF, settling, and careful decantation, the resulting brown solution was cooled to −20 °C to give bright yellow crystals of **15**. Reaction of these crystals with water gave exclusively *cis*-stilbene (^{1}H NMR); reaction with deuterium oxide gave *cis*-**14** (GCMS).

15: ^{1}H NMR ([^{2}H$_8$]THF, 200 MHz), δ 6.5–7.5.

Structure Determination and Refinement of 15. A bright yellow block-shaped crystal suitable for an X-ray structure determination was mounted under nitrogen in a Lindemann glass capillary and transferred to an Enraf-Nonius CAD-4 diffractometer for data collection. Crystal data and details of the structure determination are given in Table IX. Lattice parameters were refined by least-squares fitting of 25 reflections with 7.2 < θ < 11.1°. The unit cell parameters were checked for the presence of higher lattice symmetry.[29] Data were corrected for *Lp*, but no absorption correction was applied. During 52 h of X-ray exposure time no significant decay of the reference reflections was observed. The space group $P\bar{4}2_1c$ was established by observed systematic absences: *hhl*, $l = 2n + 1$; 00*l*, $l = 2n + 1$; *h*00, $h = 2n + 1$. The structure was solved by automated standard Patterson methods followed by tangent expansion (SHELXS86[30]). Two phenyl rings and the magnesium atoms could be located in the resultant Fourier map. Subsequent least-squares refinement and difference Fourier methods revealed the rest of the structure. At this stage ($R = 0.16$) a difference Fourier showed various peaks ($\approx$1.1 eÅ^{-3}) located in channels parallel to the *c*-axis at $x = 0$, $y = {}^1/_2$ and $x = {}^1/_2$, $y = 0$. No discrete solvent model could be fitted in this density. The BYPASS procedure[31] was used to take the electron density in this hole into account in the refinement. An electron count of 173 was found for both channels, with a total volume of 626 Å^3, which is indicative of a total of four THF molecules in the unit cell. The atomic volume of the non-hydrogen atoms (31 Å^3) is in reasonable accordance with that found in the liquid phase (27 Å^3). In the final cycles of full-matrix least-squares refinement using SHELX76,[34] 183 parameters were refined, including an overall scale factor and positional and anisotropic thermal parameters for all non-H atoms. H atoms were included in the refinement on calculated positions riding on their bonded atoms (C–H = 0.98 Å) with overall isotropic thermal parameters for the diphenylvinylene group and the coordinated THF of 0.088(12) and 0.20(3), respectively. Final atomic coordinates are listed in Table X. Scattering factors were taken from ref 32 and anomalous-dispersion corrections from ref 33. Geometric calculations were performed with the EUCLID package.[35] All calculations were performed on a MicroVAX-II.

Association Measurements of 6 and 12. The association measurements of **4** and **10** were performed using the technique of isothermal distillation.[27] The compounds were crystallized and washed with cold THF before use. Relevant data are given in Table IV.

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Supplementary Material Available: Thermal motion ellipsoid plots, tables of anisotropic thermal parameters, bond distances, and bond angles for **4** and **15** (11 pages); listings of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.