Substituted Cyclopentadienides of Magnesium from the Reaction of Dialkyl Magnesium with Fulvenes

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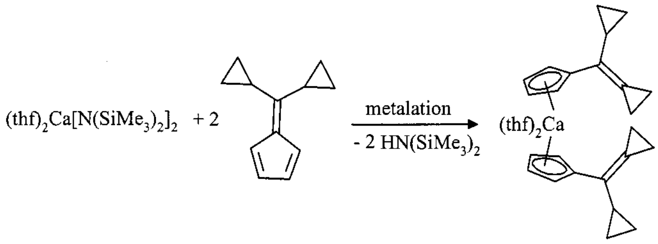
The reaction of *n/sec*-dibutyl magnesium with 6-methyl-6-phenyl- and 6,6-dicyclopropylfulvene gives the β-hydride transfer products 1,1′-bis(1-phenylethyl)- and 1,1′-bis(dicyclopropylmethyl)magnesocene, respectively. The latter crystallizes in the eclipsed conformation, whereas the first one shows an *anti* conformation in the solid state. Dimethylmagnesium deprotonates 6-methyl-6-phenylfulvene with formation of 1,1′-bis(1-phenylethen-1-yl)magnesocene, which decomposes upon isolation. The deprotonation of 6,6-dicyclopropylfulvene with $MgMe_2$ in thf solution yields [bis(tetrahydrofuran-*O*)]iro{cyclopropane-1,2′(1′-η^5-cyclopentadienyl-1′,3′,3′-tricyclopropyl-1′,2′,3′,3a′-tetrahydropenalene)}-3a′-6′-η^2-enyl]magnesium. In the absence of β-hydrogen atoms at the organometallic reagent as well as at the fulvene the addition reaction is the only possible reaction pathway. Thus, one Mg−C bond of $MgMe_2$ adds to tetramethylfulvene to give quantitatively dimeric methylmagnesium ethyltetramethylcyclopentadienide. The bridging methyl groups are sterically shielded against further attack of the fulvene.

The metalation of 6-methyl-6-phenylfulvene with calcium bis[bis(trimethylsilyl)amide] in tetrahydrofuran yields the bis(thf) complex of 1,1′-bis(1-phenyl-1-ethenyl)calcocene.[1] The bis(trimethylsilyl)amides of strontium and barium react in the same manner.[2] Enhancement of the ring strain leads to extended reaction periods. Therefore, the reaction of $(thf)_2Ca[N(SiMe_3)_2]_2$ with two equivalents of 6,6-dicyclopropylfulvene according to Eq. (1) needs several days even at elevated temperatures,[3] however, the yield of 1,1′-bis(cyclopropylcyclopropylidenemethyl)calcocene is only moderate. The cyclopentadienide fragments and the alkenyl groups show no electronic interaction, free rotation around the C−C bond between these moieties is observed. An addition of the Ca−N bond to the fulvene has never been observed. In contrast to these findings, the addition of methyl lithium to 6,6-dimethylfulvene gives tert.-butylcyclopentadienyllithium,[4] whereas sterically demanding nucleophiles favor the metalation reaction. For example, lithium diisopropylamide metalates (α-deprotonates) fulvenes in tetrahydrofuran to alkenylcyclopentadienyllithium.[5] Erker and coworkers[5g] investigated the dependency of this reaction on the solvent and observed in diethylether a β-hydride transfer from alkyl lithium to the fulvenes. Based on the investigations of Fischer and coworkers[6a] addition reactions of anionic nucleophiles such as methyllithium, potassium diphenylphosphanide or sodium cyclopentadienide to 6,6-dimethylfulvene as well as the corresponding chromium tri(carbonyl) complex were reported by Edelmann et al.[6b][6c]



We were interested in the synthesis of magnesocenes by the reaction of halogen-free magnesium compounds with fulvenes to compare the magnesocenes with the heavier homologues. In contrast to calcium bis[bis(trimethylsilyl)-amide], the homologous magnesium bis(amide)[7] does not react with fulvenes. Although a monomer-dimer equilibrium is observed for $Mg[N(SiMe_3)_2]_2$ in toluene solution,[8a] the X-ray structure reveals the steric shielding of the Mg−N bonds of the dimer in the solid state.[8b] Due to a large cone angle of the bis(trimethylsilyl)amide substituent,[9] even in the monomer the metal center is not accessible to fulvenes. Therefore, we investigated the reactivity of dimethylmagnesium as well as commercially available *n/sec*-dibutylmagnesium towards 6-methyl-6-phenyl- and 6,6-dicyclopropylfulvene. The reductive coupling of 6,6-dimethylfulvene with magnesium, calcium or strontium in the presence of a catalytic amount of $HgCl_2$ gives the corresponding *ansa*-alkaline earth metallocenes in a good yield,[10] however, our interest was centered on protonation and deprotonation reactions with fulvenes and we could show that not only the substituents at the fulvene and the

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[+] X-ray structure determinations.

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metal led to different reaction products but that the size of the alkaline earth metal influenced the reaction pathway.

Synthesis

The reaction of dimethylmagnesium[11] with 6-methyl-6-phenylfulvene yields nearly quantitatively the metalation product 1,1′-bis(1-phenyl-1-ethenyl)magnesocene **1** according to Eq. (2). The ^1H- and $^{13}C\{^1H\}$-NMR spectra are very similar to those of the heavier homologous alkaline earth metallocenes of calcium,[1] strontium and barium.[2] In Table 1 characteristic resonances are listed in comparison to the corresponding calcocene[1] and lithium derivative.[6] An isolation of **1** failed due to decomposition upon isolation. The use of butyl ligands instead of methyl groups leads to a β-hydride transfer from *n*/*sec*-dibutyl magnesium to 6-methyl-6-phenylfulvene and to the elimination of butene in a good yield. Butene was collected during the reaction and identified by IR spectroscopy. 1,1′-Bis(1-phenyl-1-ethyl)magnesocene **2** is a colorless, moisture-sensitive solid. Freshly prepared magnesium dihydride does not react with fulvenes to give 1,1′-dialkylmagnesocenes, therefore, β-hydride transfer reactions of *n*/*sec*-dibutyl magnesium with cyclic transition states as already known[12] are proposed.

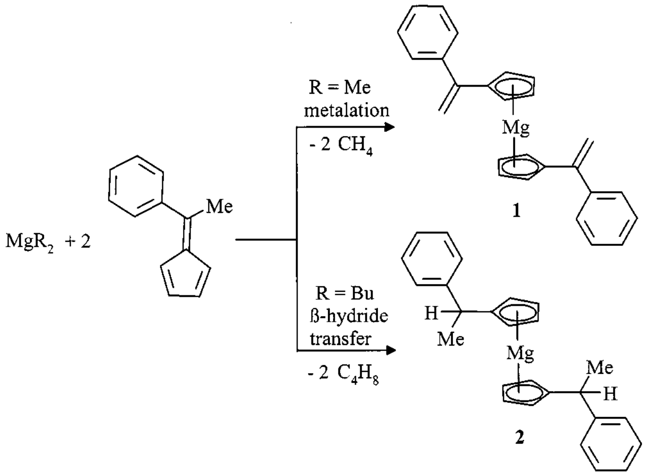
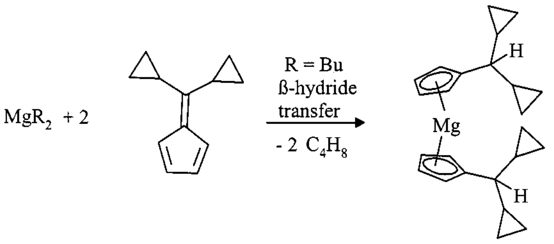


Table 1. Comparison of the NMR parameters of the homoleptic 1-phenylethen-1-ylcyclopentadienides of lithium, magnesium (**1**), and calcium (Cp′ = H_4C_5-C(=CH_2)Ph)

	LiCp′[5g]	MgCp′$_2$ (**1**)	(thf)$_2$CaCp′$_2$[1]
^1H NMR			
δ(=CH_2)	4.71, 5.30	4.92, 5.47	4.73, 5.23
^2J(H,H)	2.7	2.4	2.3
δ(C_5H_4)	5.94, 6.07	6.03, 6.28	5.79, 5.95
δ(Ph)	7.10−7.30, 7.65	7.6−7.7	7.2−7.5
^{13}C NMR			
δ(=CH_2)	101.9	105.03	104.57
^1J(C,H)	155	156	156.4
δ(C=CH_2)	149.5	147.74	148.54
δ(*i*-C/Cp)	120.5	122.13	123.13
δ(CH, Cp)	105.0, 105.1	103.69, 106.26	108.52, 108.70
δ(Ph)	126.6	126.64	127.32
δ(Ph)	127.6	127.52	128.06
δ(Ph)	129.2	128.83	129.30
δ(*i*-C, Ph)	146.1	144.78	145.21

These different reaction behaviors of dimethyl- and dibutylmagnesium allows the synthesis of two different compounds **1** and **2** without impurities stemming from the other reaction type.

To compare the reactivity of dimethyl- and dibutylmagnesium with the reactivity of $(thf)_2Ca[N(SiMe_3)_2]_2$ both the dialkylmagnesium compounds were reacted with 6,6-dicyclopropylfulvene. The calcium derivative metalates the fulvene and 1,1′-bis(cyclopropylcyclopropylidenmethyl)calcocene was isolated.[3] The use of *n*/*sec*-dibutylmagnesium gives quantitatively the β-hydride transfer product 1,1′-bis(dicyclopropylmethyl)magnesocene **3** [Eq. (3)]. Dimethylmagnesium on the other hand reacts with dicyclopropylfulvene in a completely different and unexpected manner. During the reaction methane is eliminated, however, the NMR parameters showed no similarities to the product obtained from the metalation with the above mentioned calcium bis(amide).



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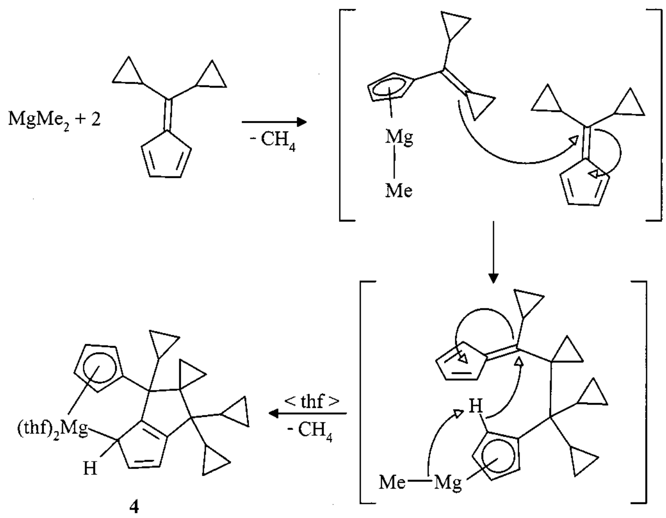
Eq. (4) describes the formation of [bis(tetrahydrofuran-*O*)]spiro{cyclopropane-1,2′(1′-η^5-cyclopentadienyl-1′,3′,3′-tricyclopropyl-1′,2′,3′,3a′-tetrahydropentalene)}-3a′-6′-η^2-enyl]magnesium **4** and proposes a reaction mechanism. The first step is the metalation of 6,6-dicyclopropylfulvene as also observed for the reaction of calcium bis[bis(trimethylsilyl)amide] according to Eq. (1).[3] This step is supported by the solvent-dependent studies of Erker and coworkers[5g] who found in tetrahydrofuran a favoring of the α-deprotonation against a β-hydride transfer. The ring strain of the thus formed cyclopropylidene fragment is released by the reaction with another molecule of 6,6-dicyclopropylfulvene. The second methyl nucleophil at the magnesium atom metalates the cyclopentadienyl moiety, a ring closure follows and a bis(cyclopentadienyl)magnesium derivative forms. Due to the enforced orientation of the cyclopentadienyl groups to each other, the aromatic fragments are not coplanar and two thf molecules occupy the coordination gap at the alkaline earth metal center. A rather similar mechanism was suggested to explain the reaction of sodium cyclopentadienide with 6,6-dimethylfulvene.[13]

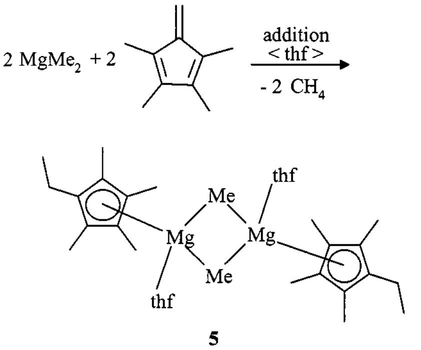
Further enhancement of ring strain during the formation of an alkenyl substituted magnesocene prevents a metalation (α-deprotonation) of the fulvene. Therefore, dimethylmagnesium shows no reaction with cyclopentadienylideneadamantane.[14] The absence of α-CH moieties in the fulvene molecule would enforce another reaction mechanism, because the formation of an alkenylcyclopentadienyl substituent as an intermediate is impossible. Consequently, also 6,6-diphenylfulvene[15] does not react with $MgMe_2$. An-



4

other conceivable reaction pathway would be the addition of a Mg-Me bond to the exocyclic C=C double bond of 6,6-diphenylfulvene, however, this reaction was not observed, probably due to steric reasons.

The reaction of dimethylmagnesium with tetramethylfulvene only allows the addition reaction, because the requirements for a β-hydride transfer reaction as well as for a α-deprotonation of the fulvene are not given. In the presence of Lewis bases such as thf and 1,4-dioxane the addition of one methyl substituent to tetramethylfulvene yields the tetrahydrofuran complex of bis(η^5-ethyltetramethylcyclopentadienyl)dimethyldimagnesium **5**. Due to the coordination of a thf molecule to the metal center and the formation of a four-membered Mg$_2$C$_2$ cycle the methylmagnesium moiety is sterically too shielded for an addition reaction to an additional molecule of tetramethylfulvene.



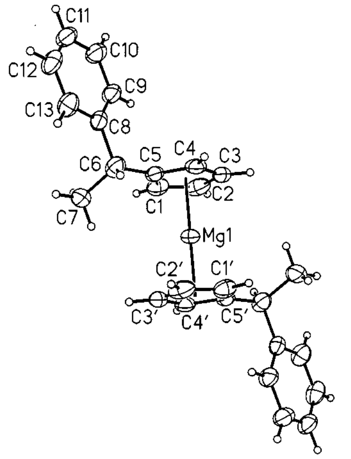
5

Heteroleptic cyclopentadienylmagnesium derivatives are well known since decades. The diethylether and tetrahydrofuran adducts of the halides RMgX are dimeric with a central Mg$_2$X$_2$ cycle[16][17] whereas the addition of tmeda yields monomeric complexes.[18] The Schlenk equilibrium interconverts Cp′MgX into magnesium dihalides and magnesocens.[19] Methylmagnesium cyclopentadienide is dimeric via methyl bridges as confirmed by IR spectroscopy,[20] however, diethyl ether leads to a partial cleavage of the dimer, whereas thf and tmeda cleave the methyl bridges completely.[20][21] In contrast to these findings neither the reaction of compound **5** with additional tetramethylfulvene occurs nor redistribution reactions to the homoleptic dimethylmagnesium and the substituted magnesocene are observable even in the presence of Lewis bases such as thf.

Molecular Structures

The alkaline earth metallocenes gained interest not only for their synthetic potential but moreover quite unusual solid state structures[22] led to theoretical investigations.[23] Although numerous magnesocenes are characterized by X-ray structure determinations we describe the molecular structures of **2** to **5**, however, only **2** and **3** show the characteristic sandwich structure. Figure 1 und 2 show the molecular structures and numbering schemes of **2** and **3**, respectively. The crystallographic inversion center in the structure of **2** lies on the magnesium atom and therefore, a *anti*-configuration of the alkyl substituents is enforced (Figure 3). The Mg−C bond lengths differ between 230.0 and 231.6 pm and the distance between Mg and the center Z of the cyclopentadienyl moiety lies at 198 pm. The molecular structure of **3** shows an eclipsed-conformation (Figure 3). This arrangement leads to steric repulsion between the dicyclopropylmethyl groups. As a consequence, the Z1−Mg−Z2 angle of 176.3° shows a small deviation from linearity and furthermore, the deviation from coplanarity of the cyclopentadienyl ligands amounts 4.4°.

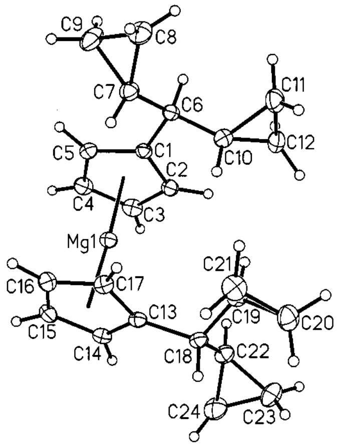
Figure 1. Molecular structure and numbering scheme of **2**; symmetry-related atoms are marked by an apostrophe. Thermal ellipsoids are drawn at a 40% probability level[a]



[a] Selected bond lengths [pm]: Mg1−C1 230.8(2), Mg1−C2 231.5(2), Mg1−C3 231.0(2), Mg1−C4 230.0(2), Mg1−C5 231.6(2), C1−C2 140.5(4), C1−C5 140.8(3), C2−C3 137.9(4), C3−C4 139.0(3), C4−C5 140.0(3), C5−C6 151.3(3), C6−C7 151.2(4), C6−C8 153.1(3).

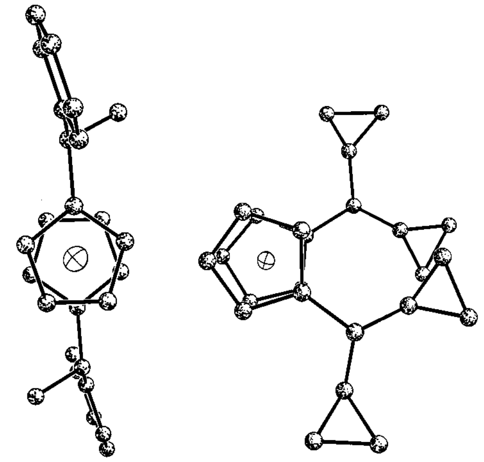
Magnesocene Mg(C$_5$H$_5$)$_2$ shows Mg−C distances of 230.4[24] and 233.9 pm[25] in the solid state and the gas phase, respectively. In contrast to the antiprismatic (staggered) conformation in the crystalline state an eclipsed (prismatic) structure is found in the gas phase. A linear arrangement is also observed for 1,1′-di-*tert*-butylmagnesocene[26] with an average Mg−C bond length of 233.6 pm. Intramolecular steric repulsion leads to a bending of hexakis(trimethylsilyl)magnesocene.[27] In contrast to these

Figure 2. Molecular structure and numbering scheme of **3**; thermal ellipsoids are drawn at a 40% probability level[a]



[a] Selected bond lengths [pm]: Mg1−C1 235.7(2), Mg1−C2 232.2(2), Mg1−C3 231.8(2), Mg1−C4 233.1(2), Mg1−C5 234.6(2), Mg1−C13 235.8(2), Mg1−C14 233.9(2), Mg1−C15 231.8(2), Mg1−C16 230.9(2), Mg1−C17 231.8(2), C1−C2 142.7(2), C1−C5 142.4(2), C1−C6 151.5(3), C2−C3 141.3(3), C3−C4 141.0(3), C4−C5 141.1(3), C13−C14 141.7(3), C13−C17 142.6(2), C13−C18 152.2(2), C14−C15 141.4(2), C15−C16 140.2(3), C16−C17 141.9(3).

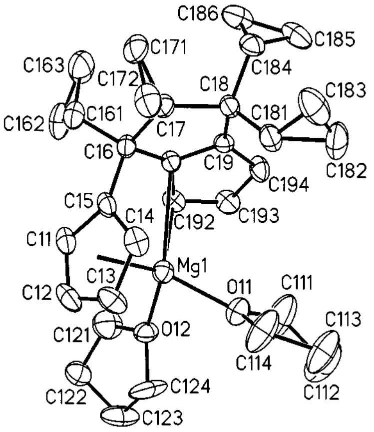
Figure 3. Comparison of the conformations of **2** (left) and **3** (right) with a view perpendicular to the cyclopentadienide ligands; the carbon atoms are drawn with arbitrary radii and the hydrogen atoms omitted for clarity. The magnesium atoms are drawn at a 40% probability level.



monomeric magnesocenes bis(indenyl)magnesium exhibits infinite chains with bridging and terminal indenyl substituents[28] bonded in η^1, η^2, or η^5 fashion.

The asymmetric unit of the crystal structure of **4** consists of two independent molecules. These two molecules are distinguished by the first number $n = 1$ or 2 following the element symbol. Due to the similar constitution the discussion of the molecular structure is limited to the molecule with $n = 1$ shown in Figure 4. The magnesium atom is η^5-bonded to the cyclopentadienyl fragment and the magnesium−carbon distances vary between 237.4 and 252.2 pm. Due to the rather unflexible backbone of the carbdianionic ligand the tetrahydropentalene unit acts as a η^2-bonded substituent with a short Mg1−C192 bond length of 227.2 pm, whereas the distance to the neighboring atom C191 is approximately 40 pm larger. Nevertheless, a delocalization of the double bonds within this five-membered cycle exists because the bonds C19−C191 (137.2 pm) and C193−C194 (139.1 pm) are only approximately 4 pm shorter than the other endocyclic C−C bonds with values of 141.0, 141.8, and 143.7 pm. In this molecule there are three neighboring quarternary carbon atoms C16, C17, and C18. Due to the steric repulsion, the C−C distances of these carbon atoms are unusual large (157.0 and 158.2 pm).

Figure 4. Molecular structure und numbering scheme of **4**; thermal ellipsoids are drawn at a 40% probability level. The hydrogen atoms are omitted for clarity[a]



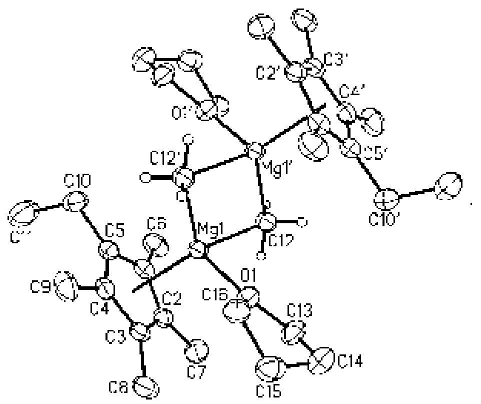
[a] Selected bond lengths [pm]: Mg1−O11 203.7(3), Mg1−O12 204.5(3), Mg1−C11 246.5(5), Mg1−C12 252.2(5), Mg1−C13 247.4(5), Mg1−C14 237.4(4), Mg1−C15 238.7(4), Mg1−C191 265.8(4), Mg1−C192 227.2(4).

The Mg−O bond lengths of 204 pm to the coordinated tetrahydrofuran molecules lie within the characteristic range and depend on the degree of steric strain. They are also influenced by the coordination number of the metal center; a comparison with published data[29] account for four to five-fold coordinated magnesium centers. Moreover, the Mg1−C192 bond length lies in the characteristic range for Mg−C σ bonds of a four or five-fold coordinated metal center[29] as for example in $(Et_2O)_2Mg(Br)CPh_3$ (225 pm[30]) and the anthracenyl derivatives $(thf)_3Mg(An)_2$ (229 pm[30]).

The molecular structure of **5** as well as the numbering scheme is represented in Figure 5. Symmetry related atoms are marked with an apostroph. The isotropic refinement of the methyl hydrogen atoms was successful and therefore, these H atoms are included in Figure 5. Bridging methyl substituents were also found in solvent-free dimethylmagnesium.[31]

Figure 5 shows the dimeric molecule of ethyltetramethylcyclopentadienylmagnesium methanide **5**. The methyl group bridges the magnesium atoms, the Mg−C bonds amount 227.0 and 228.5 pm. In polymeric dimethyl-[31] and diethylmagnesium[32] similar Mg−C distances of 224 and 226 pm were observed by Weiss. The magnesate anion

Figure 5. Molecular structure und numbering scheme of **5**; thermal ellipsoids are drawn at a 40% probability level. Only the hydrogen atoms of the bridging methyl substituents are represented[a]



[a] Selected bond lengths [pm] and angles [°]: Mg1−O1 209.2(2), Mg1−C1 242.7(2), Mg1−C2 246.9(2), Mg1−C3 251.2(2), Mg1−C4 248.4(2), Mg1−C5 243.8(2), Mg1−C12 228.5(2), Mg1···Mg1′ 280.96(12), O1−Mg1−C12 94.22(8), O1−Mg1−C12′ 96.02(8), C12−Mg1−C12′ 103.82(7), Mg1−C12−Mg1′ 76.18(7).

$[Mg_3Me_8]^{2-}$ is best described as a tetramethylmagnesate dianion, where two methyl groups are bridged by $MgMe_2$ units.[33] The central Mg−C bond lengths lie in the expected region of approximately 224 pm, whereas the bonds between the outer magnesium atoms and the bridging methyl groups are more than 10 pm longer. Terminally bonded methyl groups show approximately 10 pm shorter Mg−C bond lengths.[21]

NMR Spectroscopic Characterization

The comparison of the NMR data of **1** with those of 1-phenylethen-1-ylcyclopentadienyllithium[6] and bis(tetrahydrofuran-*O*)calcium bis(1-phenylethen-1-ylcyclopentadienide)[1] shows nearly no dependency on the nature of the metal atom. On the other hand the composition of **1** can be proven by these NMR data which are listed in Table 1. Similar findings also hold for **2** and the corresponding lithium derivative.[6]

A different situation is observed for **4**. Whereas the aromatic CH protons of the cyclopentadienyl moiety of the lithium derivative show an AA′XX′coupling pattern, the ^{1}H-NMR spectrum of **4** is more complicated due to the fixed geometry of this fragment in regard of the rotation around the C−C bond between the cyclopentadienyl and the tetrahydropentalene units. Furthermore, large differences in the chemical shifts of the CH groups of the pentalene fragment are observed. This can be explained by the mainly η^2-coordination of the pentalene unit to magnesium in **4** whereas lithium forms a η^5-complex. The chemical $^{13}C\{^1H\}$ and ^{1}H shifts of the magnesium-bonded fragment (C192 in Figure 4) are $\delta = 75.1$ and 4.6, respectively. The other CH fragments show values of approximately $\delta = 110$ for the carbon (C193 and C194 in Figure 4) and $\delta = 6$ for the ^{1}H nuclei.

The characteristic feature in the NMR spectra of **5** is the high field shift of the bridging methyl groups at $\delta = -2.1$ for the ^{1}H and $\delta = -18.1$ for the ^{13}C nuclei. The dimeric, but thf-free molecule is even present in the gas phase as shown by mass spectroscopy. Regarding the dimeric nature of this compound in solution as well as in the gas phase it is not surprising that the bridging methyl groups cannot add to another equivalent of tetramethylfulvene.

Conclusion

Erker and coworkers[5g] demonstrated the solvent dependency on the reaction of organyl lithiums whether a protonation (β-hydride transfer from alkyl lithium) or a deprotonation (metalation) of the fulvene is favored. Due to the absence of β-hydrogen atoms the alkaline earth metal bis[bis(trimethylsilyl)amides] of calcium, strontium and barium deprotonate the fulvenes to give alkenyl substituted alkaline earth metallocenes. The corresponding magnesium derivative is not reactive enough to interact with fulvenes. If β-hydrogen atoms are present in dialkylmagnesium as for example in *n*/*sec*-dibutylmagnesium only the β-hydride transfer to the fulvene is observed. Dimethylmagnesium always deprotonates the fulvene, however, the reaction with 6,6-dicyclopropylfulvene proceeds different than the reaction with 6-phenyl-6-methylfulvene, which yields 1,1′-bis(1-phenylethen-1-yl)magnesocene. One of the fulvene molecules is not metalated at the alkyl substituent but in *ortho*-position at the cyclopentadienyl fragment. Thus, the ring strain induced by the formation of a cyclopropylidene moiety is avoided. Now a ring closure reaction gives [bis(tetrahydrofuran-*O*)]spiro{cyclopropane-1,2′(1′-η^5-cyclopentadienyl-1′,3′,3′-tricyclopropyl-1′,2′,3′,3a′-tetrahydropentalene)}-3a′-6′-η^2-enyl]magnesium. Thus far, an addition of an alkyl magnesium moiety to a fulvene is only observed when both the β-hydride transfer to and the deprotonation (metalation) of a fulvene is impossible.

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Experimental Section

All experiments and manipulations were carried out under argon purified by passage through BTS catalyst and P_4O_{10}. Reactions were performed by using standard Schlenk techniques and dried, thoroughly deoxygenated solvents. The starting materials 6-methyl-6-phenylfulvene,[34] 6,6-dicyclopropylfulvene,[35] and dimethylmagnesium[11] were prepared by literature procedures. − NMR spectra were recorded on the Bruker spectrometers AM200, AC250, and AM400 or Jeol spectrometers GSX270 and EX400. − A Perkin-Elmer Paragon 1000 PC spectrophotometer was used to record the IR spectra; solid substances were measured in nujol between CsBr windows (vs very strong, s strong, m medium strong, w weak, vw very weak, sh shoulder). The frequencies in the region of the nujol vibrations were not listed. − The sensitivity towards moisture and oxygen during the handling of the compounds and the formation of carbides during combustion lead to low carbon values in the elemental analysis. Due to the moisture and air sensitivity of **4** and **5** the elemental analysis gave no reasonable results, even though if crystalline material was used. During handling of these compounds they turned dark and became waxy.

1,1′-Bis(1-phenyl-1-ethenyl)magnesocene (**1**). At 0°C 4.5 ml of 6-methyl-6-phenylfulvene were added to 13.8 mmol of dimethylmagnesium dissolved in 20 ml of the solvent mixture of thf, diethyl ether, and 1,4-dioxane. Stirring at r.t. for a few days led to quantitative formation of **1** as could be shown by NMR spectroscopy. The addition of 30 ml of pentane and cooling to 5°C yielded a precipitation of **1**. The nearly colorless precipitate turns dark upon removal of the mother liquor and drying in vacuum. Therefore, we used this solution without further purification or isolation of **1**. The NMR data is summarized in Table 1.

1,1′-Bis(1-phenyl-1-ethyl)magnesocene (**2**). At −30°C 3.3 ml (20.0 mmol) of 6-methyl-6-phenylfulvene were dropped to 10.0 ml of a 1 M solution of dibutylmagnesium in heptane. After complete addition the reaction mixture was stirred for 2 days, till the color changed from orange to bright yellow. The solution was decanted from the precipitate and reduced in vacuum. 2.6 g of compound **2** crystallized as colorless cuboids (72%), m.p. 47−48°C. − ^{1}H NMR (C_6D_6): δ = 1.48 [d, ^3J(H,H) = 7 Hz, Me], 3.85 [q, ^3J(H,H) = 7 Hz, CpC*H*], 5.7−5.9 [m, Cp], 7.0−7.2 [m, Ph]. − ^{13}C{^{1}H} NMR (C_6D_6): δ = 22.92 [Me], 40.05 [Cp-*C*H], 104.95, 105.08, 105.70, 106.56 [*C*H of Cp], 126.20 [*para*-C of Ph], 127.30, 128.58 [*meta* and *ortho*-C of Ph], 129.50 [*ipso*-C of Ph], 147.40 [*ipso*-C of Cp]. − IR (nujol): ν = 1688 cm^{-1} w, 1601 m, 1296 w, 1271 w, 1236 w, 1201 w, 1182 w, 1156 w, 1066 m, 1051 m, 1026 s, 1003 w, 978 m, 917 m, 895 sh, 862 w, 825 s, 768 s, 703 s, 632 w, 617 w, 584 w, 529 m, 504 sh, 452 w. − MS (70 eV); *m*/*z* (%): 169 (100) [$CpCHMePh^+$], 154 (99) [$CpCHPh^+$], 105 (95) [$PhCHMe^+$], 77 (42) [Ph^+]. − $C_{26}H_{26}Mg$ (362.78): calcd. C 86.07, H 7.22; found C 83.88, H 7.20.

1,1′-Bis(dicyclopropylmethyl)magnesocene (**3**). 5.0 ml (30 mmol) of 6,6-dicyclopropylfulvene were added to a cooled solution of 15.0 ml of 1 M dibutylmagnesium in heptane. After stirring for 2 days at r.t. the solution was reduced in vacuum. At 5°C 4.8 g of slightly yellow crystals of **3** precipitated (93%), m.p. 53−54°C. − ^{1}H NMR (C_6D_6): δ = 0.14−0.28 and 0.39−0.54 [m, CH_2], 0.92−1.01 [m, CH of ^{c}Pr], 1.22 [t, ^3J(H,H) = 9 Hz, CpC*H*^{c}Pr$_2$], 6.06 [s, Cp]. − ^{13}C{^{1}H} NMR (C_6D_6): δ = 3.80, 4.15 [CH_2], 17.45 [CH of ^{c}Pr], 47.90 [Cp*C*H^{c}Pr$_2$], 105.53 and 106.04 [CH of Cp], 128.72 [*ipso*-C of Cp]. − IR (nujol): $\tilde{\nu}$ = 1271 cm^{-1} s, 1261 sh, 1216 w, 1201 w, 1163 w, 1110 w, 1057 w, 1043 s, 1030 s, 1019 s, 1011 s, 973 m, 933 s, 916 m, 899 m, 855 sh, 829 s, 778 sh, 769 s, 750 s, 676 w, 530 w, 496 m, 453 m, 426 w, 321 w. − MS (70 ev); *m*/*z* (%): 158 (31) [Cp-$C(C_3H_5)_2^+$], 131 (100), 117 (63) [Cp-$CH(C_3H_5)^+$], 95 (28) [$CH(C_3H_5)_2^+$]. − $C_{24}H_{30}Mg$ (342.81): calcd. C 84.09, H 8.82; found C 83.43, H 8.64.

[Bis(tetrahydrofuran-O)]spiro{cyclopropane-1,2′(1′-η^5-cyclopentadienyl-1′,3′,3′-tricyclopropyl-1′,2′,3′,3a′-tetrahydropentalene)}-3a′-6′-η^2-enyl]magnesium (**4**). 1.6 ml (10.0 mmol) of 6,6-dicyclopropylfulvene was added at 0°C to 5.0 mmol of dimethylmagnesium dissolved in 7.1 ml of a mixture of thf, diethyl ether and 1,4-dioxane. Within 12 days the orange solution turned yellow. The addition of 10 ml of pentane led to the precipitation of 0.8 g of a reddish oil **4**, which crystallized at −5°C in the shape of yellowish cuboids (35%), m.p. 218°C (dec.). − ^{1}H NMR (C_6D_6, assignment with ^{1} ^{H,1}H-COSY45 NMR experiments): δ = 0.4−0.48 [m], 0.64−0.68 [m], 0.82−0.84 [m], 0.98−1.07 [m], 1.27−1.33 [m], 1.40−1.48 [m], 1.51−1.60 [m], 1.72−1.82 [m], 4.60 [dd, ^3J(H,H) = 1.3 Hz], 5.95 [dd], 5.96 [m, Cp], 6.11 [m, Cp], 6.14 [m, Cp], 6.17 [dd], 6.76 [m, Cp]. − ^{13}C NMR (C_6D_6, assignment with means of DEPT, ^{1}H-*J*-resolved 2D-NMR and ^{1}H,^{13}C-HMQC experiments[36]): δ = 0.01, 1.07, 2.50, 2.74, 3.89, 6.71, 13.26, 13.43 [CH_2 of ^{c}Pr]; 17.88, 19.89, 22.47 [CH of ^{c}Pr]; 46.24, 47.34, 54.25 [quart. C]; 75.06, 105.28 116.40 [CH of pentalene fragment]; 97.80, 100.66, 104.18, 106.41 [CH of Cp]; 129.96, 134.44, 140.63 [quart. aromatic C]. − IR (nujol): ν = 1309 cm^{-1} vs, 1242 vs br, 1184 vs, 1129 vs br, 1045 m, 1020 s, 998 sh, 985 vs, 933 w, 918 w, 901 w, 871 w, 845 w, 828 w, 810 w, 760 sh, 745 w, 719 sh, 702 w, 675 w, 646 w, 625 w, 532 w br, 467 w, 438 w, 405 w, 370 w. MS (70 eV); *m*/*z* (%): 316 (24), 275 (45), 209 (39), 193 (55), 165 (71), 158 (100), 128 (96), 115 (98), 91 (87).

Bis(tetrahydrofuran-O)dimethyl-bis(η^5-ethyltetramethylcyclopentadienyl)dimagnesium (**5**). At 0°C 3.8 mmol of dimethylmagnesium dissolved in thf, dioxane, and diethyl ether were added to

Table 2. Crystallographic data of **2**, **3**, **4**, and **5** as well as details of the structure solution and refinement procedures

compound	**2**	**3**	**4**	**5**
formula	$C_{26}H_{26}Mg$	$C_{24}H_{30}Mg$	$C_{32}H_{42}MgO_2$	$C_{16}H_{28}MgO$
fw [g·mol^{-1}]	362.78	342.79	482.97	260.69
T [K]	193	193	193	193
space group[38]	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a [pm]	1181.7(4)	853.8(4)	1268.6(3)	900.35(1)
b [pm]	803.1(3)	983.2(5)	2315.5(7)	1348.23(1)
c [pm]	1155.2(5)	1236.6(4)	18.41.9(5)	1297.14(2)
α [°]	90	82.442(7)	90	90
β [°]	109.24(1)	78.92(1)	97.55(1)	93.26(1)
γ [°]	90	73.347(7)	90	90
V [nm^3]	1.0352(6)	0.9729(7)	5.364(3)	1.57201(3)
Z	2	2	8	4
d_{calcd} [g·cm^3]	1.164	1.170	1.196	1.101
μ [mm^{-1}]	0.093	0.095	0.093	0.102
F(000)	388	372	2096	576
scan range [°]	$1.7 \le \theta \le 24.7$	$1.7 \le \theta \le 29.3$	$1.4 \le \theta \le 24.0$	$2.2 \le \theta \le 29.4$
measured data	4888	5505	17538	8768
unique data (R_{int})	1666 (0.0255)	2958 (0.0192)	7643 (0.0377)	2979 (0.0193)
parameters	129	227	735	180
wR_2[a] (all data)	0.1282	0.0900	0.2699	0.1516
R_1[a] (all data)	0.0570	0.0473	0.1192	0.0639
data [$I>2\sigma(I)$]	1567	2696	5647	2470
R_1 [$I>2\sigma(I)$]	0.0538	0.0416	0.0883	0.0519
goof σ[b] on F^2	1.052	1.159	1.108	1.068
residual dens [e·nm^{-3}]	561; −0.219	193; −158	599; −288	355; −325

[a] Definition of the *R* values: $R_1 = (\Sigma\|F_o| - |F_c\|)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$. − [b] $\sigma = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

1.02 g of 1,2,3,4-tetramethylfulvene in *n*-pentane. Stirring at r.t. for 4 d resulted in a yellow solution. Recrystallization from pentane yielded 0.74 g of colorless **5** (75%), m.p. 124°C. − ^{1}H NMR ([D$_8$]THF): $\delta = -2.08$ [s, Mg-Me], 0.90 [t, ^3J(H,H) = 7.6 Hz, CH$_3$ of Et], 1.76 [m, THF], 1.91 [Cp-Me], 1.94 [Cp-Me], 2.42 [q, ^3J(H,H) = 7.6 Hz], 3.60 [m, THF]. − ^{13}C{^{1}H} NMR ([D$_8$]THF): $\delta = -18.13$ [Mg-Me], 10.41 [CpCH$_3$], 10.56 [CpCH$_3$], 15.75 [CH$_3$ of Et], 19.55 [CH$_2$ of Et], 25.44 [THF], 67.35 [THF], 106.70 [Cp], 107.45 [Cp], 114.23 [Cp]. − IR (nujol): ν = 1363 cm^{-1} m, 1339 m, 1310 w, 1293 w, 1242 m, 1182 vs, 1138 sh, 1126 w, 1105 w, 1070 w, 1053 w, 1025 vs, 985 w, 956 w, 944 sh, 927 m, 912 w, 870 vs, 844 m, 675 m, 637 sh, 564 s, 494 s, 429 s, 404 s, 390 sh, 353 sh, 330 s, 295 sh. − MS (70 eV); *m/z* (%): 377 (8) [M$^+$ − 2 THF], 299 (74) [M$^+$ − Cp′ − 2 THF], 285 (91), 269 (92), 149 (100) [Cp′$^+$], 134 (99) [Cp′$^+$-CH$_4$].

X-ray Crystallography.[37] The single crystals were covered with nujol, sealed in thin-walled capillaries and mounted on a diffractometer with graphite monochromated Mo-K_α radiation (λ = 71.073 pm). A Siemens SMART-CCD area detector was used to monitor the reflections. Crystallographic parameters and details of data collection performed at −80°C are summarized in Table 2.

All structures were solved by direct methods with the software package SHELXTL Plus[39] and refined with the program SHELXL-93.[40] Neutral atom scattering factors were taken from Cromer and Mann[41] and for the hydrogen atoms from Stewart et al.[42] The non-hydrogen atoms were refined anisotropically. The H-atoms were refined with a riding model under restriction of ideal symmetry at the corresponding carbon atom. The hydrogen atoms of the bridging methyl substituents of **5** were refined isotropically.

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[37] Crystallographic data (excluding structure factors) for the structures of **2**, **3**, **4**, and **5** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101070. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

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