the intermediate complex $P_4Rh^+(acac)^-$ is first formed and slowly rearranges into the less soluble $P_3Rh^+{-}P(O)(OPh)_2^-$ species. The formation of the P_4Rh^+ species was observed very clearly in the ^{31}P NMR spectrum. The rearrangement process is significantly faster (ca. 30 min at room temperature when P_4RhClO_4 is treated with KOH. A possible intermediate with either a directly or ortho coordinated phenyl group could not be observed, whereas the formation of phenol could be unambiguosly detected by ^1H NMR spectroscopy. The novel rearrangement of $P(OPh)_3$ to $O{=}P(OPh)_2^-$ in $CDCl_3/C_6D_6$ with KOH observed here lends support to the feasibility of such a reaction in the RhP_4^+ species. Thus the main structural elements of 1 in solution could be derived from extensive NMR spectroscopic investigations without resorting to X-ray structure analysis.

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(η^5-Tris(trimethylsilyl)cyclopentadienyl)magnesium Compounds: Syntheses and Structures

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The new compounds methyl(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)(η^5-1,2,4-tris(trimethylsilyl)cyclopentadienyl)magnesium (A), bis(η^5-1,2,4-tris(trimethylsilyl)cyclopentadienyl)magnesium (B), and bromo(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)(η^5-1,2,4-tris(trimethylsilyl)cyclopentadienyl)magnesium (C) have been prepared and characterized. The crystal and molecular structures of B and C have been determined by X-ray diffraction. B: $C_{28}H_{58}MgSi_6$, $a = 18.794$ (3) Å, $b = 22.720$ (4) Å, $c = 19.803$ (1) Å, $\beta = 108.82$ (1)°, space group $P2_1/a$ (No. 14), $Z = 8$, monoclinic, $F(000) = 2576$; $R = 0.087$ for 5578 observed reflections. C: $C_{20}H_{45}BrMgN_2Si_3$, $a = 9.546$ (1) Å, $b = 10.852$ (1) Å, $c = 30.727$ (2) Å, $\alpha = 97.19$ (1)°, $\beta = 93.01$ (1)°, $\gamma = 110.41$ (1)°, space group $P\bar{1}$ (No. 2), $Z = 4$, triclinic, $F(000) = 1076$; $R = 0.050$ for 6096 observed reflections. The two cyclopentadienyl ligands in B are nonparallel, and the average Cp–Mg–Cp angle is 171.1°; this can be attributed to steric repulsion between the bulky trimethylsilyl substituents on the rings. Multinuclear NMR spectroscopy has been used to study the structure of A, B, and C in solution. Restricted rotation of the cyclopentadienyl rings in B is observed at low temperature.

Introduction

The ability of elements of groups IA and IIA (1 and 2[38]) to participate in polyhapto bonding with cyclopentadienyl ligands has received increasingly wide study in the past few years, particularly from a theoretical point of view.[1,2] Synthetic work has tended to concentrate on the organolithium compounds, and recently several structures of (η^5-cyclopentadienyl)lithium compounds have been published.[3] In comparison, the cyclopentadienyl chemistry of magnesium has been somewhat neglected, although the cyclopentadienyl Grignard reagent (C_5H_5MgBr) has been known for 70 years.[4]

Bis(η^5-cyclopentadienyl)magnesium ("magnesocene") was first prepared in 1954,[5] and arguments about the nature of the metal–ring bonding have continued sporadically ever since. Wilkinson, Cotton, and Birmingham originally proposed an ionic formulation for magnesocene on the basis of mass[6] and infrared spectral data, chemical properties, and its electrical conductance in liquid ammonia solution.[7] Lippincott et al.[8] disagreed with this and published infrared data supporting their suggestion that magnesocene should be considered as an essentially covalent compound. The reliability of these data has, how-

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ever, recently been called into question by a more detailed investigation.[9] Ford[10] has recorded UV and NMR spectra of magnesocene (and also of C_5H_5MgX (X = Br, Cl)) in THF solution and analyzed the results in terms of an ionic formulation. Fischer et al.,[11] however, treated magnesocene as a more or less covalent compound in considering its ^{13}C NMR spectrum. Recent ^{25}Mg NMR investigations[12] also support a covalent formulation.

The structure of magnesocene has been investigated by X-ray[13] and electron diffraction[14] techniques; the isomorphism of the compound with ferrocene and the relatively short Mg–C distances seem to imply at least partial covalent character in the metal–ring bonding. This view is supported by recent theoretical calculations by Faegri et al.,[2] who point out that "the classification of a sandwich compound as ionic or covalent is of interest mainly in the context of its properties and chemical behavior". Bis(η^5-pentamethylcyclopentadienyl)magnesium ("decamethylmagnesocene")[15] has recently been prepared, as have bis- and tetrakis(trimethylsilyl)magnesocenes.[17]

Monocyclopentadienyl derivatives of magnesium have received relatively little attention despite the extensive use of cyclopentadienyl Grignard reagents as synthetic intermediates. The crystal and molecular structure of bromo(η^5-cyclopentadienyl)(*N,N,N′,N′*-tetraethylethylenediamine)magnesium (CpMg(TEEDA)Br) has been determined.[16] The Mg–C(ring) distance in this compound is 0.25 Å longer than that in magnesocene, which may imply a lower bond order. NMR,[18] mass,[18] and IR[19] spectra of (η^5-cyclopentadienyl)methylmagnesium have been determined. Ashby et al. have also isolated and characterized a dimeric monoetherate of this compound. The most recent publication in this area is the most comprehensive to date: Lehmkuhl et al.[20] report a systematic investigation of the complexation of magnesocene by Lewis bases and also the structure of $[CpMg(OEt)]_4$. In view of current interest in cyclopentadienylmagnesium chemistry and stimulated by the success in preparing cyclopentadienylmetal compounds derived from polysilylated cyclopentadienes,[3,21] we have prepared several magnesium derivatives containing the η^5-1,2,4-tris(trimethylsilyl)cyclopentadienyl (Si_3Cp) ligand.

Experimental Section

All operations were carried out under a purified argon atmosphere by using standard Schlenck techniques and rigorously dried apparatus. All solvents were dried by repeated distillation from lithium aluminium hydride, stored over 4-Å molecular sieves, and degassed by boiling under reduced pressure.

NMR spectra were recorded on a Bruker AM 300 or WH 400 instrument, infrared spectra as Nujol mulls between KBr disks, prepared in a nitrogen-filled glovebox, on a Perkin-Elmer 598 infrared spectrophotometer, and mass spectra on a Varian MAT 311 A instrument using electron-impact (electron energy 70 eV) ionization. Analyses were performed by Mikroanalytisches Laboratorium Beller, Theaterstr. 23, D-3400 Göttingen, West Germany.

Tris(trimethylsilyl)cyclopentadiene (Si_3CpH)[22] and dimethylmagnesium[23] were prepared as previously described. *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) was dried by distillation from potassium hydroxide and stored over 4-Å molecular sieves.

Methyl(*N,N,N′,N′*-tetramethylethylenediamine)(η^5-1,2,4-tris(trimethylsilyl)cyclopentadienyl)magnesium, (Si_3Cp)Mg(tmeda)Me (A). Si_3CpH (2.83 g, 10. mmol) and TMEDA (2.32 g, 20 mmol) were added to a solution of dimethylmagnesium (0.54 g, 10 mmol) in diethyl ether (50 mL), and the mixture was stirred at room temperature for 5 days, allowing excess gas pressure to escape via a bubbler. The solvent and excess TMEDA then were removed by distillation under reduced pressure, and the residue was extracted with hexane. The hexane solution was filtered and cooled slowly to −10 °C to deposit colorless, prismatic crystals of A. Recrystallization from hexane gave an analytically pure sample, yield 3.37 g (77%).

Spectroscopic and analytical data for A are summarized in Tables I and IV-VIII. Compound A is extremely air- and water-sensitive and soluble in all common aprotic organic solvents.

Bis(η^5-1,2,4-tris(trimethylsilyl)cyclopentadienyl)magnesium, ($Si_3Cp)_2Mg$ (B). Si_3CpH (14.13 g, 50 mmol) and TMEDA (14 g, ca. 120 mmol) were added to a solution of dimethylmagnesium (1.36 g, 25 mmol) in diethyl ether (100 mL), and the mixture was heated at reflux for 5 days. The solvent (and TMEDA) then were removed by distillation under reduced pressure, and the residue was extracted with hexane. The hexane solution was filtered and cooled slowly to −10 °C to deposit colorless prismatic crystals of B. Recrystallization from hexane gave an analytically pure sample, yield 7.30 g (50%).

Spectroscopic and analytical data for B are summarized in Tables I and IV and VIII. Compound B is extremely air- and water-sensitive and soluble in all common aprotic organic solvents.

Bromo(*N,N,N′,N′*-tetramethylethylenediamine)(η^5-1,2,4-tris(trimethylsilyl)cyclopentadienyl)magnesium, (Si_3Cp)Mg(TMEDA)Br (C). A 0.38 M solution of methylmagnesium bromide in di-*n*-butyl ether was prepared from an excess of magnesium turnings and bromoethane and filtered. To this solution (109.2 mL, 41.5 mmol) were added Si_3CpH (11.73 g, 41.5 mmol) and TMEDA (9.65 g, 83 mmol), and the mixture was heated at reflux for 5 days. A thick white precipitate was formed on mixing, and this gradually disappeared over the course of the reaction. After 5 days the mixture was allowed to cool, filtered, concentrated by distillation of the solvent under reduced pressure, and then further cooled to −10 °C. The resulting colorless needlelike crystals were collected by decantation, washed twice with diethyl ether, and then dried in vacuo, yield 12.4 g (59.5%).

Spectroscopic and analytical data for C are summarized in Tables I and IV and VIII. Compound C is slightly soluble in hexane, fairly soluble in aromatic hydrocarbons and di-*n*-butyl ether, and very soluble in tetrahydrofuran. It is exceptionally moisture-sensitive and somewhat less oxygen-sensitive.

X-ray Analyses of B and C. I. Colorless crystals of B crystallize in the monoclinic space group $P2_1/a$ (nonstandard setting of the space group $P2_1/c$ (No. 14)). Crystal size: 0.36 × 0.54 × 0.47 mm. Two independent molecules are present in the asymmetric unit ($Z = 8$), giving $d_{calcd} = 0.975$ g cm^{-3}, μ(Mo Kα) = 2.32 cm^{-1}, and $\lambda = 0.71069$ Å (scan mode $\omega/2\theta$). Cell data were derived by a least-squares procedure on the θ values of 75 reflections: $a = 18.794$ (3) Å, $b = 22.720$ (4) Å, $c = 19.803$ (1) Å, $\beta = 108.82$ (1)°, and $V = 8003.8$ Å^3.

A total of 14851 intensities ($\pm h,k,l$) were collected on an automated diffractometer (Enraf-Nonius CAD 4), using graphite-monochromated molybdenum radiation ($(\sin\theta)/\lambda_{max} = 0.59$). These reflections were averaged to yield a unique data set of 13943

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observations, of which 5578 were considered observed (2σ level). No absorption correction was applied to the data set. The structure was solved by direct methods (SHELX 84), and all non-hydrogen atoms were located in subsequent Fourier maps. Isotropic refinement of all atoms led to a discrepancy factor of $R = 0.136$. Further refinement by block-diagonal least-squares methods indicated that disorder was present on the methyl groups of the alkylsilyl ligands, and relatively large anisotropic thermal parameters were observed for their carbon atoms. Hydrogen atoms were placed in calculated positions (C–H = 0.95 Å) and not refined, leading to a final R value of 0.087 ($R_w = 0.098$).

II. Colorless crystals of compound C crystallize in the triclinic system of space group $P\bar{1}$ (No. 2). Crystal size: 0.36 × 0.43 × 0.54 mm. As in compound B, there are two independent molecules in the asymmetric unit: $Z = 4$, $d_{\text{calcd}} = 1.13$ g cm^{-3}, and μ(Mo Kα) = 15.3 cm^{-1}, and $\lambda = 0.71069$ Å (scan mode $\omega/2\theta$); no absorption correction was applied to the data set. Cell data were derived from the θ values of 75 reflections: $a = 9.546$ (1) Å, $b = 10.852$ (1) Å, $c = 30.727$ (2) Å, $\alpha = 97.19$ (1)°, $\beta = 93.01$ (1)°, $\gamma = 110.41$ (1)°, $V = 2943.8$ Å^3; total no. of reflections 11 538 ($\pm h,\pm k,+l$); $(\sin \theta)/\lambda_{\max} = 0.62$; 11 469 unique reflections, of which 6096 were observed (2σ level).

The structure was solved by the heavy-atom method, and all non-hydrogen atoms were located in subsequent Fourier syntheses. Anisotropic refinement of all non-hydrogen atoms with hydrogen atoms placed in calculated positions (C–H = 0.95 Å) leads to a discrepancy factor of $R = 0.050$ ($R_w = 0.056$). Final refined atomic fractional coordinates for B and C are given in Tables IX and X, respectively (supplementary material).

Results and Discussion

(a) Synthesis. Ashby et al.[19] have prepared bis(η^5-cyclopentadienyl)bis(μ-methyl)bis(diethyl ether)dimagnesium, $(\mathrm{CpMgMe(OEt_2)})_2$, and magnesocene by the room temperature reaction of dimethylmagnesium with cyclopentadiene in diethyl ether. Similarly, dibutylmagnesium reacts with various cyclopentadienes to yield the corresponding magnesocenes.[17] Under analogous conditions we found no evidence for reaction between dimethylmagnesium and tris(trimethylsilyl)cyclopentadiene ($\mathrm{Si_3CpH}$). We ascribe this failure to react to the steric demands of reaction with $\mathrm{Si_3CpH}$. Only in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) did reaction take place. This presumably is a consequence of in situ adduct formation, dimethyl(*N,N,N′,N′*-tetramethylethylenediamine)magnesium[24] being more reactive toward protic reagents than dimethylmagnesium. Similar observations have previously been made concerning the reactivity of diethylzinc.[25]

Stirring a mixture of $\mathrm{Si_3CpH}$, dimethylmagnesium, and TMEDA in diethyl ether for 5 days at room temperature led to isolation of the monocyclopentadienyl compound methyl (*N,N,N′,N′*-tetramethylethylenediamine)(η^5-1,2,4-tris(trimethylsilyl)cyclopentadienyl)magnesium, A (eq 1). Prolonged reaction at higher temperatures led to formation of the bis(cyclopentadienyl) compound bis(η^5-1,2,4-tris(trimethylsilyl)cyclopentadienyl)magnesium, B (eq 2).

$$\mathrm{MgMe_2 + C_5H_3(SiMe_3)_3 + Me_2NCH_2CH_2NMe_2 \xrightarrow[\text{room temperature}]{\mathrm{Et_2O},\ \text{5 days}} MeH +} \underset{\mathrm{A}}{(\eta^5\text{-}\mathrm{C_5H_2(SiMe_3)_3)Mg(\eta^2\text{-}Me_2NCH_2CH_2NMe_2)Me}} \quad (1)$$

$$\mathrm{MgMe_2 + 2C_5H_3(SiMe_3)_3 \xrightarrow[\mathrm{Me_2NCH_2CH_2NMe_2}]{\mathrm{Et_2O}/35\ ^\circ\mathrm{C},\ \text{5 days}} 2MeH +} \underset{\mathrm{B}}{(\eta^5\text{-}\mathrm{C_5H_2(SiMe_3)_3)_2Mg}} \quad (2)$$

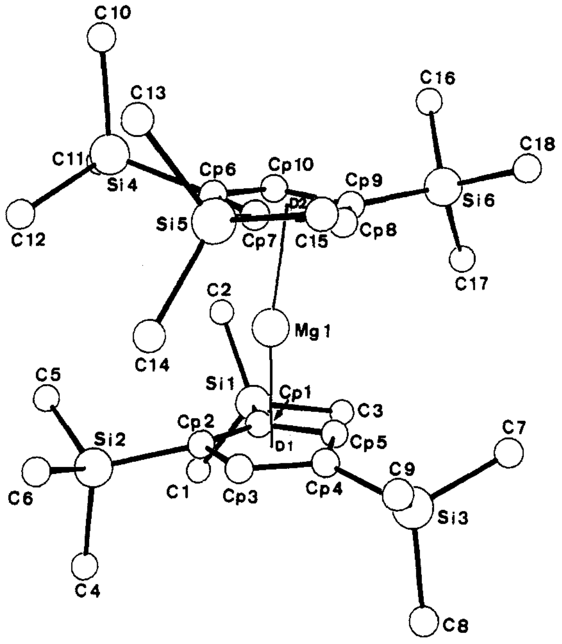

Figure 1. View of one of the two independent molecules of B.

The course of the reaction may be followed by ^{1}H NMR spectroscopy. Such studies show that A is an intermediate in the synthesis of B but that under the conditions used only low concentrations of A are ever present, i.e., that in refluxing diethyl ether the reaction of A with $\mathrm{Si_3CpH}$ is faster than that of dimethylmagnesium.

A similar reaction takes place between methylmagnesium bromide and $\mathrm{Si_3CpH}$ in the presence of TMEDA to yield bromo(*N,N,N′,N′*-tetramethylethylenediamine)(η^5-1,2,4-tris(trimethylsilyl)cyclopentadienyl)magnesium, C (eq 3).

$$\mathrm{MeMgBr + C_5H_3(SiMe_3)_3 + Me_2NCH_2CH_2NMe_2 \xrightarrow[140\ ^\circ\mathrm{C}]{n\text{-}\mathrm{Bu_2O},\ \text{5 days}} MeH +} \underset{\mathrm{C}}{(\eta^5\text{-}\mathrm{C_5H_2(SiMe_3)_3)Mg(\eta^2\text{-}Me_2NCH_2CH_2NMe_2)Br}} \quad (3)$$

The isolation of the base-free compound B is particularly noteworthy. Under the same conditions 1,2,3,4,5-pentamethylcyclopentadiene reacts with dimethylmagnesium to form a TMEDA adduct of decamethylmagnesocene.[26] NMR studies have also demonstrated the tendency of magnesocene[20] and decamethylmagnesocene[27] to form adducts with Lewis bases. That B differs in this respect even from sterically hindered analogues could be due to greater electronic saturation for the $\mathrm{Si_3Cp}$ derivative.

(b) Physical Properties. Compounds A and B are very soluble in hexane, and A, B, and C all dissolve readily in benzene. B sublimes only with decomposition. Similar behavior has been noted for (η^5-cyclopentadienyl)methylmagnesium.[18] A, B, and C all show distinct melting points and give acceptable analyses. A and C are monomeric in benzene solution, as evidenced by molecular weight determinations (see Table I). A, B, and C are particularly sensitive to traces of oxygen and moisture, forming brown decomposition products within seconds on exposure to air.

(c) Structure of Bis(η^5-1,2,4-tris(trimethylsilyl)cyclopentadienyl)magnesium (B). The molecular structure of one of the two essentially similar, independent molecules of compound B is shown in Figure 1. Each

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Table I. Analytical Data for Compounds A-C

compound	mp,[a] °C	mol wt[b,c]	anal.[b] C	anal.[b] H	anal.[b] N	anal.[b] Br
$(Si_3Cp)Mg(TMEDA)Me$ (A)	91-93	422 (437.19)	56.70 (57.69)	10.93 (11.07)	6.27 (6.40)	
$(Si_3Cp)_2Mg$ (B)	303-304		57.85[d] (63.05)	10.27[d] (11.34)		
$(Si_3Cp)Mg(TMEDA)Br$ (C)	118-120	482 (502.06)	47.99 (47.85)	9.18 (9.03)	5.58 (5.58)	15.8 (15.92)

[a] Sealed tube. [b] Calculated values in parentheses. [c] Cryoscopic in benzene. [d] Sample was spectroscopically pure: the result (8% too low) may be a consequence of in situ decomposition during analysis.

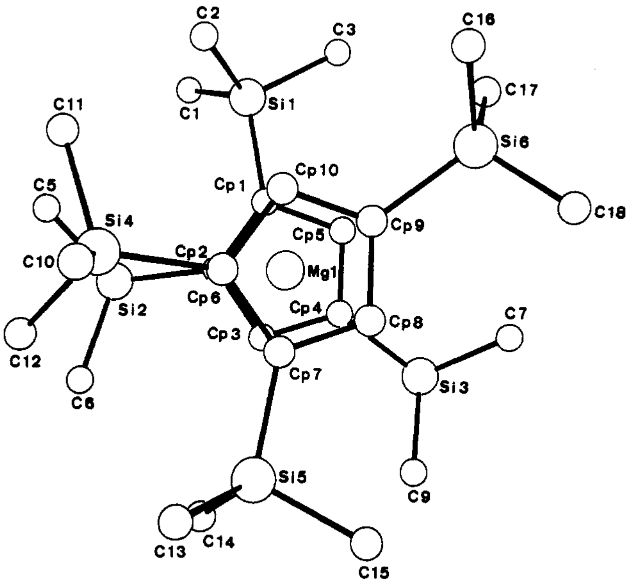

Figure 2. Silyl group ordering in B.

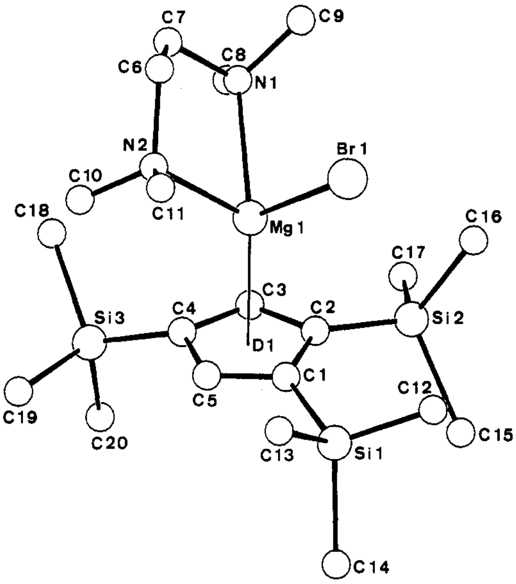

Figure 3. Molecular structure of C.

molecule has two almost parallel cyclopentadienyl rings (mean angle = 7.8°), both of which are η^5-bonded to the central magnesium atom. Viewed along the ring–metal–ring axis (Figure 2), the ring carbon atoms form an eclipsed arrangement. It is noteworthy that only one pair of silyl groups is eclipsed. The bending of the molecule may be the result of a steric interaction between the eclipsed silyl groups. All the silicon atoms are bent out of the Cp plane (average 8 (2)°) away from the metal atom, with the eclipsed Si atoms being bent the most (average 12.0 (8)°). The two independent molecules are superimposable, which indicates that this conformation is the preferred one in the solid state. The same arrangement of silyl groups has been observed in the structure of $(Si_3Cp)_2Ge$, and calculations have shown that this conformation lies in a steric energy minimum for this molecule.[28]

Table II. Selected Interatomic Distances (Å) and Angles (deg) of B[a]

molecule 1		molecule 2	
	Bond Distances		
Mg1–D1	2.02 (1)	Mg2–D3	2.02 (1)
Mg1–D2	2.04 (1)	Mg2–D4	2.03 (1)
Si1–Cp1	1.88 (1)	Si21–Cp21	1.87 (1)
Si2–Cp2	1.89 (1)	Si22–Cp22	1.88 (1)
Si3–Cp4	1.87 (1)	Si23–Cp24	1.87 (1)
Si4–Cp6	1.87 (1)	Si24–Cp26	1.89 (1)
Si5–Cp7	1.87 (1)	Si25–Cp27	1.88 (1)
Si6–Cp9	1.88 (1)	Si26–Cp29	1.87 (1)
Cp1–Cp2	1.44 (1)	Cp21–Cp22	1.45 (1)
Cp1–Cp5	1.47 (1)	Cp21–Cp25	1.44 (1)
Cp2–Cp3	1.44 (1)	Cp22–Cp23	1.45 (1)
Cp3–Cp4	1.44 (1)	Cp23–Cp24	1.42 (1)
Cp4–Cp5	1.44 (1)	Cp24–Cp25	1.44 (2)
Cp6–Cp7	1.47 (1)	Cp26–Cp27	1.46 (1)
Cp6–Cp10	1.45 (1)	Cp26–Cp30	1.42 (2)
Cp7–Cp8	1.43 (1)	Cp27–Cp28	1.45 (2)
Cp8–Cp9	1.45 (1)	Cp28–Cp29	1.45 (2)
Cp9–Cp10	1.43 (1)	Cp29–Cp30	1.43 (2)
	Bond Angles		
D2–Mg1–D1	171.8 (2)	D4–Mg2–D3	170.4 (2)
Cp5–Cp1–Cp2	106.9 (8)	Cp25–Cp21–Cp22	107.9 (8)
Cp5–Cp1–Si1	119.7 (7)	Cp25–Cp21–Si21	119.3 (7)
Cp2–Cp1–Si1	133.0 (7)	Cp22–Cp21–Si21	132.2 (7)
Cp3–Cp2–Cp1	108.9 (8)	Cp23–Cp22–Cp21	107.3 (8)
Cp3–Cp2–Si2	117.5 (7)	Cp23–Cp22–Si22	117.9 (7)
Cp1–Cp2–Si2	131.9 (7)	Cp21–Cp22–Si22	132.7 (7)
Cp4–Cp3–Cp2	108.0 (8)	Cp24–Cp23–Cp22	108.3 (8)
Cp5–Cp4–Cp3	108.1 (8)	Cp25–Cp24–Cp23	108.8 (8)
Cp5–Cp4–Si3	125.2 (7)	Cp25–Cp24Si23	125.3 (7)
Cp3–Cp4–Si3	125.7 (8)	Cp23–Cp24–Si23	124.7 (8)
Cp4–Cp5–Cp1	108.0 (8)	Cp24–Cp25–Cp21	107.7 (8)
Cp10–Cp6–Cp7	107.3 (7)	Cp30–Cp26–Cp27	109.0 (9)
Cp10–Cp6–Si4	118.6 (7)	Cp30–Cp26–Si24	117.9 (8)
Cp7–Cp6–Si4	132.0 (7)	Cp27–Cp26–Si24	131.1 (8)
Cp8–Cp7–Cp6	107.3 (8)	Cp28–Cp27–Cp26	106.3 (8)
Cp8–Cp7–Si5	120.4 (7)	Cp28–Cp27–Si25	121.7 (8)
Cp6–Cp7–Si5	131.9 (7)	Cp26–Cp27–Si25	131.7 (8)
Cp9–Cp8–Cp7	109.0 (8)	Cp29–Cp28–Cp27	108.0 (9)
Cp10–Cp9–Cp8	107.7 (8)	Cp30–Cp29–Cp28	108.6 (9)
Cp10–Cp9–Si6	124.5 (7)	Cp30–Cp29–Si26	124.7 (8)
Cp8–Cp9–Si6	126.4 (7)	Cp28–Cp29–Si26	125.9 (8)
Cp9–Cp10–Cp6	108.6 (8)	Cp29–Cp30–Cp26	108.2 (9)

[a] Abbreviations: D1, ring centroid Cp1–Cp5; D2, ring centroid Cp6–Cp10; D3, ring centroid Cp21–Cp25; D4, ring centroid Cp26–Cp30.

(d) Structure of Bromo(*N,N,N′,N′*-tetramethylethylenediamine)(η^5-1,2,4-tris(trimethylsilyl)cyclopentadienyl)magnesium (C). The molecular structure of one of the two independent molecules of compound C is shown in Figure 3. The two independent molecules differ only in the angular arrangement of the cyclopentadienyl ring with respect to the other ligands on Mg

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(28) Jutzi, P.; Schlüter, E.; Hursthouse, M. B.; Arif, A. M.; Short, R. L. *J. Organomet. Chem.* **1985**, *299*, 285.

Table III. Selected Interatomic Bond Distances (Å) and Angles (deg) of C[a]

molecule 1		molecule 2	
	Bond Distances		
Br1-Mg1	2.523 (2)	Br2-Mg2	2.510 (2)
Si1-C1	1.866 (5)	Si21-C21	1.868 (5)
Si2-C2	1.858 (4)	Si22-C22	1.865 (5)
Si3-C4	1.863 (5)	Si23-C24	1.867 (5)
Mg1-D1	2.165	Mg-D2	2.169
Mg1-N1	2.269 (5)	Mg2-N21	2.259 (5)
Mg1-N2	2.230 (5)	Mg2-N22	2.218 (5)
N1-C7	1.501 (8)	N21-C27	1.480 (9)
N2-C6	1.462 (8)	N22-C26	1.478 (9)
C1-C2	1.467 (6)	C21-C22	1.457 (6)
C1-C5	1.411 (6)	C21-C25	1.418 (7)
C2-C3	1.433 (6)	C22-C23	1.430 (6)
C3-C4	1.423 (6)	C23-C24	1.424 (6)
C4-C5	1.423 (7)	C24-C25	1.424 (6)
C6-C7	1.48 (1)	C26-C27	1.46 (1)
	Bond Angles		
Br1-Mg1-N1	99.0 (1)	Br2-Mg2-N21	97.7 (1)
Br1-Mg1-N2	94.0 (1)	Br2-Mg2-N22	95.4 (1)
N1-Mg1-N2	82.6 (2)	N21-Mg2-N22	83.0 (2)
D1-Mg1-N2	123.3	D2-Mg2-N22	122.2
D1-Mg1-N1	122.7	D2-Mg2-N21	121.6
D1-Mg1-Br1	124.9	D2-Mg2-Br2	126.3
Mg1-N1-C7	102.8 (4)	Mg2-N21-C27	103.1 (4)
Mg1-N1-C8	116.5 (4)	Mg2-N21-C28	116.3 (4)
Mg1-N1-C9	112.4 (4)	Mg2-N21-C29	113.2 (4)
Mg1-N2-C6	102.2 (3)	Mg2-N22-C26	101.4 (4)
Mg1-N2-C10	115.2 (4)	Mg2-N22-C30	115.3 (4)
Mg1-N2-C11	113.9 (4)	Mg2-N22-C31	114.1 (4)
Si1-C1-C2	131.4 (3)	Si21-C21-C22	130.8 (3)
Si1-C1-C5	121.3 (3)	Si21-C21-C25	121.2 (4)
C2-C1-C5	106.7 (4)	C22-C21-C25	106.5 (4)
S22-C2-C1	132.5 (3)	Si22-C22-C21	133.6 (3)
Si2-C2-C3	121.7 (3)	Si22-C22-C23	119.9 (3)
C1-C2-C3	105.0 (4)	C21-C22-C23	105.9 (4)
C2-C3-C4	112.1 (4)	C22-C23-C24	111.5 (4)
Si3-C4—C3	124.5 (4)	Si23-C24-C23	125.9 (4)
Si3-C4-C5	128.2 (3)	Si23-C24-C25	126.1 (3)
C3-C4C5	104.1 (4)	C23-C24-C25	104.5 (4)
C1-C5-C4	112.1 (4)	C21-C25-C24	111.6 (4)

[a] Abbreviations: D1, ring centroid C1-C5; D2, ring centroid C21-C25.

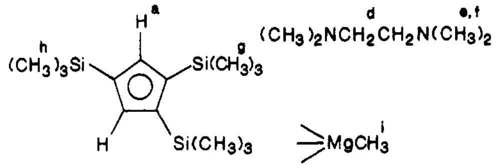
and by a slightly different rotational orientation of one trimethylsilyl group. Both differences might be induced by intermolecular packing forces. Bond distances and angles are comparable within the given experimental error, as seen from Table III.

The coordination geometry of the magnesium atoms can be thought of as tetrahedral, with two nitrogen atoms of TMEDA, bromine, and the cyclopentadienyl ring occupying the four coordination sites.

In C the average distance between the metal and the Cp ring is slightly longer than that in compound B but is shorter than that in an analogous compound containing no trimethylsilyl substituents on the cyclopentadienyl ring.[17] The shortening may imply a greater degree of covalent character induced by the trimethylsilyl groups. Comparison of these results with those for Cp_2Mg[13] suggests that the metal–ring distance in B might be even shorter were it not for the existence of overriding steric effects.

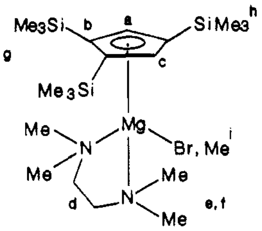
The carbon atoms of the cyclopentadienyl ring lie in a plane. The silicon atoms, however, deviate significantly from coplanarity (6.0–16°). The latter value is found for Si3, which is closest to the TMEDA ligand. Selected bond distances and angles are given in Table III.

Table IV. ^1H NMR Data (δ, C_6D_6 Solution, Room Temperature)



	A	B	C
a	6.99	6.99	7.00
d	1.46		1.34
e, f	1.82		1.85
g	0.57	0.47	0.62
h	0.27	0.41	0.22
i	−1.35		

Table V. ^{13}C NMR Data (−60 °C, C_7D_8 Solution)



	A			C		
	δ	mult	$^1J_{CH}$, Hz	δ	mult	$^1J_{CH}$, Hz
a	129.21	d	159	129.55	d	160
b	122.94	s		124.29	s	
c	115.15	s		116.89	s	
d	54.84	t	135	54.97	t	137
e	47.18	q	135	49.58	q	137
f	46.93	q	135	47.51	q	137
g	2.65	q	118	2.70	q	117
h	1.93	q	118	1.60	q	117
i	−6.39	q	106			

(e) ^1H NMR Spectra. The ^1H NMR spectra of A–C are summarized in Table IV. Resonances due to the Si_3Cp fragment are found in similar positions to those in η^5-bonded Si_3Cp compounds of other main-group elements.[29] The spectra of A and C may be compared with that of (*N,N,N′,N′*-tetramethylethylenediamine)(η^5-1,2,4-tris(trimethylsilyl)cyclopentadienyl)lithium (NMR (C_6D_6) δ 6.89 (s, 2), 1.73 (s, 12), 1.44 (s, 4), 0.53 (s, 18), 0.40 (s, 9)).[3] In the ^1H NMR spectrum of A the position of the resonance at δ −1.35 is noteworthy, coming to an unusually low field for a terminal methyl group bound to magnesium. Some comparative measurements are summarized below.

sample	solv	δ
A	C_6D_6	-1.35
A	Et_2O	-1.69
$[CpMg(Et_2O)Me]_2$	C_6H_6	-1.17[a]
$CpMg(Et_2O)_xMe$	Et_2O	-1.70[a]
$(MgMe_2)_x$	Et_2O	-1.51
$(TMEDA)MgMe_2$	Et_2O	-1.68

[a] From ref 19.

Ashby has investigated the ^1H NMR spectra of the compound with the empirical formula "$CpMg(Et_2O)Me$" and ascribes the resonance at δ −1.17 in the spectrum of a solution of this substance in benzene to the bridging methyl groups of a dimeric species. However, cryoscopic measurements show that A is monomeric in benzene. Furthermore, the position of the methyl resonance in a spectrum of A in diethyl ether is "normal". Therefore, we ascribe its unusually low-field position in benzene solution to a simple solvent effect, albeit a rather large one.

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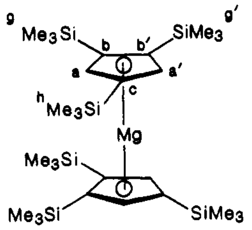
(29) Jutzi, P.; Schlüter, E. *J. Organomet. Chem.* 1983, *253*, 313.

Table VI. ^{13}C NMR Data (B, C_7D_8 Solution)



	δ(27 °C)	δ(−80 °C)	mult	$^1J_{CH}$, Hz
a	130.43	130.17 (br)	d	164
a′				
b	127.76	127.18	s	
b′		126.71		
c	123.14	122.37	s	
g	2.09	1.76	q	119
g′		1.68		
h	0.88	0.70	q	119

(f) ^{13}C NMR Spectra. The ^{13}C NMR spectra of A and C are summarized in Table V. Their similarity, together with that of the ^1H NMR spectra, leaves little doubt that A has essentially the same structure as C, at least in solution. In both molecules the two nitrogen-bound methyl groups are inequivalent at low temperature. Their apparent equivalence in the room-temperature ^1H NMR spectra may therefore possibly be due to exchange with traces of free TMEDA.

The ^{13}C NMR spectrum of B is summarized in Table VI. The spectrum is temperature-dependent in that at low temperature all the ring carbon atoms and trimethylsilyl groups become inequivalent (separate signals for carbon atoms a and a′ are not resolved at −80 °C, but a considerable broadening of the room-temperature resonance clearly indicates their approaching inequivalence). This phenomenon we attribute to the freezing out of the rotation of the Si_3Cp rings. At room temperature both rings can rotate freely and the molecule has apparent C_{2v} symmetry. The limiting low-temperature spectrum corresponds to the conformation observed in the solid state (C_2 symmetry; see Figure 2). Restricted rotation of the Si_3Cp rings has not previously been observed, though the phenomenon is known in the chemistry of *tert*-butyl-substituted cyclopentadienyl and cyclooctatetraene derivatives.[30,31]

(g) ^{25}Mg NMR Spectra. The results of ^{25}Mg NMR measurements, together with some comparative data, are listed below.

sample	solv	δ	$w_{1/2}$, Hz
$Si_3CpMg(TMEDA)Me$	toluene	15.0	1100
CpMgEt	THF	−4.0	1500
$Si_3CpMg(TMEDA)Br$	toluene	−15.0	300
CpMgBr[a]	THF	−26.8	60
$(Si_3Cp)_2Mg$	toluene	−79.6	750
Cp_2Mg[a]	toluene	−85.4	105

[a] From ref 20.

The chemical shifts observed resemble those of analogous Cp complexes. These fall well to high field of σ-bound alkyl- and arylmagnesium derivatives and are indicative of considerable covalent character in the metal–ring bonding. The line widths for the Si_3Cp derivatives are somewhat larger than for their cyclopentadienyl analogues: this is probably largely due to the lowering of the site symmetry at the quadrupolar ^{25}Mg nucleus.

Table VII. Mass Spectra for Compounds A–C

		rel abundance		
m/e	assignment[a]	A	B	C
768–776	$(Si_3Cp)_2Mg_2Br \equiv \{1\}$			8.4
756–758	$\{1\}$-Me			0.6
586–592	$(Si_3Cp)_2Mg \equiv \{2\}$	90.5	99.8	37.5
571–577	$\{2\}$-Me	41.3	47.3	9.8
513–517	$\{2\}$-$SiMe_3$	3.7	4.2	1.7
498–502	$\{2\}$-$SiMe_3$, Me	3.8	4.4	1.6
483–489	$\{2\}$-$SiMe_3$, 2Me	3.1	3.6	0.8
395–399	$\{2\}$-$SiMe_3$, 3Me	2.6	3.3	0.4
384–388	$(Si_3Cp)MgBr \equiv \{3\}$			3.2
377–382	$\{2\}$-Si_3Cp, H; +$SiMe_3$	13.4	15.6	1.6
369–374	$\{3\}$-Me			9.1
305–311	$\{2\}$-Si_3Cp	41.6	31.5	7.2
297–302	$(TMEDA)MgBr_2 \equiv \{4\}$			1.3
289–294	$\{2\}$-Si_3Cp, Me, H	12.3	13.2	2.8
282–285	Si_3CpH	9.8	10.6	28.0
217–223	$\{4\}$-Br			36.3
116–117	TMEDA			9.0
103–107	$\{4\}$-Br, TMEDA			5.5
73	$SiMe_3$	100.0	100.0	97.5
58	$SiMe_2$	3.0	0.5	100.0

[a] All major patterns show predicted isotope distribution.

(h) Mass Spectra. The mass spectra of A–C are summarized in Table VII. A gives essentially the same mass spectrum as B and thus presumably decomposes in the gas phase according to eq 4. In comparison with the spectrum

$$2(\eta^5\text{-}C_5H_2(SiMe_3)_3)Mg(\eta^2\text{-}Me_2NCH_2CH_2NMe_2)Me \rightarrow (\eta^5\text{-}C_5H_2(SiMe_3)_3)_2Mg + \ldots \quad (4)$$

of B, that of A exhibits greater intensity of the pattern ascribed to Si_3CpMg^+, which may be symptomatic of some monomolecular decomposition.

In the spectrum of B the molecular ion has high intensity. Wilkinson et al. have interpreted the mass spectra of a number of metallocenes using the simple maxim that fragmentation processes requiring the least expenditure of energy are the most probable.[6] Their results for magnesocene and ferrocene, together with ours for B, are summarized below.

	rel abundance of $Cp'M^+$ (Cp' = Cp or Si_3Cp)[a]
$(Cp)_2Mg$	1.74
$(Cp)_2Fe$	0.36
$(Si_3Cp)_2Mg$	0.32

[a] Intensity of molecular ion = 1 in each case.

The relative instability of the molecular ion for magnesocene led Wilkinson to the conclusion that the metal–ring bonding in this compound is of a quite different nature (i.e., ionic) from that in ferrocene. It can readily be seen from the intensity ratios above, however, that making the same comparison between the spectrum of B and that of ferrocene leads to a quite different conclusion: namely, that B, like ferrocene, is a covalently bonded molecule.

Further evidence for the strength of the metal–ring bond in Si_3Cp–magnesium derivatives is provided by the mass spectrum of C. Although no molecular ion could be observed, species containing the Si_3CpMg unit are still in high abundance. Two gas-phase decomposition processes seem to be indicated: the first is a process analogous to eq 4, leading to formation of B; the second is summarized in eq 5.

$$2(\eta^5\text{-}C_5H_2(SiMe_3)_3)Mg(\eta^2\text{-}Me_2NCH_2CH_2NMe_2)Br \rightarrow [(\eta^5\text{-}C_5H_2(SiMe_3)_3)MgBr]_2 + 2\ Me_2NCH_2CH_2NMe_2 \quad (5)$$

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(30) Luke, W. D.; Streitwieser, A., Jr., *J. Am. Chem. Soc.* **1981**, *103*, 3241.

(31) Erker, G.; Mühlenbernd, T.; Benn. R.; Rufinska. A.; Tsay, Y.-H.; Krüger, C. *Angew. Chem.* **1985**, *97*, 336.

Table VIII. Infrared Data[a] for Compounds A–C and Tris(trimethylsilyl)cyclopentadiene (Si_3CpH)

Si_3CpH[b]	A	B	C
1437 (m)	1427 (m)	1417 (w)	1424 (m)
1403 (w)	1404 (w)	1400 (w)	1403 (w)
	1353 (w)		1353 (w)
	1344 (w)		1344 (w)
	1289 (m)	1330 (w)	1296 (m)
		1310 (vw)	1283 (m)
1248 (s)	1248 (s)	1246 (vs)	1249 (vs)
			1240 (s)
	1185 (w)		1192 (w)
	1160 (w)		1166 (w)
	1144 (w)	1133 (w)	1142 (w)
1114 (w)	1113 (w)		1120 (w)
	1084 (m, br)	1082 (s)	1083 (s)
	1062 (w)		1062 (m)
	1042 (w)		1042 (m)
	1024 (m)		1021 (s)
977 (m)	1010 (m)	1004 (m)	1010 (s)
916 (w)	952 (m)		953 (m)
907 (m)	941 (m)	943 (m)	942 (s)
879 (s)	929 (w)		930 (w)
828 (vs)	830 (vs, br)	835 (vs, br)	830 (vs, br)
	795 (m)		798 (s)
754 (m)	755 (s)	753 (s)	753 (s)
740 (s)			
690 (m)	683 (m)	689 (m)	684 (s)
	647 (w)	645 (w)	649 (m)
633 (m)	638 (m)	640 (m)	641 (m)
628 (m)	629 (s)	630 (m)	630 (m)
619 (m)	581 (w)		586 (m)
	528 (w)		
	499 (m)	498 (w)	500 (s)
444 (s)	473 (m)		463 (w)
	432 (w)	425 (w)	432 (m)
			394 (m)
			375 (w)
			362 (w)

[a] Band positions (cm^{-1}) and strengths (vw = very weak, w = weak, m = medium, s = strong, vs = very strong, br = broad). Only bands observed between 1500 and 300 cm^{-1} are listed. [b] Recorded as a thin film between KBr disks.

(i) Infrared Spectra. The infrared spectra of A–C together with that of Si_3CpH are summarized in Table VIII. The spectrum of B is similar to that of bis(η^5-1,2,4-tris(trimethylsilyl)cyclopentadienyl)iron, a ferrocene derivative whose IR spectrum has been reported.[32]

The spectra of A and C are in accord with the presence of bidendate TMEDA.[33] We assign the band common to their spectra at 581/586 cm^{-1} to a magnesium–nitrogen absorption (cf. metal–nitrogen bands in ((TMEDA)$_2$RhCl$_2$)Cl, 537, 517 cm^{-1};[34] (TMEDA)Pt(SCN)$_2$, 532, 511 cm^{-1} [35]). The spectrum of A contains two bands in the 470–530 cm^{-1} range that probably are due to skeletal vibrations associated with the methyl group. The spectra of (η^5-cyclopentadienyl)methylmagnesium and other methylmagnesium compounds also exhibit absorptions in this region.[19] The low-frequency region of B's spectrum (bands at 498 and 425 cm^{-1}) may be compared with those of magnesocene (524 (m), 461 (s) cm^{-1})[9] and decamethylmagnesocene (517 (s), 427 (m) cm^{-1}).[15] The spectrum of C is almost the same as that of A above 550 cm^{-1}; at a lower frequency, three, presumably magnesium–bromine, absorptions are present in the range 360–400 cm^{-1}.

(j) Electron Configuration. We note that A–C are all 12-electron compounds, but in our experience organometallic compounds of main-group elements, aside from the marked stability of the eight-electron configuration, often are able to accommodate varying numbers of valence electrons by a geometrical distortion,[36] so that this coincidence may not be significant. For magnesocene, however, 12 electrons do represent a filling of all metal–ring bonding and nonbonding orbitals, and Böhm[37] has calculated that the HOMO–LUMO energy gap is about 3 eV in this molecule.

Conclusion

The new (η^5-Si_3Cp)Mg^{II} compounds A–C, prepared by reaction of Si_3CpH with an appropriate methylmagnesium precursor, exhibit interesting physical and spectroscopic features. There are several indications of covalent character in the metal–ring bond: (i) the failure of B to form a coordination complex with TMEDA and the monomeric nature of A and C in benzene solution; (ii) the high solubility of A–C in hydrocarbon solvents, the low melting points of A and C, and the relatively high volatility of B; (iii) the comparatively short metal–ring carbon distances in the structures of B and C; (iv) the high-field position of the ^{25}Mg NMR resonances of A–C; (v) the high intensity of the molecular ion in the mass spectrum of B and the observation of the ion $[(Si_3Cp)MgBr]_2^+$ in the mass spectrum of C.

A stark preference for the least sterically hindered conformer in the structure of B, both in the solid state, as determined by X-ray diffraction, and in solution, as determined by ^{13}C NMR spectroscopy, has been observed.

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Supplementary Material Available: Detailed information on the crystal structure determination of B and C including tables of final atomic positional parameters, final thermal parameters, and interatomic distances and angles (20 pages); lists of observed and calculated structure factors for B and C (59 pages). Ordering information is given on any current masthead page.

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(38) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)