Magnesiation of Isodicyclopentadiene. Formation of Sandwich and Monomeric Complexes and the Stereoselectivity of Their Reactions with Transition Metal Halides

Olivier Gobley,[†] Sébastien Gentil,[†] Jeffrey D. Schloss,[‡] Robin D. Rogers,[§]
Judith C. Gallucci,[‡] Philippe Meunier,[†] Bernard Gautheron,*,[†] and
Leo A. Paquette*,[‡]

*Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS, UMR 5632,
Université de Bourgogne, BP 138, 21004 Dijon Cedex France, Department of Chemistry,
The Ohio State University, Columbus, Ohio 43210, and Department of Chemistry,
The University of Alabama, Tuscaloosa, Alabama 35487*

The *exo,exo*-bis(isodicyclopentadienyl)magnesium sandwich and the monomeric *exo*-(isodicyclopentadienyl)butylmagnesium TMEDA complex have been synthesized and characterized by ^{1}H and ^{13}C NMR spectroscopy in C_6D_6 solution. The solid-state structures were determined by X-ray crystallography. The stereoselectivity with which both moisture-sensitive compounds react with $TiCl_3 \cdot 3THF$ and $ZrCl_4$ was assessed and suitably compared to related observations recorded for alkali metal (Li^+, Na^+, and K^+) complexes of isodicyclopentadiene.

The molecular array isodicyclopentadiene (**1**) is the linchpin of a growing family of bicyclo-fused cyclopentadienes that possess the ability to discriminate between their two π-surfaces when ligating to metal ions under the proper conditions. As part of a long-standing interest in this phenomenon,[1] we have recently accorded attention to the stereoselectivity of complexation of the isodicyclopentadienide (isodiCp) anion **2** with alkali metal ions. The lithium salt was examined first because

1   **2**

of the remarkable temperature-dependent behavior exhibited by this species toward various electrophiles.[2] Detailed multinuclear NMR studies revealed the existence of a monomer−dimer equilibrium involving **3** and **4**.[3] In agreement with theory, a preponderance of the contact ion pair **3** is favored at room temperature and at higher concentrations.[4]

3   **4**
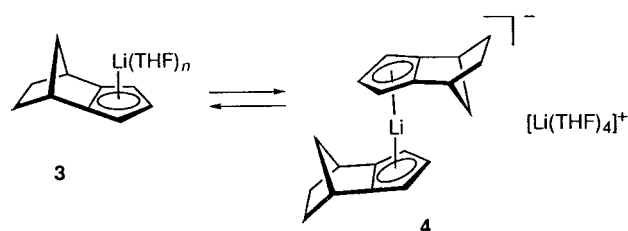
Success has also been achieved in isolating crystalline forms of these salts for X-ray diffraction analysis.[5] In the presence of TMEDA, Li isodiCp slowly deposits colorless crystals of **5** from ether solution. In a similar experiment, dropwise introduction of 12-crown-4 in THF affords the less robust pale yellow complex **6**,

5   **6**
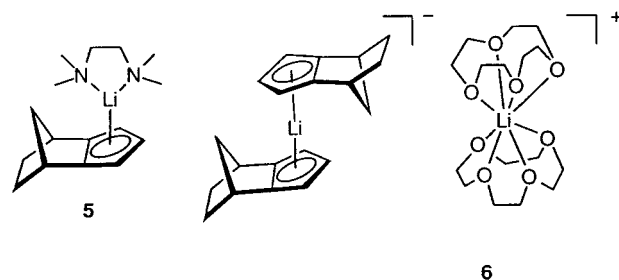
with the oxygen atoms about the Li^+ ion adopting a distorted square antiprism geometry with approximate D_{4d} symmetry. These observations lend strong

[†] Université de Bourgogne.
[‡] The Ohio State University.
[§] The University of Alabama.
(1) (a) Hsu, L.-Y.; Hathaway, S. J.; Paquette, L. A. *Tetrahedron Lett.* **1984,** *25,* 259. (b) Paquette, L. A.; Moriarty, K. J.; Meunier, P.; Gautheron, B.; Sornay, C.; Rogers, R. D.; Rheingold, A. L. *Organometallics* **1989,** *8,* 2159. (c) Sornay, C.; Meunier, P.; Gautheron, B.; O'Doherty, G. A.; Paquette, L. A. *Organometallics* **1991,** *10,* 2082.
(2) (a) Paquette, L. A.; Charumilind, P.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1983,** *105,* 3126. (b) Paquette, L. A.; Charumilind, P.; Gallucci, J. C. *J. Am. Chem. Soc.* **1983,** *105,* 7364.
(3) Paquette, L. A.; Bauer, W.; Sivik, M. R.; Bühl, M.; Feigel, M.; Schleyer, P. von R. *J. Am. Chem. Soc.* **1990,** *112,* 8776.

(4) The unsaturated congener of the lithium salt of **2** shows greater stability for the endo lithium monomer: Paquette, L. A.; Sivik, M. R.; Bauer, W.; Schleyer, P. von R. *Organometallics* **1994,** *13,* 4919.
(5) (a) Zaegel, F.; Gallucci, J. C.; Meunier, P.; Gautheron, B.; Sivik, M. R.; Paquette, L. A. *J. Am. Chem. Soc.* **1994,** *116,* 6466. (b) Gallucci, J. C.; Sivik, M. R.; Paquette, L. A.; Zaegel, F.; Meunier, P.; Gautheron, B. *Acta Crystallogr.* **1996,** *C52,* 1673.

Table 1. Comparative 500 MHz ^{1}H and 125 MHz ^{13}C NMR Spectral Data for 7 and 8 (δ, C_6D_6 Solution)

					^{1}H NMR				
compd	central	peripheral	bridgehead	*exo*-ethano	*endo*-ethano	*syn*-methano	*anti*-methano	butyl	TMEDA
7	5.99	5.92	3.33	1.69	0.95	1.76	1.61		
8	6.10	6.02	3.56	2.00	1.39	2.01	1.81	1.96, 1.87, 1.42, −0.55	1.93, 1.89

				^{13}C NMR				
compn	central	peripheral	quaternary	bridgehead	ethano bridge	methano bridge	butyl	TMEDA
7	106.6	98.6	133.5	40.9	29.2	52.0		
8	103.6	94.9	132.1	42.1	30.6	51.4	34.6, 33.2, 14.9, 11.5	56.0, 46.9

support to the NMR investigations while demonstrating the preference of the Cp rings for exo coordination and adoption of a staggered arrangement in the solid state.

In the case of Na isodiCp, exposure to 15-crown-5 furnished pale green crystals of an exo monomeric complex similar to **5** but with the sodium ion now ligated to the crown ether.[6] Extension to K isodiCp provided the opportunity to involve (2.2.2) cryptand. The resulting purple-tinted crystals feature the potassium ion totally encapsulated by the cryptand, such that no interaction occurs with the naked isodiCp anion.[6]

A structural feature common to all four crystalline complexes is the bend about the C1−C5 bond, which is shared by the norbornene framework and the Cp ring. Notwithstanding the complete dissociation that exists in [K-cryptand(2.2.2)]$^+$(isodiCp)$^-$, a dihedral angle of 8.3° in an endo direction persists and is therefore considered to be an integral structural characteristic of **2**.[7]

Although (η^5-cyclopentadienyl)lithium derivatives abound, their magnesium counterparts have been accorded far less attention. Although X-ray[8] and electron diffraction studies[9] on magnesocene reveal this complex to be isostructural with ferrocene, few of its more highly substituted derivatives have been comparably examined.[10−12] Monocyclopentadienyl derivatives of magnesium have similarly been largely ignored.[12−15] The relatively short Mg−C distances that have been observed by X-ray diffraction provide modest indication of possible covalent character in the Mg−ring bonds. However, if the chemical behavior of the magnesocenes[16] is used as the guiding principle, their classification as

ionic sandwich compounds would appear more appropriate.[17]

Inspired by our successful efforts in developing stereoselective processes based upon the isodiCp anion **2** and analogues thereof,[18] we have now sought to rigorously define the behavior exhibited by magnesium complexes in related contexts.

Results and Discussion

With an atomic diameter of 1.30 Å, Mg^{2+} compares closely in size to Li$^+$ (1.20 Å) and is significantly smaller than Na$^+$ (1.90 Å), Ca^{2+} (1.98 Å), K$^+$ (2.66 Å), or Ba^{2+} (2.70 Å). On this basis, the coordination of the magnesium ion to the exo π-surface of **2** was anticipated. Indeed, heating isodicyclopentadiene (**1**) with dibutylmagnesium[11] in heptane for 44 h gave rise after solvent evaporation to a white powder. Sublimation of this substance at reduced pressure afforded clear colorless crystals of **7** in 47% yield.
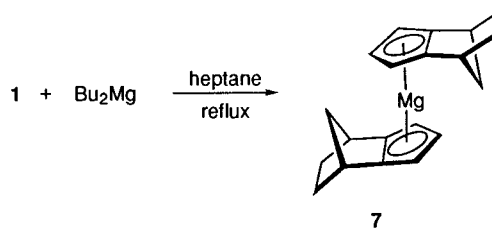
For reasons of solubility, it was not possible to record the ^{1}H and ^{13}C NMR spectra of **7** in the same solvent as that used earlier for **3**−**6**, thereby making direct comparison difficult. On the other hand, the use of C_6D_6 allowed for measurements to be made without degradation (Table 1).

The crystal and molecular structure of **7** has been determined at 173 K because of the instability of this complex under the conditions of measurement at more elevated temperatures. As depicted in Figure 1, a crystallographic 2-fold axis passes through the magnesium center and relates the two isodiCp anions. The

(6) Gallucci, J. C.; Gobley, O.; Zaegel, F.; Meunier, P.; Gautheron, B.; Lange, H.; Gleiter, R.; Kozmina, N.; Paquette, L. A. *Organometallics* **1998**, *17*, 111.

(7) For a more extreme situation, see: Paquette, L. A.; Shen, C. C. *J. Am. Chem. Soc.* **1990**, *112*, 1159.

(8) (a) Weiss, E.; Fischer, E. O. *Z. Anorg. Allg. Chem.* **1955**, *278*, 219. (b) Bünder, W.; Weiss, E. *J. Organomet. Chem.* **1975**, *92*, 1.

(9) Haaland, A.; Lusztyk, J.; Brunvoll, J.; Starowieyski, K. *J. Organomet. Chem.* **1975**, *85*, 279.

(10) Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882.

(11) Duff, A. W.; Hitchcock, P. B.; Lappert, M. F.; Taylor, R. G.; Segal, J. A. *J. Organomet. Chem.* **1985**, *293*, 271.

(12) Morley, C. P.; Jutzi, P.; Krüger, C.; Wallis, J. M. *Organometallics* **1987**, *6*, 1084.

(13) Johnson, C.; Toney, J.; Stucky, G. D. *J. Organomet. Chem.* **1972**, *40*, C11.

(14) House, H. O.; Latham, R. A.; Whitesides, G. M. *J. Org. Chem.* **1967**, *32*, 2481.

(15) Parris, G. E.; Ashby, E. C. *J. Organomet. Chem.* **1974**, *72*, 1.

(16) For example see: Collins, S.; Hong, Y.; Taylor, N. J. *Organometallics* **1990**, *9*, 2695.

(17) Faegri, K., Jr.; Almlöf, J.; Lüthi, H. P. *J. Organomet. Chem.* **1983**, *249*, 303.

(18) (a) Paquette, L. A.; Schirch, P. F. T.; Hathaway, S. J.; Hsu, Y.-L.; Gallucci, J. C. *Organometallics* **1986**, *5*, 490. (b) Paquette, L. A.; Hathaway, S. J.; Schirch, P. F. T.; Gallucci, J. C. *Organometallics* **1986**, *5*, 500. (c) Gallucci, J. C.; Gautheron, B.; Gugelchuck, M.; Meunier, P.; Paquette, L. A. *Organometallics* **1987**, *6*, 15. (d) Paquette, L. A.; Gugelchuk, M.; McLaughlin, M. L. *J. Org. Chem.* **1987**, *52*, 4732. (e) Paquette, L. A.; Moriarty, K. J.; Meunier, P.; Gautheron, B.; Crocq, V. *Organometallics* **1988**, *7*, 1873. (f) Paquette, L. A.; Moriarty, K. J.; McKinney, J. A.; Rogers, R. D. *Organometallics* **1989**, *8*, 1707. (g) Paquette, L. A.; Moriarty, K. J.; Rogers, R. D. *Organometallics* **1989**, *8*, 1506.
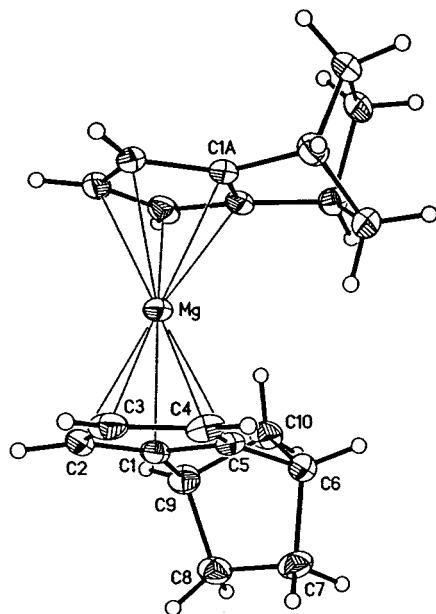
Figure 1. Computer-generated perspective drawing of the final X-ray model of **7**.

Table 2. Selected Bond Lengths (Å) for 7

atom	atom	distance	atom	atom	distance
Mg	C(3)	2.3141(16)	C(2)	C(3)	1.424(3)
Mg	C(5)	2.3352(15)	C(3)	C(4)	1.425(3)
Mg	C(4)	2.3381(16)	C(4)	C(5)	1.413(2)
Mg	C(1)	2.3438(15)	C(5)	C(6)	1.517(2)
Mg	C(2)	2.3470(16)	C(6)	C(10)	1.548(2)
Mg	cent^a	1.9997(7)	C(6)	C(7)	1.556(2)
C(1)	C(5)	1.415(2)	C(7)	C(8)	1.557(3)
C(1)	C(2)	1.416(2)	C(8)	C(9)	1.558(2)
C(1)	C(9)	1.512(2)	C(9)	C(10)	1.547(2)

^{a} Cent is the centroid of atoms C(1)−C(5).

cyclopentadienyl rings are staggered. Pentahapto coordination between the Mg and the aromatic Cp rings is clearly in effect. The Mg−C bond lengths involved are seen to range from 2.3141 to 2.3470 Å (Table 2). The distance between the magnesium atom and the center of each Cp ring is approximately 2.0 Å. This value corresponds very closely to that observed for the parent magnesocene (1.98 Å).

The two isodiCp ligands are slightly deformed to the exterior of the sandwich, as revealed by the interannular Cp−Mg−Cp angle of 174.7° (Table 3). This deformation is believed to originate from the steric interaction involving the two norbornyl subunits.

Although the size of Mg^{2+} is not too different from the size of Li^+, the conformations of **6** and **7** are very different. Because the Li^+ occupies an inversion center in Li(isodiCp)₂, the isodiCp ligands point in opposite directions, and the (ring centroid−Li−ring centroid) angle is restricted to 180°. In Mg(isodiCp)₂, the Mg^{2+} is on a 2-fold axis and the isodiCp ligands are oriented differently than in Li(isodiCp)₂. We have no rationale at present regarding why these two conformations exist. Perhaps there is another isomer of Mg(isodiCp)₂ in which the Mg is on an inversiton center, and maybe there is an isomer for Li(isodiCp)₂ with the Li on a 2-fold axis.

In a companion study, access to a mono isodiCp derivative of magnesium was gained by reacting **7** with

Table 3. Selected Bond Angles (deg) for 7^a

cent−Mg−cent#1	174.7(1)
C(5)−C(1)−C(2)	108.63(14)
C(5)−C(1)−C(9)	106.78(14)
C(2)−C(1)−C(9)	143.59(16)
C(1)−C(2)−C(3)	106.75(15)
C(2)−C(3)−C(4)	109.09(15)
C(5)−C(4)−C(3)	106.82(15)
C(4)−C(5)−C(1)	108.69(15)
C(4)−C(5)−C(6)	143.64(15)
C(1)−C(5)−C(6)	106.73(14)
C(5)−C(6)−C(10)	99.93(13)
C(5)−C(6)−C(7)	106.51(13)
C(10)−C(6)−C(7)	99.49(13)
C(6)−C(7)−C(8)	103.41(13)
C(7)−C(8)−C(9)	103.76(13)
C(1)−C(9)−C(10)	99.95(13)
C(1)−C(9)−C(8)	106.72(13)
C(10)−C(9)−C(8)	99.24(14)
C(9)−C(10)−C(6)	95.34(13)

^{a} Symmetry transformations used to generate equivalent atoms: #1 −x,y,−z$^{+3/2}$.

dibutylmagnesium in ether containing TMEDA at room temperature for 72 h. Orange crystals of **8** suitable for
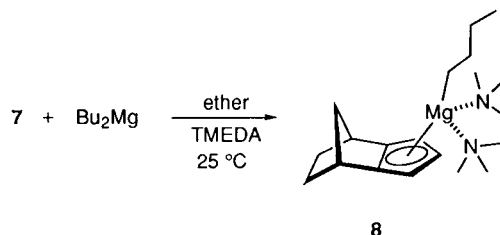
X-ray diffraction were isolated by recrystallization from pentane. The significantly altered electronic environment at the Mg center in **8**, which is brought on chiefly by complexation to TMEDA, is reflected in the significant deshielding ($\Delta\delta$ = 0.10 to 0.44 ppm) experienced by the entire ensemble of protons relative to those in **7** (Table 1). The transition from a sandwich dimer to a monomeric species does not have a similar dramatic effect on ^{13}C chemical shifts.

The molecular structure of **8** as derived from X-ray diffraction measurements at 223 K is shown in Figure 2. As is the case with **5** and Na isodiCp·15-crown-5, the metal is positioned on the exo face and interacts in η^5 fashion with the cyclopentadienide ring. The relevant Mg−C distances are in the range of 2.439−2.545 Å (Table 4). At 2.189 Å, the distance between the Mg and the center of the Cp ring compares quite favorably with the values observed for (Cp)Mg(Br)(TMEDA)[13] and {1,2,4-(SiMe₃)₃Cp}Mg(Br)(TMEDA),[12] which are 2.21 and 2.167 Å, respectively. The dihedral angle for the downward bending across C-1 and C-5 has increased somewhat to 10.0° (Table 5). A more detailed comparison of structural parameters can be found in Table 6. To the present time, three structural forms of π-complexes involving magnesium have been identified (Figure 3). Of these, **7** is best represented by **B** and **8** by **C**.

At this stage, we were in a position to implement a comparative analysis of the stereoselectivity with which **7**, **8**, and the alkali metal complexes of isodiCp react with organometallic electrophiles. One of the several objectives of this effort was to uncover the best means for preparing individual transition metal complexes
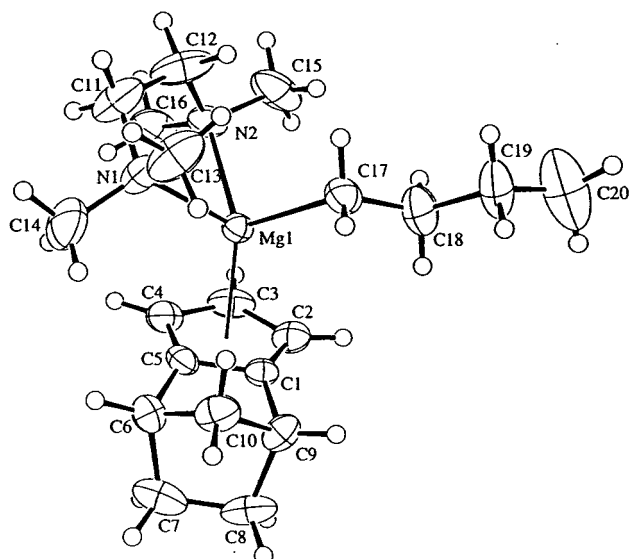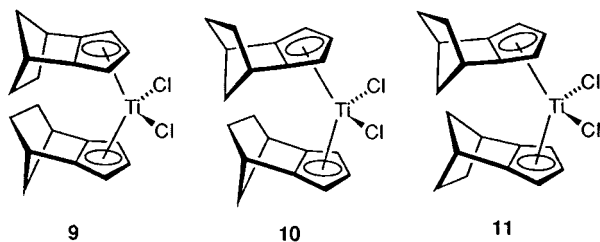
Figure 2. Computer-generated perspective drawing of the final X-ray model of **8**.

Table 4. Selected Bond Lengths (Å) for 8

atom	atom	distance	atom	atom	distance
Mg(1)	N(1)	2.318(4)	C(1)	C(5)	1.389(5)
Mg(1)	N(2)	2.255(5)	C(1)	C(9)	1.507(5)
Mg(1)	C(1)	2.542(4)	C(2)	C(3)	1.398(6)
Mg(1)	C(2)	2.545(4)	C(3)	C(4)	1.395(6)
Mg(1)	C(3)	2.441(4)	C(4)	C(5)	1.411(5)
Mg(1)	C(4)	2.439(4)	C(5)	C(6)	1.511(5)
Mg(1)	C(5)	2.489(4)	C(6)	C(7)	1.545(7)
Mg(1)	C(17)	2.145(4)	C(6)	C(10)	1.539(6)
N(1)	C(11)	1.475(6)	C(7)	C(8)	1.532(7)
N(1)	C(13)	1.473(6)	C(8)	C(9)	1.535(6)
N(1)	C(14)	1.475(6)	C(9)	C(10)	1.527(5)
N(2)	C(12)	1.475(6)	C(11)	C(12)	1.470(7)
N(2)	C(15)	1.471(5)	C(17)	C(18)	1.506(6)
N(2)	C(16)	1.460(6)	C(18)	C(19)	1.551(6)
C(1)	C(2)	1.402(5)	C(19)	C(20)	1.377(7)
Mg(1)	cent*a*	2.189(2)			

a Cent is the ring centroid of C(1)−C(5).

conveniently in as pure a form as possible. The prospects offered by TiCl$_3$·3THF were pursued first (Table 7). The reactions were performed for a standard 5 h at one of two temperatures followed by a classical workup. The proportions of the *endo,endo*-**9**, *endo,exo*-**10**, and *exo,exo*-titanocene dichloride (**11**) were determined by integra-

tion of ¹H NMR spectra. The complexes isodiCpLi-(TMEDA) and [isodiCpLi(12-C-4]$_2$ give rise at ambient temperature to 40% and 25% of **10** in addition to 20% and 15%, respectively, of **9** (expts 3 and 4). In contrast, isodiCpLi(THF)$_n$ leads almost exclusively to **9** at low temperature (expt 2). The impressive crossover in stereoselectivity exhibited by **3** at 25 °C (expt 1) has been attributed to a pronounced shift in the **3** $\rightleftarrows$ **4**

Table 5. Selected Bond Angles (deg) for 8

atom	atom	atom	angle	atom	atom	atom	angle
N(1)	Mg(1)	N(2)	79.9(1)	C(1)	C(2)	C(3)	106.1(4)
N(1)	Mg(1)	C(17)	100.5(2)	C(2)	C(3)	C(4)	110.0(4)
N(2)	Mg(1)	C(17)	103.9(2)	C(3)	C(4)	C(5)	106.6(4)
N(1)	Mg(1)	cent*a*	123.5(1)	C(1)	C(5)	C(4)	107.9(4)
N(2)	Mg(1)	cent*a*	118.9(1)	C(1)	C(5)	C(6)	106.3(4)
C(17)	Mg(1)	cent*a*	121.6(1)	C(4)	C(5)	C(6)	144.2(4)
Mg(1)	N(1)	C(11)	105.5(3)	C(5)	C(6)	C(7)	106.2(4)
Mg(1)	N(1)	C(13)	108.3(3)	C(5)	C(6)	C(10)	99.9(3)
Mg(1)	N(1)	C(14)	116.9(3)	C(7)	C(6)	C(10)	99.1(4)
C(11)	N(1)	C(13)	109.3(4)	C(6)	C(7)	C(8)	104.2(4)
C(11)	N(1)	C(14)	108.6(4)	C(7)	C(8)	C(9)	103.2(4)
C(13)	N(1)	C(14)	108.0(4)	C(1)	C(9)	C(8)	106.8(3)
Mg(1)	N(2)	C(12)	101.0(2)	C(1)	C(9)	C(10)	100.0(3)
Mg(1)	N(2)	C(15)	108.9(3)	C(8)	C(9)	C(10)	99.7(3)
Mg(1)	N(2)	C(16)	119.5(3)	C(6)	C(10)	C(9)	95.1(3)
C(12)	N(2)	C(15)	107.0(4)	N(1)	C(11)	C(12)	113.0(4)
C(12)	N(2)	C(16)	111.7(4)	N(2)	C(12)	C(11)	112.5(5)
C(15)	N(2)	C(16)	108.0(4)	Mg(1)	C(17)	C(18)	120.0(3)
C(2)	C(1)	C(5)	109.4(4)	C(17)	C(18)	C(19)	115.7(4)
C(2)	C(1)	C(9)	142.0(4)	C(18)	C(19)	C(20)	114.8(5)
C(5)	C(1)	C(9)	107.3(3)				

a Cent is the ring centroid of C(1)−C(5).

equilibrium.[3] The lack of reactivity of **6** at −64 °C (expt 9) can be rationalized in terms of competitive sequestration of titanium(III) by the crown ether, because the diameter of this ion (1.52 Å) is well-matched with the cavity present in 12-crown-4 (1.2−1.5 Å).

As concerns the isodicyclopentadienyl sodium (15-C-5) complex, no comparable amelioration of the selectivity of complexation is seen as the temperature is changed (expts 5 and 10). The response of the potassium salt is likewise independent of temperature; noteworthily, however, exclusive conversion to **11** now operates (expts 6 and 11).

The magnesocene **7** was found to exhibit behavior most closely paralleling that exhibited by isodiCpLi-(TMEDA) (expts 7 and 12).

Passage from the titanium series into the zirconium realm is invariably met with a diminution in reactivity. For this reason, the reactions undertaken between **3**, isodiCpNa (15-C-5), and **7** and ZrCl$_4$ were performed at 25 °C and at the reflux temperature of THF (expts 13−15). The most notable feature of this subset of reactions is the overwhelming exo,exo bias exhibited by isodiCpLi-(THF)$_n$.

In conclusion, dimeric and monomeric complexes of isodicyclopentadiene to the alkaline earth metal magnesium have been prepared and characterized in solution and the solid state. When reacted with TiCl$_3$·3THF and ZrCl$_4$, these compounds give rise to mixtures of all three possible transition metal complexes.

Experimental Section

***exo,exo*-Bis(isodicyclopentadienyl)magnesium (7).** A solution of isodicyclopentadiene (471 mg, 3.56 mmol) in dry heptane (10 mL) was prepared under argon at 0 °C. Following the addition of dibutylmagnesium (3.6 mL, 1.8 mmol), the reaction mixture was allowed to warm to room temperature and then refluxed for 44 h. The solvent was evaporated, and

Table 6. Comparison of Structural Parameters for Several Magnesium Complexes

complex	structural type[a]	av Mg−C distance (Å)	Mg−Cp centroid (Å)	av C−C(Cp) distance (Å)	ref
(Cp)$_2$Mg	A	2.304	1.98	1.39	8a
{1,2,4-(SiMe$_3$)$_3$Cp}$_2$Mg	B		2.03	1.44	12
(isodiCp)$_2$Mg	B	2.336	2.000	1.419	b
(Cp)Mg(Br)(TMEDA)	C	2.55	2.21	1.43	13
{1,2,4-(SiMe$_3$)$_3$Cp}Mg(Br)(TMEDA)	C		2.167	1.431	12
(isodiCp)Mg(Bu)(TMEDA)	C	2.491	2.189	1.399	b

[a] See Figure 3. [b] Present work.

Table 7. Product Distributions (THF solutions)

expt	complex	reaction temp (°C)	*endo,endo*-**9**	*endo,exo*-**10**	*exo,exo*-**11**
				composition, %	
		TiCl$_3$·3THF			
1	isodiCpLi(THF)$_n$	25	3	2	95
2	isodiCpLi(THF)$_n$	−64	95	5	0
3	isodiCpLi(TMEDA)	25	20	40	40
4	[isodiCpLi(12-C-4)]$_2$	25	15	25	60
5	isodiCpNa(15-C-5)	25	0	5	95
6	isodiCpK(cryptand [2.2.2])	25	0	0	100
7	(isodiCp)$_2$Mg	25	16	41	43
8	isodiCpLi(TMEDA)	−64	55	35	10
9	[isodiCpLi(12-C-4)]$_2$	−64		no reaction	
10	isodiCpNa(15-C-5)	−64	0	10	90
11	isodiCpK(cryptand [2.2.2])	−64	0	0	100
12	(isodiCp)$_2$Mg	−64	15	41	44
		ZrCl$_4$			
13	isodiCpLi(THF)$_n$	reflux	0	0	100
14	isodiCpNa(15-C-5)	25	70	30	0
15	(isodiCp)$_2$Mg	25	62	30	8
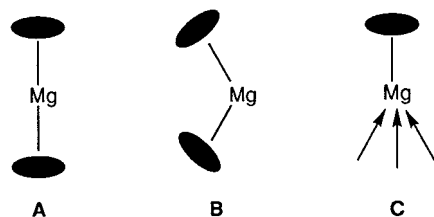
Figure 3. Schematic diagrams of the diverse types of π-complexes to magnesium.

the white solid residue was sublimed to give 239 mg (47%) of **7** as colorless crystals.

***exo*-(Isodicyclopentadienyl)(butyl)magnesium *N,N,N′,N′*-Tetramethylethylenediamine (8).** A solution of **7** (3.6 mL, 1.8 mmol) in dry ether (10 mL) was prepared under argon. Dibutylmagnesium (261 mg, 0.91 mmol) and TMEDA (0.14 mL, 0.91 mmol) were slowly introduced at room temperature. The mixture was stirred for 72 h and freed of solvent. Recrystallization of the residue from pentane afforded **8** as orange crystals (284 mg, 47%).

General Procedure for Reactions Involving TiCl$_3$·3THF. The complex to be reached (0.037 mmol) was dissolved in dry THF (2 mL) under argon and brought to the appropriate temperature (−64 °C or 25 °C). This solution was added to a magnetically stirred solution of TiCl$_3$·3THF (0.020 mmol) in THF (3 mL) at the same temperature. After 5 h, freshly distilled CCl$_4$ (0.2 mL) was introduced, and the agitation was maintained for an additional 15 min. The reaction mixture was poured into concentrated HCl (1 mL) and extracted with CHCl$_3$ (3 × 2 mL). The combined organic phases were washed with water, dried, and concentrated to leave a red-brown solid, which was directly analyzed in CDCl$_3$ by ^{1}H NMR at 200 MHz. The following peaks are characteristic:

endo,endo-**9** δ 6.33, 5.84, 3.34, 1.91, 1.85, 1.73; *endo,exo*-**10** δ 6.29, 6.17, 6.09, 5.86, 3.34, 3.29, 1.94, 1.85, 1.76, 1.32, 1.18, 1.09; *exo,exo* **11** δ 6.27, 6.08, 3.32, 1.86, 1.38, 1.22, 1.11.

General Procedure for Reactions Involving ZrCl$_4$. A flask charged with 10 mL of dry THF under argon is cooled to −78 °C, and zirconium tetrachloride (91 mg, 0.39 mmol) is added in portions. The reaction mixture is allowed to warm to room temperature, whereupon a solution of the complex (0.61 mmol) in THF (10 mL) is introduced dropwise. After 14 h of stirring, the solvent is evaporated, and the residue is taken up in toluene and filtered in order to remove excess ZrCl$_4$, sodium chloride, and magnesium chloride. Evaporation of the filtrate was followed by ^{1}H NMR analysis at 200 MHz on CDCl$_3$ solutions. The following peaks are characteristic:

endo,endo-**9** δ 6.10, 5.90, 3.30, 2.02−1.78; *endo,exo* **10** δ 6.25, 6.04, 5.94, 5.86, 3.31, 3.29, 1.82−1.03; *exo,exo* **11** δ 6.27, 5.82, 3.29, 1.80, 1.46, 0.99.

Supporting Information Available: Crystallographic details and tables of atomic coordinates, isotropic and anisotropic displacement parameters, and positional parameters for **7** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990200N