

Bis(η^3 -indenyl)bis(tetrahydrofuran)magnesium(II)

Holger Gritzko, Frank Schaper
and Hans-Herbert Brintzinger*

Fachbereich Chemie, Universität Konstanz,
Postfach 5560, 78434 Konstanz, Germany

Correspondence e-mail:
hans.brintzinger@uni-konstanz.de

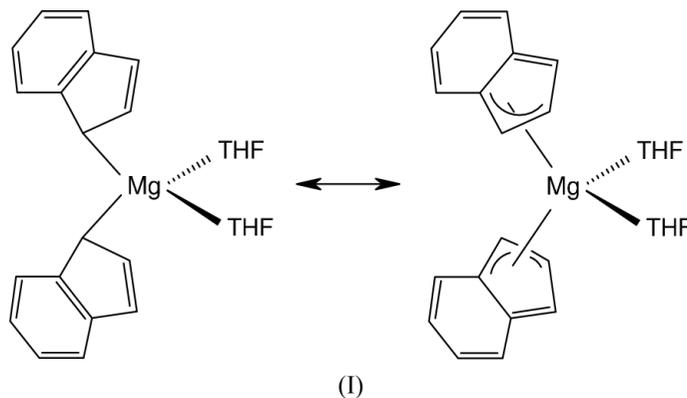
Key indicators

Single-crystal X-ray study
 $T = 188$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.070
 wR factor = 0.190
Data-to-parameter ratio = 18.2

In the crystal structure of the title compound, $[\text{Mg}(\text{C}_4\text{H}_8\text{O})_2(\text{C}_9\text{H}_7)_2]$, the two indenyl ligands are bound to the Mg atom in a manner intermediate between η^1 - and η^3 -coordination; the latter is untypical, as it includes one of the ring-sharing C atoms. The O—Mg—O angle $[101.01^\circ]$ is larger than for any other magnesocene-(THF)₂ adduct (THF is tetrahydrofuran). A crystallographic C_2 axis bisects the O—Mg—O angle.

Comment

The title compound, (I), was prepared as a precursor for syntheses of other metallocenes. $(\text{Ind})_2\text{Mg}$ is known to be polymeric in the solid state, with indenyl (Ind) groups coordinated in monohapto, dihapto or pentahapto arrangements to one or two Mg centres (Atwood & Smith, 1974). By addition of tetrahydrofuran (THF) to this complex, which was prepared *via* a ligand-exchange reaction (Eisch & Sanchez, 1985), we obtained its THF adduct, (I), which is monomeric in the solid state.



A crystallographic C_2 axis bisects the $\text{O}1-\text{Mg}-\text{O}1^i$ angle (symmetry code as in Table 1) and the two indenyl ligands are thus equivalent by symmetry. Unusual features of the coordination geometry of (I) are revealed by comparison with other magnesocene structures. The shortest Mg—C(Cp) distance (Cp is cyclopentadienyl) of 2.256 (3) Å in (I) is similar to the *bona fide* Mg—C(η^1) distance of 2.282 (2) Å for the related compound $(\eta^1\text{-Cp})(\eta^5\text{-Cp})\text{Mg}(\text{THF})_2$, (II) (Jaenschke *et al.*, 2003). The next two Mg—C distances in increasing length are 2.723 (3) and 2.738 (3) Å for (I), compared with 2.736 (2) and 2.880 (2) Å for (II). The shortening of one of these Mg—C bond distances indicates that the hapticity of the indenyl ligands in (I) is slightly higher than the η^1 -coordination assigned to (II). In (I), one of the three

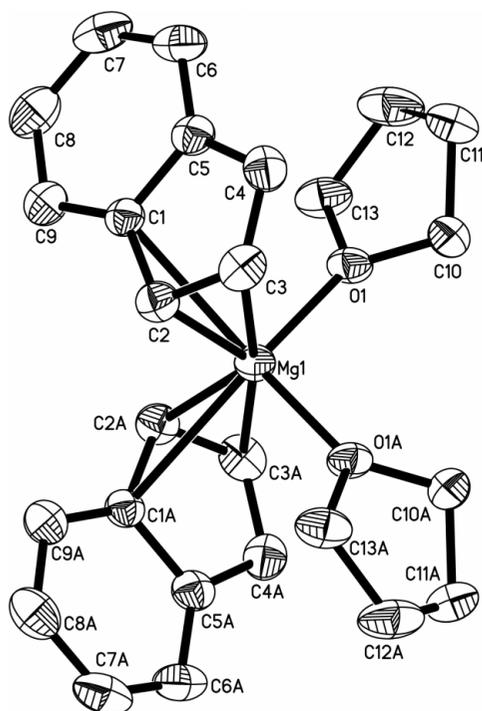


Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. Suffix *A* corresponds to symmetry code (i) in Table 1.

closest-bound C atoms is in a ring-sharing position of the indenyl ligand.

In another comparable structure, *viz.* $C_2H_4(\eta^3\text{-Ind})_2\text{-Mg}(\text{THF})_2$, (III) (Damrau *et al.*, 1998), one of the η^3 -coordinated indenyl ligands has one of its Mg-bound C atoms in a ring-sharing position, as in (I). The three shortest Mg–C distances in (III) [2.328 (3), 2.451 (3) and 2.682 (3) Å] are closer to each other than those in (I). This and their smaller average indicate that the hapticity of the indenyl ligands in (I) is lower than their η^3 -coordination in (III). Corresponding C–C distances of the indenyl fragments are quite similar for (I) and (III); however, the maximum difference is 0.02 Å.

Normally, an allylic η^3 -coordination of an indenyl ligand involves those three C atoms which are not part of the C_6 ring (O'Connor & Casey, 1987). Coordination of an indenyl fragment to an Mg atom involving a ring-sharing C atom, as in (I), has so far been seen only in two bridged magnesocenes [Cambridge Structural Database (CSD, Version 5.25 of November 2003) refcodes PUBREY and PUBROT; Allen, 2002].

The Mg–O distance of the magnesium–THF fragments [Mg–O = 1.993 (2) Å] is comparable with those found for other magnesocene–THF adducts (Mg–O = 1.989–2.098 Å (CSD refcodes HUXSAU, NUZZIP, NUZXOF, PUBREJ, PUBRIN, PUBROT, PUBRUZ, ROBCUG, TACXIF, VITZUT, WIDYAJ, WIDYEN, XILZIB and ZEHYUG). The O1–Mg–O1ⁱ angle in (I) [101.01 (12)°] is the largest observed so far for any magnesocene with two THF ligands (O–Mg–O = 88.20–94.40°; CSD refcodes HUXSAU,

NUZZIP, PUBREJ, PUBROT, PUBRUZ and XILZIB). This opening of the O–Mg–O angle is probably connected with the unusually low hapticity of both indenyl ligands in (I).

Experimental

All manipulations were performed using conventional Schlenk techniques under an atmosphere of argon or in a glove-box under an atmosphere of nitrogen. (Ind)₂Mg (Eisch & Sanchez, 1985) (5.0 g, 20 mmol) was stirred in a mixture of 50 ml pentane and 30 ml tetrahydrofuran for 3 d at room temperature. The yellow suspension was decanted and the precipitate washed twice with 20 ml pentane. Drying *in vacuo* yielded 6.4 g (16 mmol, 82%) of a pale-yellow powder. For crystallization, a small amount was dissolved in tetrahydrofuran. While the solvent was slowly evaporated in a glove-box at room temperature colourless crystals were formed. ¹H NMR (600 MHz, CD₂Cl₂, 298 K): δ 7.54 (4H, *m*, Ind-H6), 6.89 (4H, *m*, Ind-H7), 6.79 (2H, *s*, Ind-H3), 5.85 (4H, *s*, Ind-H2), 3.18 (8H, *bs*, THF), 1.71 (8H, *bs*, THF). ¹³C NMR (600 MHz, CD₂Cl₂, 298 K): δ 133.9 (Ind-C1), 120.6 (Ind-C3), 120.2 (Ind-C6), 117.9 (Ind-C7), 89.5 (Ind-C2), 70.4 (THF), 25.3 (THF). Analysis calculated for C₂₆H₃₀MgO₂: C 78.30, H 7.58%; found: C 76.68, H 7.65%.

Crystal data

[Mg(C₉H₈O)₂(C₉H₇)₂]
M_r = 398.81
 Monoclinic, *C*2/*c*
a = 10.958 (4) Å
b = 9.683 (6) Å
c = 20.861 (9) Å
 β = 96.56 (5)°
V = 2199.0 (18) Å³
Z = 4

D_x = 1.205 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 5.1–12.5°
 μ = 0.10 mm⁻¹
T = 188 K
 Plate, colourless
 0.4 × 0.2 × 0.2 mm

Data collection

Bruker *P4* diffractometer
 ω scans
 5253 measured reflections
 2399 independent reflections
 1658 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.077
 θ_{max} = 27.0°

h = –13 → 12
k = –12 → 12
l = –26 → 26
 3 standard reflections
 every 97 reflections
 intensity decay: 0.2%

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.070$
 $wR(F^2) = 0.190$
S = 1.04
 2399 reflections
 132 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0986P)^2 + 1.492P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.73 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Mg1–O1	1.993 (2)	C2–C3	1.429 (4)
Mg1–C2	2.256 (3)	C3–C4	1.391 (4)
Mg1–C3	2.723 (3)	C4–C5	1.423 (4)
Mg1–C1	2.738 (3)	C5–C6	1.412 (4)
C1–C9	1.408 (4)	C6–C7	1.361 (4)
C1–C2	1.441 (4)	C7–C8	1.418 (5)
C1–C5	1.447 (4)	C8–C9	1.378 (4)

O1–Mg1–O1ⁱ 101.01 (12)

Symmetry code: (i) $-x, y, \frac{3}{2} - z$.

H atoms were positioned geometrically and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$.

Data collection: *XSCANS* (Siemens, 1992); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1997); software used to prepare material for publication: *SHELXTL*.

References

Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.

Atwood, J. L. & Smith, K. D. (1974). *J. Am. Chem. Soc.* **96**, 994–998.

Damrau, H. R. H., Geyer, A., Prosenc, M. H., Weeber, A., Schaper, F. & Brintzinger, H. H. (1998). *J. Organomet. Chem.* **553**, 331–343.

Eisch, J. J. & Sanchez, R. (1985). *J. Organomet. Chem.* **296**, C27–C31.

Jaenschke, A., Paap, J. & Behrens, U. (2003). *Organometallics*, **22**, 1167–1169.

O'Connor, J. M. & Casey, C. P. (1987). *Chem. Rev.* **87**, 307–318.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Siemens (1992). *XSCANS*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1997). *SHELXTL*. Version 5.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.