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Di-μ-bromido-bis[benzyl(diethyl ether)-magnesium]

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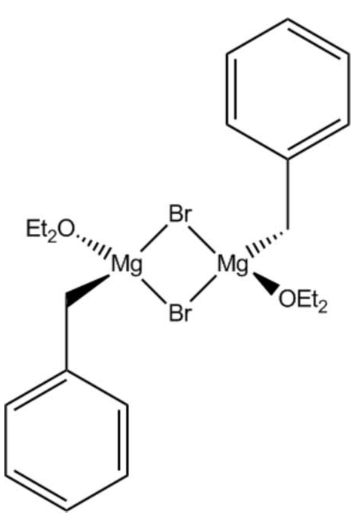
Key indicators: single-crystal X-ray study; T = 193 K; mean σ(C–C) = 0.004 Å; R factor = 0.031; wR factor = 0.073; data-to-parameter ratio = 18.6.

The title benzyl Grignard reagent, $[Mg_2Br_2(C_7H_7)_2(C_4H_{10}O)_2]$, was obtained by reaction of benzyl bromide with magnesium in diethyl ether, followed by crystallization from toluene. The asymmetric unit comprises one half-molecule, the structural dimeric unit being generated by inversion symmetry with an Mg···Mg distance of 3.469 (2) Å. The Mg(II) atom exhibits a distorted tetrahedral coordination geometry. The crystal packing is defined by van der Waals interactions only.

Related literature

For the structures of some other diethyl ether adducts of Grignard reagents, see: Stucky & Rundle (1964); Guggenberger & Rundle (1968); Engelhardt *et al.* (1988); Antolini *et al.* (2003); Avent *et al.* (2004). For the structures of some tetrahydrofuran and diisopropyl ether adducts of Grignard reagents, see: Maurice (1969); Spek *et al.* (1974); Krieck *et al.* (2009).



Experimental

Crystal data

$[Mg_2Br_2(C_7H_7)_2(C_4H_{10}O)_2]$
M_r = 538.93
Monoclinic, $P2_1/c$
a = 8.0657 (4) Å
b = 12.4288 (6) Å
c = 13.1840 (6) Å
β = 96.370 (3)°
V = 1313.50 (11) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 3.15 mm^{-1}
T = 193 K
0.38 × 0.27 × 0.23 mm

Data collection

Bruker Platform APEXII CCD diffractometer
Absorption correction: integration (*SADABS*; Bruker, 2007)
T_{min} = 0.440, T_{max} = 0.635
22801 measured reflections
2396 independent reflections
1808 reflections with $I > 2\sigma(I)$
R_{int} = 0.078

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.073
S = 1.04
2396 reflections
129 parameters
H-atom parameters not refined
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Selected bond lengths (Å).

Mg1—O1	2.0006 (18)	Mg1—Br1^{i}	2.5448 (9)
Mg1—C7	2.115 (3)	Mg1—Br1	2.5659 (9)

Symmetry code: (i) $-x+2, -y+1, -z$.

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT* and *XPREP* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *XCIF* (Bruker, 2005).

This work was supported financially by the National Science Foundation (CHE-1112360). X-ray data were collected in the Materials Chemistry Laboratory at the University of Illinois (supported in part by grants NSF CHE 95–03145 and NSF CHE 03–43032 from the National Science Foundation).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2423).

References

Antolini, F., Hitchcock, P. B., Lappert, M. F. & Wei, X.-H. (2003). *Organometallics*, **22**, 2505–2516.
Avent, A. G., Caro, C. F., Hitchcock, P. B., Lappert, M. F., Li, Z. & Wei, X.-H. (2004). *Dalton Trans.* pp. 1567–1577.
Bruker (2005). *SAINT*, *XCIF* and *XPREP*. Bruker AXS, Inc., Madison, Wisconsin, USA.
Bruker (2007). *SADABS*. Bruker AXS, Inc., Madison, Wisconsin, USA.
Bruker (2010). *APEX2*. Bruker AXS, Inc., Madison, Wisconsin, USA.
Engelhardt, L. M., Harvey, S., Raston, C. L. & White, A. H. (1988). *J. Organomet. Chem.* **341**, 39–51.
Guggenberger, L. J. & Rundle, R. E. (1968). *J. Am. Chem. Soc.* **90**, 5375–5378.
Krieck, S., Görls, H., Yu, L., Reiher, M. & Westerhausen, M. (2009). *J. Am. Chem. Soc.* **131**, 2977–2985.
Maurice, V. J. (1969). *J. Organomet. Chem.* **20**, 1–10.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L., Voorbergen, P., Schat, G., Blomberg, C. & Bickelhaupt, F. J. (1974). *J. Organomet. Chem.* **77**, 147–151.
Stucky, G. & Rundle, R. E. (1964). *J. Am. Chem. Soc.* **86**, 4825–4830.

supplementary materials

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Di-*μ*-bromido-bis[benzyl(diethyl ether)magnesium]

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Comment

Similar dimeric structures have been reported for the bromo Grignard reagents [Mg(*μ*-Br){CH($SiMe_2Ph$)($SiMe_3$)}(OEt_2)]$_2$ (Antolini, *et al.*, 2003), [Mg(*μ*-Br){CH($SiMe_3$)$_2$}(OEt_2)]$_2$ (Avent, *et al.*, 2004), and [Mg(*μ*-Br)Et(O-*i*-Pr_2)]$_2$ (Spek, *et al.*, 1974). In all three of these molecules, the magnesium centres each bear one ether ligand, and two Mg–Br–Mg bridges join the metal centres. Most bromo Grignard reagents with two ether molecule per Mg centre are monomeric; examples include MgBrPh(OEt_2)$_2$ (Stucky & Rundle, 1964), MgBrEt(OEt_2)$_2$ (Guggenberger & Rundle, 1968), MgBr(CPh_3)(OEt_2)$_2$ (Engelhardt *et al.*, 1988) and MgBr(2,4,6-$C_6H_2Ph_3$)(thf)$_2$ (Krieck *et al.*, 2009). Finally, there are some monomeric bromo Grignard reagents in which the magnesium centre bears three ether ligands and very small organic groups, such as in MgBrMe(thf)$_3$ (Maurice, 1969).

Experimental

A 250 mL round bottom flask was charged with Mg turnings (2.6 g, 107 mmol) and diethyl ether (90 mL). To the stirred suspension was added benzyl bromide (10 mL, 84 mmol) dropwise by means of an addition funnel over 30 min. After the slight exotherm had subsided, the solution was brought to reflux for two h. The solution was filtered and the filtrate was stored at 253 K. Titration with 0.13 *M* HCl showed the solution to have a concentration of 0.93 *M*.

An aliquot of the benzyl magnesium bromide solution (11.5 mL, 10.7 mmol) was taken to dryness under reduced pressure at 263 K and the residue was extracted with 1:1 benzene/toluene (50 mL). The clear yellow extract was concentrated to *ca* 20 mL and stored at 253 K overnight affording large colourless crystals.

Refinement

A structural dimeric model of (I) is [Mg(*μ*-Br)(CH_2Ph)(OEt_2)]$_2$ whereas an asymmetric unit comprises a half of the molecule. All non-H atoms were located from the difference map and refined anisotropically. H atom treatment: methyl H atom positions, R–CH_3, were optimised by rotation about R–C bonds with idealised C–H, R–H and H–H distances; the remaining H atoms were included as riding idealised contributors. Methyl H atom *U*'s were assigned as 1.5 times U_{eq} of the carrier atom; remaining H atom *U*'s were assigned as 1.2 times carrier U_{eq}.

Computing details

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT* and *XPREP* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: XCIF (Bruker, 2005).

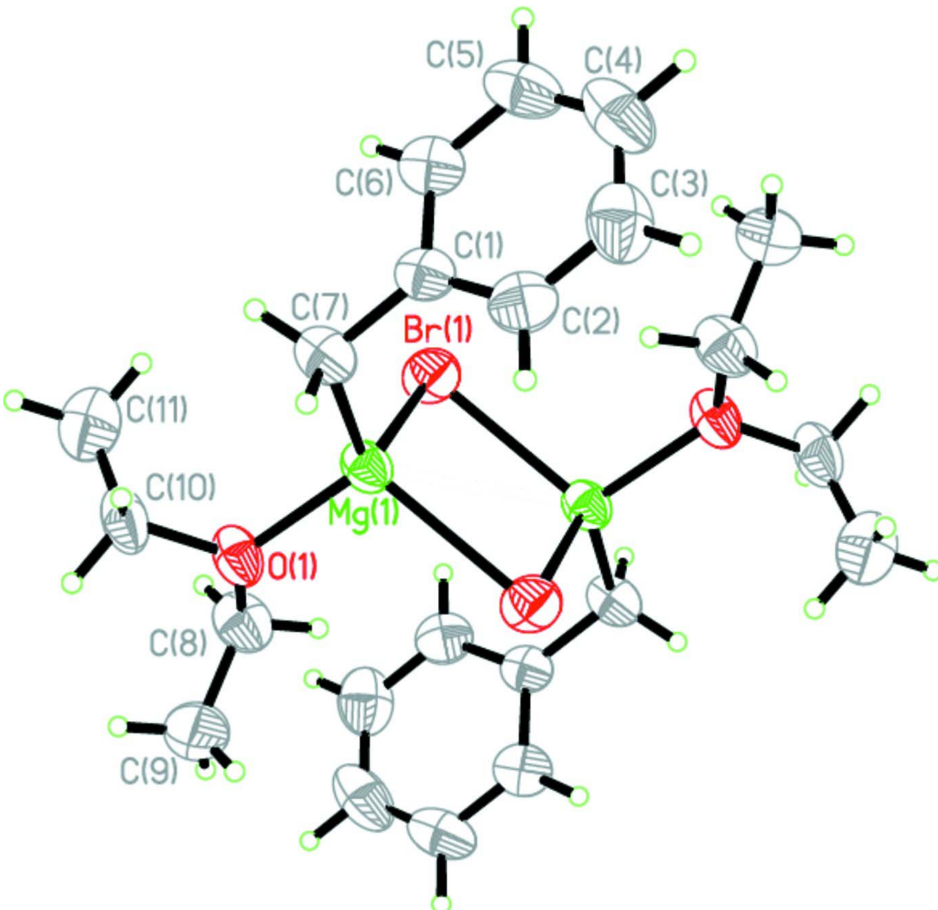

Figure 1

Structural unit of (I) with 50% probability displacement ellipsoids for non-H atoms. Arbitrary radii for H atoms are used. The unlabeled atoms are related by the symmetry operator (-*x* + 2, -*y* + 1, -*z*).

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Crystal data

$[Mg_2Br_2(C_7H_7)_2(C_4H_{10}O)_2]$
$M_r = 538.93$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 8.0657$ (4) Å
$b = 12.4288$ (6) Å
$c = 13.1840$ (6) Å
$\beta = 96.370$ (3)°
$V = 1313.50$ (11) Å^3
$Z = 2$
$F(000) = 552$
$D_x = 1.363$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5006 reflections
$\theta = 2.3$–23.5°
$\mu = 3.15$ mm^{-1}
$T = 193$ K
Prism, colourless
0.38 × 0.27 × 0.23 mm

Data collection

Bruker Platform APEXII CCD diffractometer
Radiation source: normal-focus sealed tube
Graphite monochromator
profile data from φ and ω scans
Absorption correction: integration (*SADABS*; Bruker, 2007)
$T_{min} = 0.440$, $T_{max} = 0.635$
22801 measured reflections
2396 independent reflections

1808 reflections with $I > 2\sigma(I)$
$R_{int} = 0.078$
$\theta_{max} = 25.3°$, $\theta_{min} = 2.3°$
$h = -9 \rightarrow 9$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.073$
$S = 1.04$
2396 reflections
129 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0305P)^2 + 0.0177P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Special details

Experimental. One distinct cell was identified using *APEX2* (Bruker, 2010). Ten frame series were integrated and filtered for statistical outliers using *SAINT* (Bruker, 2005) then corrected for absorption by integration using *SHELXTL*/*XPREP* V2005/2 (Bruker, 2005) before using *SADABS* (Bruker, 2005) to sort, merge, and scale the combined data. No decay correction was applied.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. The structure was phased by direct methods (Sheldrick, 2008). The systematic conditions suggested the unambiguous space group. The space group choice was confirmed by successful convergence of the full-matrix least-squares refinement on F^2. The highest peaks in the final difference Fourier map were in the vicinity of atom Br1; the final map had no other significant features. A final analysis of variance between observed and calculated structure factors showed little dependence on amplitude or resolution.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Mg1	1.18152 (11)	0.47556 (7)	0.08013 (7)	0.0396 (2)
Br1	0.89572 (3)	0.55206 (2)	0.11052 (2)	0.05037 (13)
O1	1.1776 (2)	0.32859 (13)	0.14171 (14)	0.0459 (5)
C1	1.3770 (3)	0.6793 (2)	0.0998 (2)	0.0396 (7)
C2	1.4242 (4)	0.7119 (2)	0.0058 (2)	0.0521 (8)
H2	1.4702	0.6604	−0.0364	0.063*
C3	1.4058 (4)	0.8173 (3)	−0.0276 (3)	0.0655 (10)
H3	1.4394	0.8370	−0.0919	0.079*
C4	1.3403 (4)	0.8927 (3)	0.0310 (3)	0.0712 (10)
H4	1.3288	0.9651	0.0080	0.085*
C5	1.2908 (4)	0.8638 (2)	0.1233 (3)	0.0624 (9)
H5	1.2448	0.9164	0.1644	0.075*
C6	1.3072 (3)	0.7593 (2)	0.1567 (2)	0.0488 (7)
H6	1.2702	0.7407	0.2203	0.059*
C7	1.3934 (3)	0.56671 (19)	0.1365 (2)	0.0468 (7)
H7A	1.4057	0.5658	0.2120	0.056*
H7B	1.4947	0.5340	0.1134	0.056*
C8	1.0390 (4)	0.2534 (2)	0.1235 (2)	0.0545 (8)

H8A	0.9597	0.2804	0.0665	0.065*
H8B	0.9794	0.2499	0.1852	0.065*
C9	1.0940 (4)	0.1444 (2)	0.0986 (2)	0.0708 (10)
H9A	0.9964	0.0977	0.0838	0.106*
H9B	1.1665	0.1153	0.1567	0.106*
H9C	1.1557	0.1477	0.0387	0.106*
C10	1.2862 (4)	0.3105 (2)	0.2361 (2)	0.0547 (8)
H10A	1.3958	0.3446	0.2307	0.066*
H10B	1.3047	0.2322	0.2457	0.066*
C11	1.2145 (4)	0.3549 (3)	0.3267 (2)	0.0777 (10)
H11A	1.2928	0.3431	0.3880	0.117*
H11B	1.1088	0.3187	0.3345	0.117*
H11C	1.1948	0.4323	0.3173	0.117*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mg1	0.0341 (5)	0.0340 (5)	0.0493 (6)	0.0000 (4)	−0.0015 (4)	0.0023 (4)
Br1	0.0424 (2)	0.0587 (2)	0.0502 (2)	0.00999 (14)	0.00602 (14)	−0.00680 (14)
O1	0.0356 (11)	0.0375 (10)	0.0617 (12)	−0.0040 (8)	−0.0073 (9)	0.0111 (9)
C1	0.0255 (16)	0.0405 (16)	0.0514 (18)	−0.0041 (12)	−0.0023 (13)	−0.0063 (13)
C2	0.0464 (19)	0.0541 (19)	0.056 (2)	−0.0063 (15)	0.0071 (16)	−0.0068 (15)
C3	0.059 (2)	0.069 (2)	0.069 (2)	−0.0160 (18)	0.0071 (19)	0.0179 (18)
C4	0.059 (2)	0.042 (2)	0.109 (3)	−0.0042 (17)	−0.005 (2)	0.015 (2)
C5	0.050 (2)	0.0429 (19)	0.093 (3)	0.0043 (16)	0.0063 (19)	−0.0131 (18)
C6	0.0376 (18)	0.0501 (18)	0.0593 (19)	−0.0034 (14)	0.0081 (15)	−0.0048 (14)
C7	0.0356 (17)	0.0392 (16)	0.064 (2)	−0.0012 (13)	−0.0001 (14)	0.0002 (13)
C8	0.0441 (18)	0.0441 (17)	0.074 (2)	−0.0092 (15)	0.0004 (16)	0.0044 (15)
C9	0.093 (3)	0.0498 (19)	0.068 (2)	−0.0076 (19)	0.001 (2)	−0.0049 (16)
C10	0.0472 (19)	0.0471 (18)	0.065 (2)	0.0049 (14)	−0.0134 (17)	0.0164 (15)
C11	0.087 (3)	0.085 (3)	0.060 (2)	0.004 (2)	0.002 (2)	0.0078 (19)

Geometric parameters (Å, º)

Mg1—O1	2.0006 (18)	C5—C6	1.373 (4)
Mg1—C7	2.115 (3)	C5—H5	0.9500
Mg1—Br1^{i}	2.5448 (9)	C6—H6	0.9500
Mg1—Br1	2.5659 (9)	C7—H7A	0.9900
Mg1—Mg1^{i}	3.4690 (17)	C7—H7B	0.9900
Br1—Mg1^{i}	2.5448 (9)	C8—C9	1.474 (4)
O1—C8	1.456 (3)	C8—H8A	0.9900
O1—C10	1.458 (3)	C8—H8B	0.9900
C1—C2	1.396 (4)	C9—H9A	0.9800
C1—C6	1.401 (3)	C9—H9B	0.9800
C1—C7	1.482 (3)	C9—H9C	0.9800
C2—C3	1.385 (4)	C10—C11	1.490 (4)
C2—H2	0.9500	C10—H10A	0.9900
C3—C4	1.358 (4)	C10—H10B	0.9900
C3—H3	0.9500	C11—H11A	0.9800
C4—C5	1.371 (4)	C11—H11B	0.9800

C4—H4	0.9500	C11—H11C	0.9800
O1—Mg1—C7	113.26 (9)	C1—C6—H6	119.0
O1—Mg1—Br1^{i}	105.34 (6)	C1—C7—Mg1	110.56 (17)
C7—Mg1—Br1^{i}	121.26 (9)	C1—C7—H7A	109.5
O1—Mg1—Br1	102.71 (6)	Mg1—C7—H7A	109.5
C7—Mg1—Br1	116.84 (8)	C1—C7—H7B	109.5
Br1^{i}—Mg1—Br1	94.50 (3)	Mg1—C7—H7B	109.5
O1—Mg1—Mg1^{i}	110.90 (6)	H7A—C7—H7B	108.1
C7—Mg1—Mg1^{i}	135.62 (8)	O1—C8—C9	112.5 (3)
Br1^{i}—Mg1—Mg1^{i}	47.51 (2)	O1—C8—H8A	109.1
Br1—Mg1—Mg1^{i}	47.00 (2)	C9—C8—H8A	109.1
Mg1^{i}—Br1—Mg1	85.50 (3)	O1—C8—H8B	109.1
C8—O1—C10	114.8 (2)	C9—C8—H8B	109.1
C8—O1—Mg1	124.43 (16)	H8A—C8—H8B	107.8
C10—O1—Mg1	116.89 (15)	C8—C9—H9A	109.5
C2—C1—C6	115.8 (3)	C8—C9—H9B	109.5
C2—C1—C7	122.7 (3)	H9A—C9—H9B	109.5
C6—C1—C7	121.5 (3)	C8—C9—H9C	109.5
C3—C2—C1	121.7 (3)	H9A—C9—H9C	109.5
C3—C2—H2	119.1	H9B—C9—H9C	109.5
C1—C2—H2	119.1	O1—C10—C11	112.2 (2)
C4—C3—C2	120.5 (3)	O1—C10—H10A	109.2
C4—C3—H3	119.7	C11—C10—H10A	109.2
C2—C3—H3	119.7	O1—C10—H10B	109.2
C3—C4—C5	119.6 (3)	C11—C10—H10B	109.2
C3—C4—H4	120.2	H10A—C10—H10B	107.9
C5—C4—H4	120.2	C10—C11—H11A	109.5
C4—C5—C6	120.3 (3)	C10—C11—H11B	109.5
C4—C5—H5	119.8	H11A—C11—H11B	109.5
C6—C5—H5	119.8	C10—C11—H11C	109.5
C5—C6—C1	122.0 (3)	H11A—C11—H11C	109.5
C5—C6—H6	119.0	H11B—C11—H11C	109.5

Symmetry code: (i) $-x+2, -y+1, -z$.