metal-organic compounds

Polymeric [dihydrobis(pyrazol-1-yl)borato]potassium(I) and three dihydrobis(pyrazol-1-yl)borate–magnesium(I) compounds obtained by disproportionation of the Grignard reagent

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Reaction of the Grignard reagent with polydentate nitrogen-donor ligands yields new species with rare magnesium coordination and possible catalytic activity. In the first of the title compounds, poly[[μ_4-dihydrobis(pyrazol-1-yl)borato-$\kappa^2 N,N'$]potassium(I)], [K($C_6H_8BN_4$)]$_n$, (I), polymeric chains form a two-dimensional network in the [100] plane. Each potassium ion is coordinated by four N atoms of pyrazolyl ligands, while weak (μ-BH)···K$^+$ interactions additionally stabilize the structure. The K and B atoms both lie on a mirror plane. In three new structures obtained by disproportionation of the Grignard reagent, each Mg atom is bound to a $\kappa^2 N,N'$-type ligand, forming the basal plane, and tetrahydrofuran molecules occupy the axial positions. Di-μ-chlorido-bis[dihydridobis(pyrazol-1-yl)borato]tris(tetrahydrofuran)dimagnesium(II), [$Mg_2(C_6H_8BN_4)_2Cl_2(C_4H_8O)_3$], (II), adopts a dimeric structure with μ-Cl—Mg interactions. One of the Mg atoms has an octahedral coordination, while the other has a distorted square-pyramidal environment. However, in the bis-chelate compounds bis[dihydridobis(pyrazol-1-yl)borato-$\kappa^2 N,N'$](tetrahydrofuran-κO)magnesium(II), [$Mg(C_6H_8BN_4)_2(C_4H_8O)$], (III), and bis[dihydridobis(pyrazol-1-yl)borato-$\kappa^2 N,N'$]bis(tetrahydrofuran-κO)magnesium(II), [$Mg(C_6H_8BN_4)_2(C_4H_8O)_2$], (IV), the Mg atoms have square-pyramidal and octahedral environments, respectively. The Mg atom in (IV) lies on an inversion centre.

Comment

The geometric characteristics of dihydrobis(pyrazol-1-yl)borate ligands are very similar to those of β-diketonate ions, though cyclopentadienyl (Cp) or pentamethylcyclopentadienyl (Cp*) ligands are comparable to hydrotris(pyrazol-1-yl)borate ligands (Trofimenko, 1993). Although pyrazolyl ligands have been considered widely, their solid-state struc-

tures have not been well studied. There is a lack of structural information on dihydrobis(pyrazol-1-yl)borate and hydrotris(1-pyrazolyl)borate ligands with a Cp behaviour. Dias *et al.* (1995) have reported an interaction of σ-bonding type between potassium ions and highly fluorinated bis(pyrazol-1-yl)borate ligands, while (μ-BH)···K interactions have been observed only for dihydrobis(pyrazol-1-yl)borate ligands. Hu & Gorun (2001), however, have reported that hydrotris(1-pyrazolyl)borate ligands may function not only as σ donors but also as Cp-like π donors.

(I)

(II)

(III)

(IV)
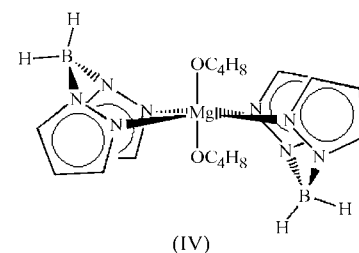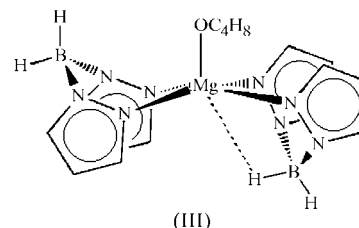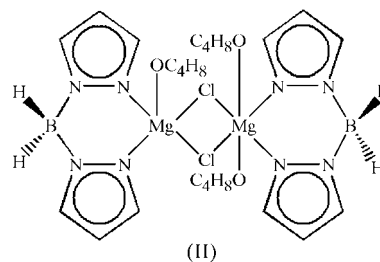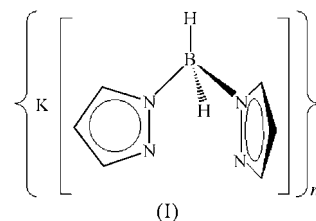
The search for new species with catalytic activity has led to increased attention being paid to studies of reactivity between Grignard reagents and polydentate nitrogen-donor ligands. Reports on this area, dealing with magnesium halides and magnesium alkyls with different solvents, have been published (Ashby & Arnott, 1968), but little information about their chemical and physical properties is available (Gibson *et al.*, 2000; Bailey *et al.*, 2003).

The present paper reports the structure of ligand (I) in its polymeric form, representing the first example with η^5-pyrazole-, $\kappa^2 N,N'$- and μ-BH binding modes. Several side products, (II)–(IV), can be obtained by reaction of the corresponding tetrahydrofuran (THF) solution of complex (I) (Trofimenko,

1966, 1993) and a THF solution of MeMgCl at room temperature.

In the polymeric molecular structure of (I) (Fig. 1), each monomer ligand has a butterfly arrangement of three condensed rings, namely two pyrazole rings and a boat-shaped central BN_4K unit. The K and B atoms lie on a mirror plane. Selected bond lengths are listed in Table 1. The short B—N bond distances in the H_2BN_2 group [1.561 (2) Å] are comparable to the average value for pyrazolyl groups (1.562 Å) retrieved from the Cambridge Structural Database (Version of May 2005; Allen, 2002). The acute dihedral angle of 58.78 (16)° (at atom B1) suggests a deeper boat conformation than that found in similar pyrazabole complexes [35.5 (1) and 33.4 (3)°; Hanecker et al., 1985]. In (I), the η^5-pyrazole—K^+ distances range from 3.025 (2) to 3.473 (2) Å [with a $K^+\cdots$centroid distance of 3.035 (2) Å]. Comparison of the η^5-pyrazole—K^+ contacts in highly fluorinated bis(pyrazol-1-yl)borate ligands [3.355 (2) Å] and η^5-indole—K^+ contacts [3.640 (2) Å] (Hu & Gorun, 2001; Dunbar, 1998; Dias & Gorden, 1996) with the η^5-pyrazole—K^+ distances in (I) suggests that there is a strong π bond with the potassium ion in

the latter. In addition, the $(\eta^5$-pyrazole centroid)$\cdots K^+$ distances are longer than the corresponding $Cp\cdots K$ interactions (2.699 Å; Forbes et al., 2002). The pyrazolyl rings in (I) are located on opposite sides of the K atom, with a corresponding angle between the ring centroids of 92.2 (2)°. The σ-N bonding interactions with the potassium ion (the average K—N bond distance is 2.787 Å) are similar to those found in $(\{HB[3,5-(CF_3)_2Pz]_3\}K(DMAC))_2$ [2.885 (7) Å] and $(\{HB[3-(CF_3),5-(CH_3)Pz]_3\}K(DMAC))_2$ [2.827 (4) Å] (Pz is pyrazole and DMAC is dimethylacetamide; Dias & Gorden, 1996). The $(\mu\text{-}BH)\cdots K$ contacts (2.88 Å) are shorter than π interactions and can be described as s-block agostic interactions (a donor–acceptor interaction type), providing an extra stability to the polymeric complex. The intrachain $K\cdots K(x, y-1, z)$ separation is equal to the b unit-cell dimension, i.e. 5.843 (3) Å, while the interchain separation is equal to half of the a unit-cell dimension [8.584 (3) Å]. Several Csp^2—H$\cdots\pi$ interactions (average distance 2.88 Å) are strong enough to direct the crystal packing through interpolymeric chain interactions between equivalent planes ([100] and [200]; Fig. 2).

The formation of the by-product complexes (II)–(IV) is explained by a disproportionation of the Grignard reagent known as the Schlenk equilibrium. Complex (II) suggests solvation and association, by which $MgCl_2$ is also formed in solution, and associations by bridging halide atoms predominate. In addition, in complexes (III) and (IV), a large solvent effect is present during the reaction, especially when a strong donor solvent such as tetrahydrofuran (THF) is used. In general, in complexes (II)–(IV), ligand (I) coordinates in a κ^2N,N' fashion, with boat-shaped central BN_4Mg units. The B—N bond distances in the H_2BN_2 group for compounds (II)–(IV) (average 1.551 Å) are not significantly different from those in pyrazolyl groups (average 1.562 Å; Allen, 2002). The average Mg—N bond distances for complexes (II) and (III) (2.138 Å) are shorter than the average distance for complex
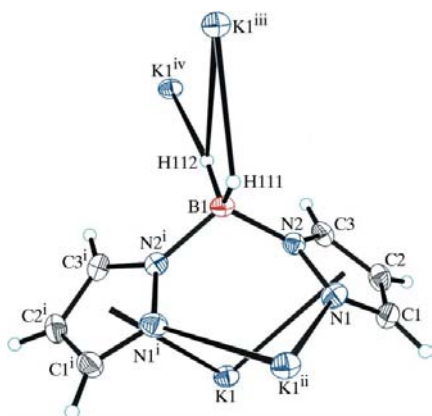

Figure 1
The asymmetric unit of (I) and some symmetry-related atoms. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x+1, y, z$; (ii) $-x+1, -y+1, z+\frac{1}{2}$; (iii) $-x+1, -y, z+\frac{1}{2}$; (iv) $x, y-1, z$.]

Figure 2
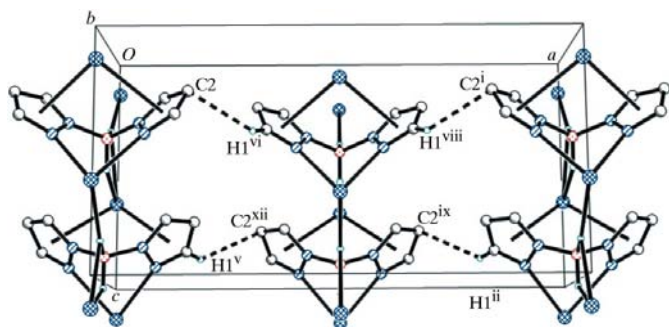Part of the crystal packing of (I), showing Csp^2—H$\cdots\pi$ interactions between chains. [Symmetry codes: (i) $-x+1, y, z$; (ii) $-x+1, -y+1, z+\frac{1}{2}$; (v) $x, -y+1, z+\frac{1}{2}$; (vi) $-x+\frac{1}{2}, y-\frac{1}{2}, z$; (vii) $-x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (viii) $x+\frac{1}{2}, y-\frac{1}{2}, z$; (ix) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$.]
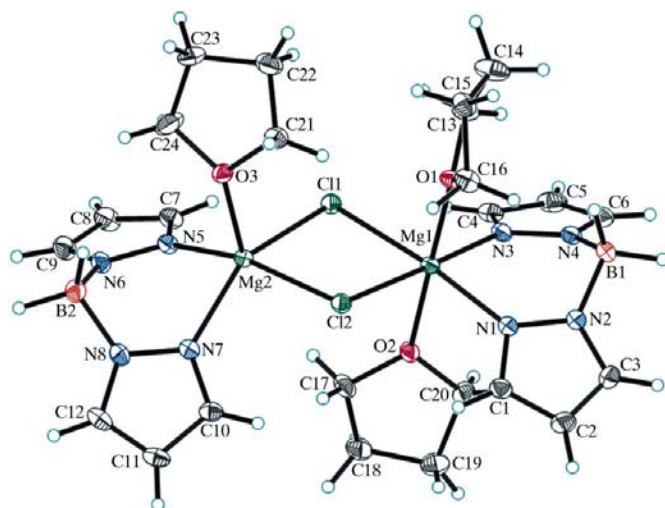

Figure 3
The major disorder component of (II), with displacement ellipsoids shown at the 50% probability level.

(IV) (2.186 Å). All these Mg—N bond distances are typical of the σ-bonding distances in similar magnesium complexes (Takahashi *et al.*, 1998; Malbosc *et al.*, 1999; Viebrock & Weiss, 1994; Bailey *et al.*, 2000, 2003).

In the asymmetric molecular structure (II) (Fig. 3), two Mg atoms are bridged by two Cl atoms, forming a square Mg_2Cl_2 core in which the Mg—Cl—Mg angles are 94.05 (3) and 94.55 (3)°, while the Cl—Mg—Cl angles are 84.08 (3) and 85.99 (3)°. An octahedral environment is observed for atom Mg1, while a rare distorted square-pyramidal environment is
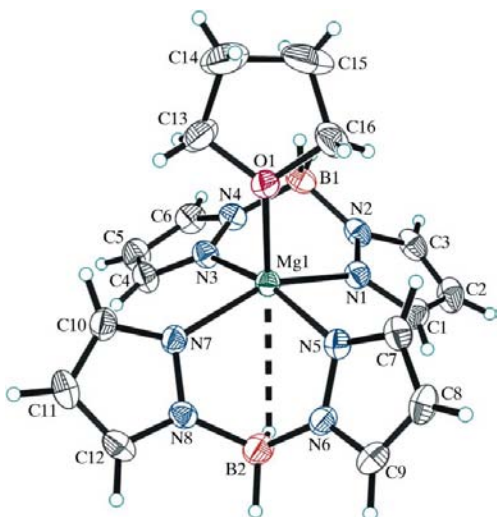

Figure 4
The molecular structure of (III). Displacement ellipsoids are drawn at the 50% probability level. The dashed line indicates a pseudo-axial B—H···Mg interaction.
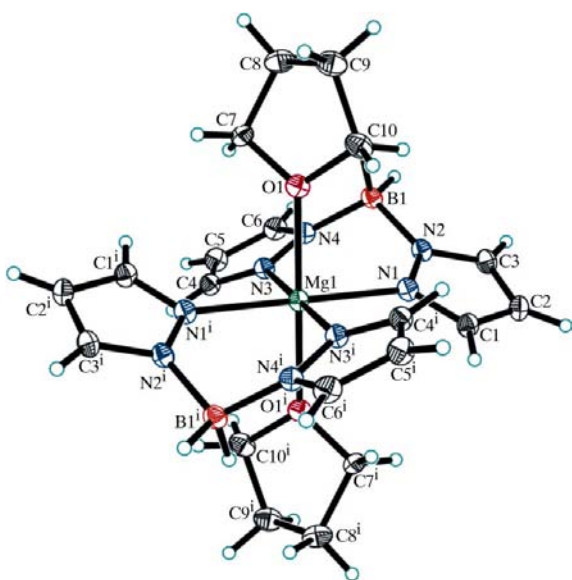

Figure 5
The major disorder component of one of the two independent molecules of (IV), with displacement ellipsoids shown at the 50% probability level. [Symmetry code: (i) −x, −y + 1, −z + 1.]

adopted by atom Mg2. The boat conformation of the ring containing atom Mg1 is characterized by dihedral angles at atoms B1 and Mg1 of 46.48 (17) and 13.92 (15)°, respectively, which results in a boat slightly flatter than that in (I). In the case of the six-coordinated Mg1 atom, both disordered THF molecules are in axial positions, with Mg1—O1 and Mg1—O2 bond distances of 2.0920 (15) and 2.1477 (15) Å, respectively. It should be noted that the Mg1—O1 and Mg1—O2 bonds are both almost perpendicular to the Cl1/Cl2/N1/N3 plane [with angles of 93.07 (4) and 87.49 (4)°, respectively]. The boat conformation of the Mg2-containing ring is characterized by dihedral angles at atoms B2 and Mg2 of 47.59 (15) and 27.80 (16)°, respectively. In addition, the distorted square-pyramidal environment of atom Mg2 involves a rather short Mg2—O3 bond distance [2.0201 (15) Å], with atom Mg2 lying 0.40 (3) Å out of the N5/N7/Cl1/Cl2 plane. Selected bond lengths and angles are listed in Table 2.

The X-ray structure of compound (III) (Fig. 4) reveals a bis-chelate complex, with a square-pyramidal geometry around the two Mg atoms in the asymmetric unit. The short Mg—O interactions [2.0397 (16) and 2.0233 (17) Å] agree well with previously reported values (Takahashi *et al.*, 1998; Malbosc *et al.*, 1999; Viebrock & Weiss, 1994; Bailey *et al.*, 2000, 2003). Selected bond lengths and angles for (III) are listed in Table 3. The boat conformation of the B1-containing ring is characterized by dihedral angles at atoms B1 and Mg1 of 48.43 (15) and 23.52 (17)°, respectively. However, a more pronounced boat conformation, with dihedral angles of 53.81 (15) and 41.29 (16)° for atoms B2 and Mg1, is observed for the other chelate ring; this conformation could be related to a weak pseudo-axial B—H···Mg interaction (distance 2.69 Å) (Takahashi *et al.*, 1998; Malbosc *et al.*, 1999). Moreover, the observed strong Mg—O interaction induces the Mg atom to be located 0.39 (3) Å out of the N1/N3/N5/N7 plane.

The X-ray crystal structure of (IV) (Fig. 5), on the other hand, also reveals a bis-chelate complex, but with an octahedral environment for the Mg atoms. The two Mg atoms in the asymmetric unit are located on inversion centres, while the average σ-N—Mg bond distance (2.186 Å) is a little longer than the corresponding distance in complex (III). The axial positions are occupied by two disordered THF molecules, with Mg—O bond lengths [2.1735 (10) and 2.1989 (10) Å] longer than those in complex (III). As a result, the boat conformation in complex (IV) is flatter than that in complex (III), with dihedral angles at atoms B2 and Mg1 of 45.60 (17) and 18.44 (18)°, respectively. Selected bond lengths and angles for (IV) are listed in Table 4, and more information about the dihedral angles for all complexes is given in Table 5.

Experimental

All solvents and reagents were used as received from Aldrich and Fisher. The starting material (I) was prepared as described by Trofimenko (1966). Colourless needle-shaped crystals were grown from a concentrated THF solution at room temperature. A suitable crystal was selected from the resulting batch. A solution of (I) (1.000 g, 5.358 mmol) in THF (5 ml) was treated with MeMgCl

(1.8 ml, 3.0 M in THF, 5.358 mmol) at room temperature. After 3 h, the solvent and volatile components were removed under vacuum, diethyl ether was added (10 ml) and the suspension was filtered under nitrogen atmosphere through Celite 521. The final solution was concentrated (5 ml) and left at room temperature for 2 d to give colourless plate-shaped crystals of (II) (1.69 mmol, yield 63%). Colourless plate-shaped crystals of complexes (III) and (IV) were obtained in a similar manner to (II), but the reaction times were 10 and 24 h, respectively [(III): 1.82 mmol, yield 68%; (IV): 1.91 mmol, yield 72%]. Suitable crystals were selected from the resulting batch. Owing to the air- and moisture-sensitive nature of the final product, reliable microanalysis was not possible.

Compound (I)

Crystal data

[K(C6H8BN4)]	$V = 878.1$ (7) Å^3
$M_r = 186.07$	$Z = 4$
Orthorhombic, $Cmc2_1$	Mo $K\alpha$ radiation
$a = 17.167$ (3) Å	$\mu = 0.55$ mm^{-1}
$b = 5.843$ (4) Å	$T = 150$ (2) K
$c = 8.754$ (3) Å	$0.32 \times 0.06 \times 0.06$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	2664 measured reflections
	926 independent reflections
Absorption correction: multi-scan ($SADABS$; Sheldrick, 1996)	893 reflections with $I > 2\sigma(I)$
$T_{min} = 0.958$, $T_{max} = 0.965$	$R_{int} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	H-atom parameters constrained
$wR(F^2) = 0.056$	$\Delta\rho_{max} = 0.27$ e Å^{-3}
$S = 1.00$	$\Delta\rho_{min} = -0.17$ e Å^{-3}
926 reflections	Absolute structure: Flack (1983),
64 parameters	373 Friedel pairs
1 restraint	Flack parameter: 0.10 (5)

Table 1
Selected geometric parameters (Å, °) for (I).

K1—N1^x	2.7870 (15)	K1—C1	3.3481 (18)
K1—N1^{xi}	2.7870 (15)	K1—C2	3.4734 (18)
K1—N2	3.0252 (14)	K1—C3	3.2721 (17)
K1—N1	3.1003 (15)		
K1⋯H111^{xii}	2.67	K1⋯H111^{xiii}	2.67
K1⋯H112^{xii}	3.01	K1⋯H112^{xiii}	3.01
K1⋯H112^{iv}	2.78	C2⋯H1^{xiv}	2.88
K1⋯H111^x	3.48		
N1^x—K1—N1^{xi}	71.71 (6)	N2^i—B1—N2	110.6 (2)

Symmetry codes: (i) $-x+1, y, z$; (iv) $x, y-1, z$; (x) $-x+1, -y+1, z-\frac{1}{2}$; (xi) $x, -y+1, z-\frac{1}{2}$; (xii) $-x+1, -y+2, z-\frac{1}{2}$; (xiii) $x, -y+2, z-\frac{1}{2}$; (xiv) $-x+\frac{3}{2}, y+\frac{1}{2}, z$.

Table 2
Selected geometric parameters (Å, °) for (II).

Cl1—Mg1	2.5229 (8)	Mg2—N5	2.1310 (18)
Cl1—Mg2	2.4579 (8)	Mg2—N7	2.1393 (17)
Cl2—Mg1	2.4932 (8)	B1—N2	1.556 (3)
Cl2—Mg2	2.4681 (8)	B1—N4	1.554 (3)
Mg1—N1	2.1352 (18)	B2—N6	1.550 (3)
Mg1—N3	2.1301 (17)	B2—N8	1.549 (3)
N1—Mg1—N3	90.34 (7)	N5—Mg2—N7	87.15 (7)
O1—Mg1—O2	178.09 (6)		

Compound (II)

Crystal data

[Mg2(C6H8BN4)2Cl2(C4H8O)3]	$V = 3195.9$ (10) Å^3
$M_r = 629.78$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 15.119$ (3) Å	$\mu = 0.28$ mm^{-1}
$b = 13.862$ (2) Å	$T = 150$ (2) K
$c = 15.453$ (3) Å	$0.48 \times 0.32 \times 0.18$ mm
$\beta = 99.319$ (3)°	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	38733 measured reflections
	8068 independent reflections
Absorption correction: multi-scan ($SADABS$; Sheldrick, 1996)	6406 reflections with $I > 2\sigma(I)$
$T_{min} = 0.894$, $T_{max} = 0.951$	$R_{int} = 0.051$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$	114 restraints
$wR(F^2) = 0.133$	H-atom parameters constrained
$S = 1.08$	$\Delta\rho_{max} = 0.54$ e Å^{-3}
8068 reflections	$\Delta\rho_{min} = -0.32$ e Å^{-3}
400 parameters	

Table 3
Selected geometric parameters (Å, °) for (III).

Mg1—N1	2.119 (2)	Mg2—N9	2.1199 (19)
Mg1—N3	2.150 (2)	Mg2—N11	2.1434 (19)
Mg1—N5	2.165 (2)	Mg2—N13	2.1642 (19)
Mg1—N7	2.126 (2)	Mg2—N15	2.1462 (19)
B1—N2	1.546 (3)	B3—N10	1.545 (3)
B1—N4	1.547 (3)	B3—N12	1.554 (3)
B2—N6	1.549 (3)	B4—N14	1.543 (3)
B2—N8	1.550 (3)	B4—N16	1.543 (3)
N1—Mg1—N3	88.04 (8)	N9—Mg2—N11	87.56 (7)
N5—Mg1—N7	87.06 (8)	N13—Mg2—N15	87.39 (7)

Compound (III)

Crystal data

[Mg(C6H8BN4)2(C4H8O)]	$\gamma = 107.909$ (3)°
$M_r = 390.36$	$V = 2070.2$ (8) Å^3
Triclinic, $P\overline{1}$	$Z = 4$
$a = 9.951$ (3) Å	Mo $K\alpha$ radiation
$b = 10.741$ (2) Å	$\mu = 0.11$ mm^{-1}
$c = 20.996$ (3) Å	$T = 150$ (2) K
$\alpha = 99.137$ (5)°	$0.42 \times 0.26 \times 0.12$ mm
$\beta = 97.410$ (4)°	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	17263 measured reflections
	8386 independent reflections
Absorption correction: multi-scan ($SADABS$; Sheldrick, 1996)	5502 reflections with $I > 2\sigma(I)$
$T_{min} = 0.982$, $T_{max} = 0.997$	$R_{int} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$	537 parameters
$wR(F^2) = 0.115$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{max} = 0.25$ e Å^{-3}
8386 reflections	$\Delta\rho_{min} = -0.20$ e Å^{-3}

Table 4
Selected geometric parameters (Å, °) for (IV).

Mg1—N1	2.1958 (11)	Mg2—N5	2.1894 (12)
Mg1—N1^i	2.1958 (11)	Mg2—N5^{ii}	2.1894 (12)
Mg1—N3	2.1904 (11)	Mg2—N7	2.1690 (12)
Mg1—N3^i	2.1904 (12)	Mg2—N7^{ii}	2.1690 (12)
B1—N2	1.5487 (19)	B2—N6	1.561 (2)
B1—N4	1.5470 (19)	B2—N8	1.545 (2)
N1—Mg1—N3	88.24 (4)	N5—Mg2—N7	88.99 (4)
N1^i—Mg1—N3	91.76 (4)	N5^{ii}—Mg2—N7	91.01 (4)

Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x, -y, -z$.

Compound (IV)

Crystal data

[Mg(C$_6$H$_8$BN$_4$)$_2$(C$_4$H$_8$O)$_2$]	$\gamma = 105.568\ (3)°$
$M_r = 462.47$	$V = 1199.3\ (4)$ Å^3
Triclinic, $P\bar{1}$	$Z = 2$
$a = 9.4171\ (19)$ Å	Mo $K\alpha$ radiation
$b = 10.936\ (2)$ Å	$\mu = 0.11$ mm^{-1}
$c = 13.013\ (3)$ Å	$T = 150\ (2)$ K
$\alpha = 94.069\ (3)°$	$0.40 \times 0.26 \times 0.12$ mm
$\beta = 109.329\ (3)°$	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	10757 measured reflections
	6335 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	4305 reflections with $I > 2\sigma(I)$
$T_{min} = 0.962$, $T_{max} = 0.984$	$R_{int} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$	48 restraints
$wR(F^2) = 0.109$	H-atom parameters constrained
$S = 1.01$	$\Delta\rho_{max} = 0.29$ e Å^{-3}
6335 reflections	$\Delta\rho_{min} = -0.32$ e Å^{-3}
329 parameters	

Table 5
Selected dihedral angles (°) between planes 1 and 2 for compounds (I)–(IV).

Compound	Plane 1	Plane 2	Angle
(I)	N1/N2/N3/N4	N2/B1/N4	58.78 (16)
(II)	N1/N2/N3/N4	N2/B1/N4	46.48 (17)
	N1/N2/N3/N4	N1/Mg1/N3	13.92 (15)
	N5/N6/N7/N8	N6/B2/N8	47.59 (15)
	N5/N6/N7/N8	N5/Mg2/N7	27.80 (16)
(III)	N1/N2/N3/N4	N2/B1/N4	48.43 (15)
	N1/N2/N3/N4	N1/Mg1/N3	32.52 (17)
	N5/N6/N7/N8	N6/B2/N8	53.81 (15)
	N5/N6/N7/N8	N5/Mg1/N7	41.29 (16)
(IV)	N1/N2/N3/N4	N2/B1/N4	45.60 (17)
	N1/N2/N3/N4	N1/Mg1/N3	18.44 (18)

H atoms were included in the refinement at calculated positions, in the riding-model approximation, with C—H distances of 0.93–0.99 Å and B—H distances of 1.11 Å. The U_{iso}(H) values were set equal to $1.2U_{eq}$(C,B). The refinement of positional disorder in complexes (II) and (IV) was resolved with two components and the use of similarity restraints. The THF molecules in (II) are disordered, and the pairs of atoms C15/C15A, C18/C18A and C23/C23A have occupancy ratios of 80:20, 79:21 and 86:14%, respectively. One disordered THF molecule is also found in the asymmetric unit of complex (IV); atom pairs C7/C7A, C8/C8A and C9/C9A each have an occupancy ratio of 82:18%.

For all compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Version 5.03; Sheldrick, 2008), plus *WinGX2003* (Farrugia, 1999) for (I); software used to prepare material for publication: *SHELXL97*.

References

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