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Imino Sulfinamidines: Synthesis and Coordination Chemistry of a Novel Class of Chiral Bidentate Ligands

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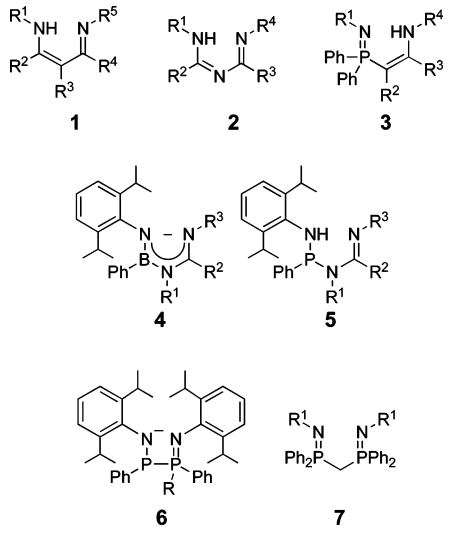
The new imino sulfinamidine ligand PhS(NH*t*-Bu)═NC(Me)═N(C_6H_3-2,6-*i*Pr_2), **LH (11)** was synthesized from *N*-(2,6-diisopropylphenyl)acetamidine (**9**) and *N*-*tert*-butyl phenylsulfinimidoyl chloride (**10**). Reaction of **LH** (**11**) with $ZnEt_2$ or $AlMe_3$ gave the complexes **LZnEt (12)** and **LAlMe$_2$ (13)**, respectively. The structures of **12** and **13** were determined by X-ray diffraction and were shown to contain **L** as a κ^2-N^1,N^5 bidentate ligand in a six-membered chelate. Formation of the magnesium complex (**L**MgN(TMS)$_2$•**L**$_2$Mg) **(14)** from **11**, MgI_2, and $KN(SiMe_3)_2$ highlighted a secondary coordination mode of **L**, binding through the sulfinamidine nitrogens in a four-membered chelate.

Introduction

The development of ancillary ligands in homogeneous catalysis has resulted in a diverse range of catalytic systems. While increasing ligand sophistication has resulted in dramatic improvements in activity, the desire for stereocontrol in organometallic reactions is still of high priority, and consequently, a plethora of chiral ligands have been developed. Notable successful moieties include the chiral diphosphines,[1] salen derivatives,[2] oxazolines,[3−6] and *N*-heterocyclic carbenes.[7,8] The β-diketimines **1** are a class of monoanionic ligands that have been used to stabilize low metal (transition and main group) oxidation states and/or coordination numbers to effect a variety of catalytic processes by means of their coordinative and electronic unsaturation.[9] The success of the β-diketiminates lies in the ease with which the steric bulk of the substituents may be modified at both the coordinating nitrogens and hydrocarbon ligand "backbone."



Although there have been significant studies of the effects of varying backbone substituents,[10−24] there have been only

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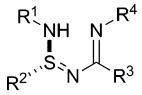
limited attempts to alter the backbone itself in order to further modify the coordination sphere around the metal. These include the synthesis of various triazapentadienyl ligands **2**, which have been used to form a variety of metal complexes.[25−33] Recently, phosphinimine donors have been incorporated into the ligand backbone, resulting in phosphonium diketimide analogues **3**, which have been successfully utilized in the synthesis of Group 13 complexes.[34,35] Chivers et al. have achieved the synthesis of hybrid boraamidinate/amidinate ligands **4** isoelectronic to the diketiminates and successfully applied their magnesium complexes in lactide polymerization.[36] The same group has also synthesized chiral phosphine analogues **5**. Attempts at metalation, however, resulted in nucleophilic attack at the phosphine to generate phosphine−phosphonium anions of the type **6**.[37] Coordination studies of bis(phosphinimino)-methanide ligands of type **7** have been performed, and the monoanions have been shown to complex as bidentate *N*,*N*′ ligands when $R^1 = SiMe_3$[38−42] or 2,4,6-$Me_3C_6H_2$.[43,44]

Despite these efforts, an efficient, versatile route to a β-diketiminate analogue in which the chirality is well expressed in the vicinity of the ligated metal center has yet to be realized. We envisioned that placing a chiral sulfinamidine functionality into the backbone would lead to significant distortion of the planar diketimine framework, inducing a highly discriminating asymmetric environment around the metal center by means of the pseudo-tetrahedral sulfur. Ligand **8** would combine the easily variable steric



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demand of the β-diketimines with the asymmetric potential of sulfur(IV) to introduce chirality proximal to the metal. To this end, we describe the synthesis of a novel ligand containing the imino sulfinamidine moiety and some exploratory coordination complexes of this ligand, which displays at least two coordination modes.

Experimental Section

General Procedures. All manipulations were carried out using a standard Schlenk line or within a glovebox (operating at < 2 ppm O_2) containing an inert dinitrogen atmosphere. Hexane and PhMe were redistilled from Na and THF over Na and Ph_2CO. C_6D_6 and toluene-d_8 were dried with molten K and vacuum-transferred to a Youngs' storage ampule prior to use. *tert*-Butyldichloroamine was synthesized from *tert*-butyl alcohol as described by Kovacic et al.[45] All other reagents were used as commercially supplied.

***N*-(2,6-Diisopropylphenyl)acetamidine (9).** MeCN (4.20 mL, 80.00 mmol) and 2,6-diisopropylaniline (15.76 g, 80.00 mmol) were added to freshly ground $AlCl_3$ (10.64 g, 80.00 mmol), and the mixture was heated at 180 °C for 2 h.[46] After this time, the mixture was cooled and hydrochloric acid (1.2 M, 160 mL) carefully added, followed by decolorizing charcoal (2 g), and the mixture heated to reflux for 10 min. The mixture was allowed to cool to room temperature before filtering, giving a dark green solution, which was extracted with CH_2Cl_2 (3 × 100 mL) to remove a dark purple impurity. The aqueous layer was basified with 15% NaOH (200 mL) to give an off-white precipitate, which was extracted with CH_2Cl_2 (3 × 100 mL). The organic extracts were combined, dried ($MgSO_4$), filtered, and evaporated to yield amidine **9** (12.20 g, 70%) as a gray solid: mp 118−120 °C (MeOH); R_f 0.14 (CH_2Cl_2:MeOH:NH_3, 92:7:1); IR (thin film) 3454, 3305, 3168, 1643, 1460 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.12−1.20 (m, 12H), 2.15 (s, 3H), 3.01 (sept, J = 6.9 Hz, 2H), 4.27 (br s, 2H), 7.00−7.16 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.8, 23.7, 28.0, 123.3, 123.5, 139.8, 143.3, 154.0; MS (CI) *m*/*z* 219 $(M + H)^+$; HRMS (CI) *m*/*z* calcd for $C_{14}H_{23}N_2$ $(M + H)^+$, 219.1861; found: 219.1868. Anal. Calcd for $C_{14}H_{22}N_2$: C, 77.01; H, 10.16; N, 12.83. Found: C, 76.95; H, 10.19; N, 12.74.

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***N-tert*-Butyl Phenylsulfinimidoyl Chloride (10).** Using a slightly modified procedure of Mukaiyama,[47] *tert*-butyldichloroamine (6.24 g, 43.98 mmol) was added to PhSAc (6.36 g, 41.78 mmol, 0.95 equiv) in PhH (18 mL), and the solution was heated at 80 °C for 20 min, after which time the color changed from yellow to orange. Evaporation under reduced pressure yielded sulfinimidoyl chloride **10** (8.50 g, 97%) as a yellow moisture-sensitive solid: IR (thin film) 1630, 1303, 1140 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.57 (s, 9H), 7.57−7.59 (m, 3H), 8.10−8.13 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.8, 64.4, 125.8, 129.l, 133.8, 142.9.

***N-tert*-Butyl Phenylsulfinimidoyl *N*-(2,6-Diisopropylphenyl)-acetamidine (11).** Amidine **9** (5.00 g, 22.93 mmol) was added portionwise to a suspension of KH (3.15 g, 27.56 mmol) in THF (120 mL) at 0 °C. The mixture was stirred for 1 h, cooled to −78 °C, and sulfinimidoyl chloride **10** (5.95 g, 27.61 mmol) in THF (25 mL) added dropwise. The reaction mixture was stirred for 1 h, allowed to warm to room temperature, stirred for a further 1 h, and quenched with saturated aqueous NH_4Cl (50 mL). The mixture was extracted with CH_2Cl_2 (3 × 75 mL), and the combined organic extracts were dried ($MgSO_4$), filtered, and evaporated. The residue was chromatographed on neutral alumina (hexane; hexane/CH_2Cl_2, 3:17; EtOAc/CH_2Cl_2/NEt_3 10:90:1) to yield **11** (7.21 g, 79%) as a yellow oil, which solidified upon standing: mp 130−132 °C (DMSO); R_f 0.20 (CH_2Cl_2:MeOH:NH_3, 240:10:1); IR (thin film) 3192, 1568, 1460, 1363, 1280, 1239 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 0.62−1.10 (4d, J = 6.9 Hz, 12H), 1.36 (s, 9H), 1.58 (s, 3H), 2.12−2.28, 2.88 (2m, overlapping sept, J = 6.9 Hz, 2H), 6.77 (br s, 1H, N*H*), 6.81 (t, J = 7.6 Hz, 1H), 6.87 (dd, J = 7.6, 1.2 Hz, 1H), 6.95 (dd, J = 7.6, 1.2 Hz, 1H), 7.49−7.57 (m, 3H), 7.76 (d, J = 7.3 Hz, 2H); ^{13}C NMR (75 MHz, C_6D_6) δ 21.4, 23.3, 24.1, 24.9, 27.3, 28.0, 30.2, 53.4, 123.1, 122.9, 127.0, 128.9, 129.4, 138.5, 139.4, 143.9, 146.8, 167.5; MS (CI) *m*/*z* 398 $(M + H)^+$; HRMS (CI) *m*/*z* calcd for $C_{24}H_{36}N_3S$ $(M + H)^+$, 398.2630; found: 398.2619. Anal. Calcd for $C_{24}H_{35}N_3S$: C, 72.50; H, 8.87; N, 10.57. Found: C, 72.60; H, 8.93; N, 10.49.

LZnEt (12). $ZnEt_2$ (1M, 5.0 mL, 5.00 mmol) in hexane was added to **11** (1.00 g, 2.52 mmol) in PhMe (15 mL) at 0 °C. The solution was allowed to warm to room temperature, stirred overnight, evaporated under reduced pressure, and the residue dissolved in hexane (25 mL) and filtered. The filtrate was evaporated to yield **12** (1.09 g, 88%) as a yellow solid. Crystals suitable for an X-ray structure determination were obtained from a concentrated solution of **12** in hexane: IR (solid) 1738, 1479, 1364, 1217 cm^{-1}; ^1H NMR (400 MHz, $CD_3C_6D_5$) δ −0.07−0.05 (m, 2H, ZnC*H*$_2$), 0.52 (d, J = 6.9 Hz, 3H), 0.79 (d, J = 6.9 Hz, 3H), 0.96 (t, J = 8.1 Hz, 3H, $ZnCH_2CH_3$), 1.12 (d, J = 6.9 Hz, 3H), 1.15 (d, J = 6.9 Hz, 3H), 1.33 (s, 9H), 1.70 (s, 3H), 1.85 (sept, 1H, J = 6.9 Hz), 3.11 (sept, 1H, J = 7.3 Hz), 6.82−6.86 (m, 1H), 6.91−7.07 (m, 5H), 7.77−7.80 (m, 2H); ^{13}C NMR (100 MHz, $CD_3C_6D_5$) δ 0.6, 12.2, 23.1, 23.5, 24.0, 24.7, 27.6, 28.3, 33.0, 55.4, 123.6, 125.7, 127.2, 129.9, 141.6, 141.8, 144.6, 146.2, 170.9.

LAlMe$_2$ (13). $AlMe_3$ (2M, 0.6 mL, 1.20 mmol) in hexane was added to **11** (432 mg, 1.09 mmol) in PhMe (8 mL) at −78 °C. The solution was allowed to warm to room temperature, stirred overnight, evaporated under reduced pressure, and the residue dissolved in hexane (20 mL) and filtered. The filtrate was evaporated to yield **13** (400 mg, 81%) as a crystalline yellow solid. Crystals suitable for an X-ray structure determination were obtained from a concentrated solution of **13** in hexane: IR (solid) 1738, 1571, 1366, 1217 $cm^{-1;}$ ^1H NMR (300 MHz, C_6D_6) δ −0.77 (s, 3H, AlC*H*$_3$), −0.26 (s, 3H, AlC*H*$_3$), 0.77 (d, J = 6.0 Hz, 1H), 0.94 (d, J = 6.0 Hz, 1H), 1.08 (d, J = 6.4 Hz, 3H), 1.15 (s, 3H), 1.23 (d, J = 6.4 Hz, 3H), 1.32 (d, J = 6.0 Hz, 2H), 1.37 (d, J = 6.0 Hz, 2H), 1.51 (s, 9H), 2.15−2.31 (m, 0.5H), 2.8 (s, 3H), 3.29−3.36 (m, 1.5H), 7.03−7.21 (m, 6H), 7.84−7.88 (m, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ −4.4, 16.4, 23.1, 23.3, 23.7, 25.3, 25.5, 25.7, 27.4, 27.7, 27.8, 28.7, 31.3, 52.5, 57.6, 123.0, 123.3, 124.9, 126.8, 127.4, 128.4, 129.2, 130.4, 131.9, 139.3, 144.5. Anal. Calcd for $C_{26}H_{40}AlN_3S$: C, 68.84; H, 8.89; N, 9.26. Found: C, 68.78; H, 8.99; N, 9.23.

LMgN(TMS)$_2$·L$_2$Mg (14). Precooled THF (15 mL) was added at −78 °C to a rapidly stirred mixture of **11** (500 mg, 1.26 mmol), $KN(SiMe_3)_2$ (502 mg, 2.52 mmol), and MgI_2 (350 mg, 1.26 mmol). The mixture was allowed to warm to room temperature and was stirred overnight to produce a tan slurry. After evaporation under reduced pressure, the tan solid residue was extracted with hexane (20 mL). Filtration and slow cooling of a warm saturated solution afforded colorless crystals of **14** (150 mg, 34%) suitable for an X-ray structure determination: ^1H NMR (400 MHz, $CD_3C_6D_5$) δ 0.07 (s, 7H), 0.36−0.64 (m, 9H), 0.75−1.04 (m, 16H), 1.05−1.36 (m, 44H), 1.44−1.59 (m, 8H), 1.71−2.09 (m, 7H), 2.31−2.59 (m, 2H), 3.12−3.63 (m, 3H), 6.85−7.14 (m, 20H), 7.92−8.30 (m, 4H); ^{13}C NMR (100 MHz, $CD_3C_6D_5$) δ 2.2, 14.0, 21.2, 22.7, 22.8, 23.0, 23.1, 23.3, 23.4, 23.8, 24.0, 24.7, 27.2, 27.3, 27.8, 28.7, 30.1, 31.7, 32.9, 53.2, 122.7, 122.8, 125.8, 126.9, 128.6, 129.1, 130.5, 136.8, 138.3, 138.9, 139.2, 144.0, 143.9, 146.7, 147.0, 148.0, 167.5. Anal. Calcd for $C_{78}H_{120}Mg_2N_{10}S_3Si_2$: C, 66.97; H, 8.65; N, 10.01. Found: C, 66.94; H, 8.57; N, 9.98.

Crystallographic Structural Determination. Table 1 provides a summary of the crystallographic data for compounds **11**−**14**. Data for **11** ($2\theta_{max}$ = 46°) and **13** ($2\theta_{max}$ = 52°) were collected on an Enraf Nonius KappaCCD diffractometer, while those for **12** ($2\theta_{max}$ = 66°) and **14** ($2\theta_{max}$ = 66°) were collected on an Oxford Diffraction Xcalibur3 diffractometer. CCDC 289163 to 289166, respectively.

Results and Discussions

The synthesis of racemic imino sulfinamidine **11** was achieved in two steps from amidine **9**. Deprotonation with KH followed by treatment with *N*-*tert*-butyl phenylsulfinimidoyl chloride at −78 °C afforded ligand **11** in 79% yield (Scheme 1). The X-ray structural analysis of crystals of **11** revealed the presence of two independent molecules (**A** and **B**) in the asymmetric unit (molecule **A** is shown in Figure 1, and molecule **B** is shown in Figure S1 in the Supporting Information). The two molecules have similar conformations, the rms fit of the {N−S−N−C(Me)−N} ligand backbone (including the attached carbons of the *tert*-butyl, phenyl, and 2,6-diisopropylphenyl substituents) being ca. 0.14 Å. The largest difference between the two independent molecules is the orientation of the S-phenyl ring, this ring being almost orthogonal (ca. 86°) to the S(1)−N(2) bond in molecule **A** compared to ca. 57° in molecule **B**.

Despite the N−H proton being located on N(1) [meaning that S(1)−N(2) is formally a double bond], the N(1)−S(1) and S(1)−N(2) bond distances are the same [1.644(3) and 1.640(3) Å, respectively, in molecule **A**, 1.645(3) and 1.631(3) Å, respectively, in molecule **B**]. The N(2)−C(11) and C(11)−N(3) bond lengths are unexceptional (Table 2). Presumably, the intermolecular N−H···N hydrogen bonds are the cause of the comparable bond lengths of N(1)−S(1)

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Table 1. Crystallographic Data for Compounds **11**−**14**

data	**11**	**12**	**13**	**14**
chemical formula	$C_{24}H_{35}N_3S$	$C_{26}H_{39}N_3SZn$	$C_{26}H_{40}AlN_3S$	$C_{78}H_{120}Mg_2N_{10}S_3Si_2$
solvent	−	−	$0.5C_6H_{14}$	C_6H_{14}
fw	397.61	491.03	496.74	1484.99
T (°C)	−100	−100	−100	−100
space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
a (Å)	10.4125(4)	13.5781(4)	8.4281(2)	21.9499(7)
b (Å)	11.9105(7)	11.6793(4)	15.3512(4)	18.8731(6)
c (Å)	20.7215(11)	16.7892(5)	23.3402(3)	23.4952(7)
α (deg)	102.952(3)	−	−	−
β (deg)	94.096(3)	93.342(3)	99.795(1)	107.934(3)
γ (deg)	107.637(3)	−	−	−
V (Å^3)	2359.7(2)	2657.95(14)	2975.77(11)	9260.3(5)
Z	4[a]	4	4	4
ρ_{calcd} (g cm^{-3})	1.119	1.227	1.109	1.065
λ (Å)	0.71073	0.71073	0.71073	0.71073
μ (mm^{-1})	0.151	1.019	0.159	0.164
R1[b]	0.059	0.037	0.044	0.103
wR2[c]	0.150	0.101	0.115	0.150

[a] There are two crystallographically independent molecules in the asymmetric unit. [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

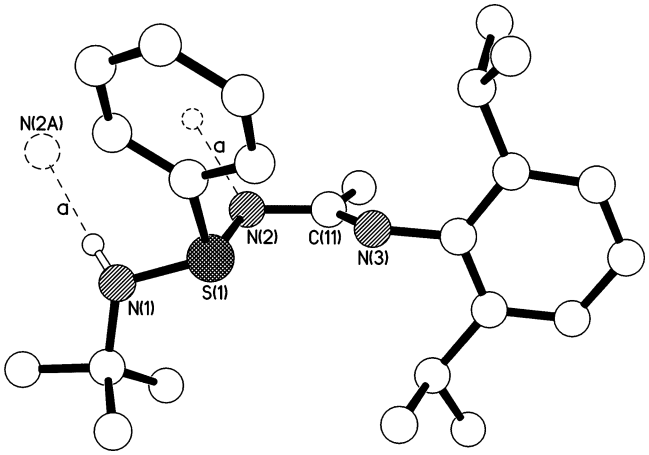

Figure 1. Molecular structure of one (**A**) of the two independent molecules present in the crystals of **11**. The N−H···N hydrogen bond (**a**) has N···N 2.989(4) Å, H···N 2.09 Å, and N−H···N 175°.

Scheme 1. Synthesis of Imino Sulfinamidine **11**

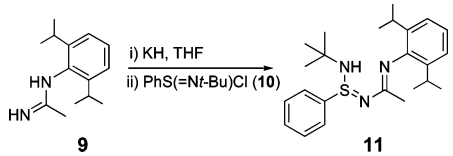

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Two Independent Molecules (**A** and **B**) Present in the Crystals of **11**

	A	**B**
N(1)−S(1)	1.644(3)	1.645(3)
N(2)−C(11)	1.383(4)	1.380(4)
S(1)−N(2)	1.640(3)	1.631(3)
C(11)−N(3)	1.291(4)	1.289(4)
N(2)−S(1)−N(1)	104.18(14)	107.16(14)
N(2)−S(1)−C(5)	106.39(15)	105.39(15)
N(1)−S(1)−C(5)	101.50(15)	100.32(16)
C(11)−N(2)−S(1)	110.9(2)	112.7(2)
N(3)−C(11)−N(2)	121.4(3)	122.1(3)

and S(1)−N(2). While the S(1)−N(2)−C(11)−N(3) portion of the backbone adopts a syn conformation (see Table 6 for the torsion angles along the ligand backbone), N(1) is oriented distal from the N(3) nitrogen, rather than forming an intramolecular hydrogen bond as was seen in the structure of the LiI species **(LH**·LiI·thf)$_2$ (see the Supporting Information).

In both independent molecules, the 2,6-diisopropylphenyl ring is oriented almost orthogonally to the plane at the parent nitrogen, the N(3)−Ar torsion angle being ca. 83° and 74° in **A** and **B**, respectively. Each of the two independent molecules is linked across a center of symmetry to a neighboring molecule of the same type (i.e., **A** to **A**′ and **B** to **B**′) by a pair of N−H···N hydrogen bonds from the N(1)−H proton in one molecule to the N(2) nitrogen in the C_i-related counterpart, forming discrete dimer pairs in each case. For molecule **A**, the N−H···N hydrogen bonds have N···N 2.989(4) Å, H···N 2.09 Å, and N−H···N 175°, while for molecule **B**, the parameters are N···N 2.963(4) Å, H···N 2.06 Å, and N−H···N 180°.

With ligand precursor **11** in hand, studies into its coordination behavior were commenced by reaction of **11** with an excess of $ZnEt_2$ in toluene. Upon removal of volatile components, the ^{1}H NMR spectrum of the crude residue was consistent with the formation of a single product. Extraction with hexane followed by crystallization gave material suitable for an X-ray solid-state structure determination, and this showed a 1:1 complex between ligand **L**, an ethylzinc moiety with a distorted trigonal planar coordination geometry at the metal center [{Zn,N(1),N(5),C(30)} is coplanar to better than 0.01 Å], and a six-membered *N*,*N*′ chelate ring (Figure 2). The angles at the metal are 98.36(4)°, 125.15(6)°, and 136.49(6)°, the smallest being associated with the bite of the chelating ligand (Table 3). It is not immediately clear why the ethyl ligand is situated away from the exterior bisector of the N(1)−Zn−N(5) angle toward N(5), there being no noticeable steric hindrance.

While the Zn−N(5) bond length of 2.0209(10) Å is comparable to other three-coordinate-zinc-to-imino-nitrogen distances in other complexes,[48−51] there are no close ana-

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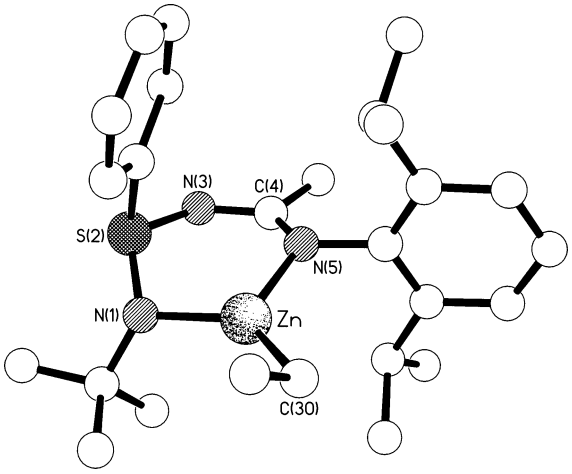

Figure 2. Molecular structure of **12**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **12**

Zn−N(1)	1.9655(11)	Zn−N(5)	2.0209(10)
Zn−C(30)	1.9570(14)	N(1)−S(2)	1.6198(12)
S(2)−N(3)	1.6390(11)	N(3)−C(4)	1.3419(17)
C(4)−N(5)	1.3161(16)		
N(1)−Zn−N(5)	98.36(4)	N(1)−Zn−C(30)	136.49(6)
N(5)−Zn−C(30)	125.15(6)		

logues for the Zn−N(1) linkage. One of the closest is for a four-coordinate zinc to a *tert*-butyl-substituted imine nitrogen in bis(1,4-di-*tert*-butyl-1,4-diazabutadiene-*N*,*N*′) zinc[52] where the Zn−N separations are 1.999 and 2.014 Å, though this is formally zinc(0) cf. zinc(II) here in **12**. The Zn−C distance of 1.9570(14) Å is very similar to those seen in related three-coordinate mono-zinc structures with six-membered *N*,*N*′ chelate rings [1.947(4), 1.951(5), 1.955(5), and 1.963(5) Å].[53−55] The most noticeable changes in the bonding pattern within the ligand backbone on going from the free ligand **11** to the zinc complex **12** (Table 6) are a marked contraction of the N(1)−S(2) [1.6198(12) Å cf. 1.644(3) and 1.645(3) Å for the two independent molecules **A** and **B** in the structure of **11**] and N(3)−C(4) linkages [1.3419(17) cf. 1.383(4) and 1.380(4) Å in **11**] and a lengthening of the C(4)−N(5) bond [1.3161(16) Å cf. 1.291(4) and 1.289(4) Å in **11**]. The S(2)−N(3) distance is unchanged [1.6390(11) cf. 1.640(3) and 1.631(3) Å in **11**].

The chelate ring adopts a folded conformation, {Zn,N-(1),C(4),N(5)} being coplanar to within ca. 0.01 Å with S(2) and N(3) ca. 0.73 and 0.22 Å out of this plane, respectively, in the direction of the S-phenyl group (Table 6). As was seen for both independent molecules in the structure of the free ligand **11**, the 2,6-diisopropylphenyl unit is oriented almost orthogonally to the chelate ring, the N(5)−Ar torsion angle being ca. 88°.

A selected portion of the ^{1}H NMR spectrum of **12** is shown in Figure 3 with assignments obtained from 2D-COSY

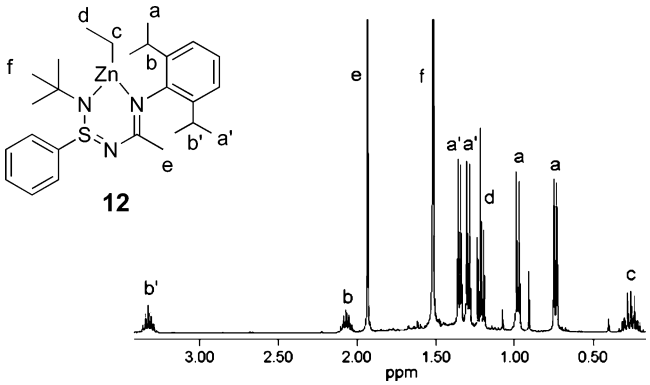

Figure 3. ^{1}H NMR spectrum of **12** at 298 K in $CD_3C_6D_5$.

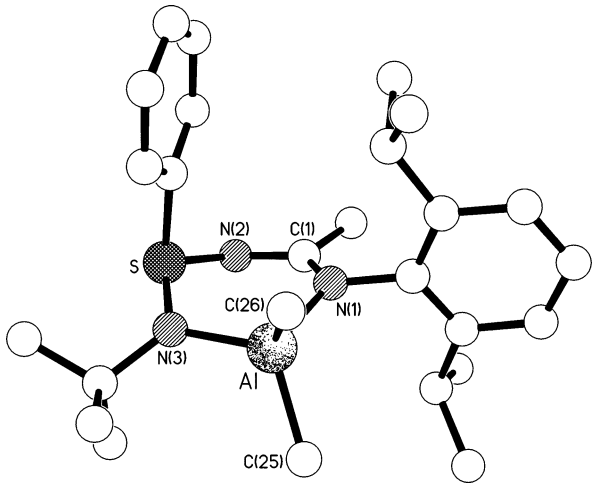

Figure 4. Molecular structure of **13**.

spectra. The highly asymmetric nature of complex **12** is highlighted by the presence of two distinct chemical environments for the isopropyl groups of the aniline. The large difference in shift for the two methine signals can be rationalized by examination of the X-ray structure: the isopropyl group vicinal to the phenyl group is at a distance of 3.00 Å to the sulfinamidine phenyl ring, which is likely to be close enough to encounter the shielding effect of the phenyl ring current.

To further evaluate the ability of ligand **11** to act as a bidentate ligand, it was allowed to react with 1 equiv of $AlMe_3$ followed by crystallization of the product from hexane to give the complex **13**. The single-crystal structure of the dimethyl-aluminum complex **13** (Figure 4) is similar to that of its ethyl-zinc counterpart **12**. The ligand coordinates with a six-membered *N*,*N*′ chelate ring that adopts a twisted geometry, {N(1),C(1),N(2),N(3)} being coplanar to better than 0.01 Å with Al and S(2) ca. −0.22 and +0.54 Å out of this plane, respectively, (the positive direction being toward the C(26) side of the plane). The geometry at the metal center is distorted tetrahedral with X−Al−Y angles in the range 99.18(6)−113.07(8)°, the smallest being associated with the bite of the chelating ligand (Table 4). The Al−N distances are asymmetric with that to N(3) [1.9076(16) Å] being ca. 0.06 Å shorter than that to N(1) [1.9716(14) Å]. The latter bond length is similar to those seen for some other Me_2Al−N(imide) linkages with another nitrogen in the fourth coordination site.[56−58] There are no good analogues for the

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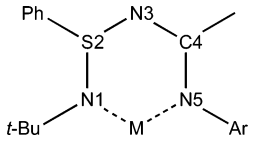
Table 4. Selected Bond Lengths (Å) and Angles (deg) for **13**

Al−N(1)	1.9716(14)	Al−N(3)	1.9076(16)
Al−C(25)	1.969(2)	Al−C(26)	1.961(2)
N(3)−S	1.6242(15)	S−N(2)	1.6297(14)
N(2)−C(1)	1.337(2)	N(1)−C(1)	1.329(2)
N(1)−Al−N(3)	99.18(6)	N(1)−Al−C(25)	109.21(7)
N(1)−Al−C(26)	111.49(7)	N(3)−Al−C(25)	111.56(8)
N(3)−Al−C(26)	113.07(8)	C(25)−Al−C(26)	111.66(9)

Scheme 2. Numbered Schematic of the Ligand Backbone in **11**−**14**



Al−N(3) linkage (with the adjacent sulfur), one of the closer being (*N*,*N*′,*N*″-tri-*tert*-butyl-methanesulfonodi-imidamide-*N*,*N*′)-dimethylaluminum where the Al−N distances in the two independent molecules range between 1.903 and 1.916 Å.[59]

The pattern of bonding in the ligand backbone shows a couple of interesting features (Table 6). Using the numbering system illustrated in Scheme 2, compared to the free ligand **11**, the N1−S2 linkage in **13** has contracted slightly [1.6242(15) cf. 1.645(3) Å in **11**], but unlike the zinc complex **12**, both N−S linkages are still the same (in the zinc complex, N1−S2 was markedly shorter than S2−N3). The N3−C4 bond is also shorter than in **11** [1.337(2) Å cf. 1.380(4) and 1.383(4) Å in **11**], a contraction that was also noticed in the zinc species [1.3419(17) Å]. The imino linkage C4−N5 is lengthened compared to the free ligand [1.329(2) Å cf. 1.289(4) and 1.291(4) Å in **11**], a feature that was also seen, though to a lesser extent, for the zinc complex [1.3161(16) Å]. The 2,6-diisopropylphenyl unit is oriented approximately orthogonally to the chelate ring, the N(1)−Ar torsion angle being ca. 84°.

In an effort to prepare a magnesium amide complex, **11** was allowed to react with 2 equiv of $KN(SiMe_3)_2$ and 1 equiv of MgI_2. Evaporation of volatile components and extraction into hexane followed by slow cooling of a saturated solution yielded complex **14** as a crystalline solid. The X-ray analysis revealed a 2:3 metal/ligand complex with three different coordination modes (Figure 5). The S(2) ligand coordinates to the Mg(1) center in an analogous manner to that seen in both the zinc (**12**) and aluminum (**13**) complexes. The six-membered chelate ring adopts a folded geometry, {Mg(1),N(3),C(4),N(5)} being coplanar to within ca. 0.05 Å with N(1) and S(2) lying ca. 0.30 and 0.76 Å out of this plane in the direction of the S-phenyl ring. Additionally, the S(2) ligand bridges to the Mg(2) center via N(3) [the longest of all the Mg−N contacts at 2.162(2) Å] and is thus overall tridentate. By contrast, the S(32) and S(62) ligands, though bidentate,

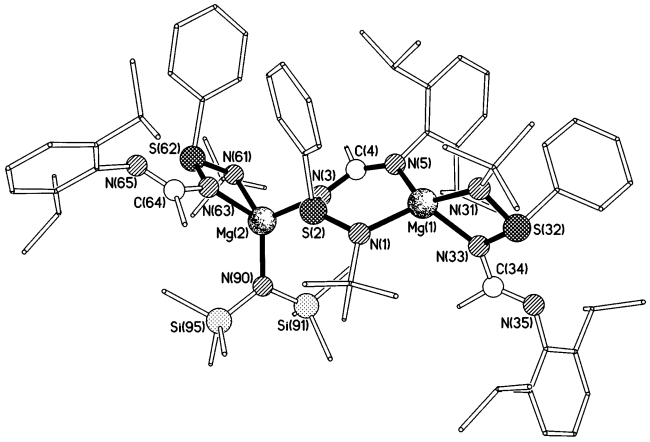


Figure 5. Molecular structure of **14**.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **14**

Mg(1)−N(1)	2.035(2)	Mg(1)−N(5)	2.117(2)
Mg(1)−N(31)	2.055(2)	Mg(1)−N(33)	2.064(2)
Mg(2)−N(3)	2.162(2)	Mg(2)−N(61)	2.103(2)
Mg(2)−N(63)	2.114(2)	Mg(2)−N(90)	2.020(2)
N(1)−S(2)	1.605(2)	S(2)−N(3)	1.662(2)
N(3)−C(4)	1.370(3)	C(4)−N(5)	1.307(3)
N(31)−S(32)	1.619(2)	S(32)−N(33)	1.668(2)
N(33)−C(34)	1.379(3)	C(34)−N(35)	1.282(3)
N(61)−S(62)	1.623(2)	S(62)−N(63)	1.675(2)
N(63)−C(64)	1.377(3)	C(64)−N(65)	1.285(3)
N(90)−Si(91)	1.713(2)	N(90)−Si(95)	1.708(2)
N(1)−Mg(1)−N(5)	95.64(9)	N(1)−Mg(1)−N(31)	123.75(10)
N(1)−Mg(1)−N(33)	119.52(10)	N(5)−Mg(1)−N(31)	131.06(10)
N(5)−Mg(1)−N(33)	115.54(9)	N(31)−Mg(1)−N(33)	71.90(9)
N(3)−Mg(2)−N(61)	113.99(9)	N(3)−Mg(2)−N(63)	100.68(9)
N(3)−Mg(2)−N(90)	115.62(9)	N(61)−Mg(2)− N(63)	70.68(9)
N(61)−Mg(2)−N(90)	122.42(9)	N(63)−Mg(2)−N(90)	124.42(10)

coordinate using the N1 and N3 nitrogens to form four-membered N_2SMg chelate rings. The four-membered chelate ring formed by the S(32) ligand is coplanar to within ca. 0.01 Å, while that formed by the S(62) ligand is folded with Mg(2) lying ca. 0.24 Å out of the {N(61),S(62),N(63)} plane. For each of the three ligands, the 2,6-diisopropylphenyl unit is oriented approximately orthogonally to the chelate ring, the N(5)−Ar, N(35)−Ar, and N(65)−Ar torsion angles being ca. 86°, 77°, and 75°, respectively. The geometry at the Mg(1) center is severely distorted from ideal tetrahedral (Table 5), the angles subtended at the metal center ranging between 71.90(9)° and 131.06(10)° [the most acute angle is, unsurprisingly, associated with the bite of the four-membered chelate ring]. The coordination geometry at Mg(2) is also distorted from ideal tetrahedral, but to a slightly lesser extent, the X−Mg(2)−Y angles being in the range 70.68(9)−124.42(10)° [again the most acute angle is associated with the bite of the four-membered chelate ring].

The Mg−N distances within the two four-membered chelate rings are 2.055(2) and 2.064(2) Å for the S(32) ligand to Mg(1) and 2.103(3) and 2.114(2) Å for the S(62) ligand to Mg(2). In each case, these are symmetric, with those to Mg(2) noticeably longer than their counterparts to Mg(1); the reason for this lengthening at Mg(2) is not immediately apparent, though it may be associated with the steric bulk of the adjacent trimethylsilyl moieties. The distances at Mg(1) are similar to those seen in related four-membered bis(*N*,*N*′) magnesium complexes.[60−64] By contrast, the Mg−N

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Table 6. Comparative Bond Lengths (Å) and Torsion Angles (deg) for the Ligand Backbone in the Structures of **11**, **12**, **13**, and **14**[a]

	11 A	**11 B**	**12**	**13**	**14**[b]		
			Bond Lengths				
N1−S2	1.644(3)	1.645(3)	1.6198(12)	1.6242(15)	1.605(2)	1.619(2)	1.623(2)
S2−N3	1.640(3)	1.631(3)	1.6390(11)	1.6297(14)	1.662(2)	1.668(2)	1.675(2)
N3−C4	1.383(4)	1.380(4)	1.3419(17)	1.337(2)	1.370(3)	1.379(3)	1.377(3)
C4−N5	1.291(4)	1.289(4)	1.3161(16)	1.329(2)	1.307(3)	1.282(3)	1.285(3)
			Torsion Angles				
C−N1−S2−N3	94.7	100.8	−100.2	−131.1	−125.1	166.0	147.8
N1−S2−N3−C4	−145.5	−158.7	−42.7	−45.4	−50.4	−165.4	−167.3
S2−N3−C4−N5	−20.4	−14.1	6.5	21.7	22.0	−7.6	−9.9
N3−C4−N5−C	174.7	173.6	−179.6	−178.2	−175.2	171.7	176.9

[a] Atom numbering from Scheme 2. [b] The three columns for structure **14** are for the three separate ligands in the structure, based around S(2), S(32), and S(62), respectively.

distances between the S(2) ligand and Mg(1) [2.035(2) and 2.117(2) Å] are asymmetric, showing the difference between the two nitrogen donors.

The pattern of bonding in the backbones of all three ligands is roughly similar (Table 6) though two differences are noticeable; for the S(2) ligand, the N1−S2 distance is slightly shorter than in the other two [1.605(2) Å cf. 1.619(2) and 1.623(2) Å] and the C4−N5 separation is slightly longer [1.307(3) cf. 1.282(3) and 1.285(3) Å]. The N1−S2 distances are all shorter than seen in the free ligand (**11**) [as was the case for the zinc (**12**) and aluminum (**13**) species], and presumably the relative lengthening of this bond in the S(32) and S(62) ligands is a consequence of the increased steric congestion of the four-membered chelate rings. In all three ligands, the N1−S2 bond lengths are significantly shorter than the S2−N3 distances. For the C4−N5 bond length, that for the S(2) ligand resembles those seen in the zinc (**12**) and aluminum (**13**) species, which have very similar coordination modes, whereas those for the S(32) and S(62) ligands resemble the distances seen for the two independent molecules in the structure of the free ligand (**11**). This is not surprising given that the coordination modes of the S(32) and S(62) ligands do not make use of the N5 nitrogen. The N3−C4 distances in all three ligands are similar to those in the free ligand (**11**).

We have also observed an analogous homoleptic zinc complex $\mathbf{L_2Zn}$ where both six-membered and four-membered chelates were present (see the Supporting Information). The preference of the mixed chelation modes over the expected double six-membered chelate is attributed to the steric bulk around the metal center. By switching to the four-membered coordination mode, the bulky 2,6-diisopropylaniline can reposition further from the metal, thus releasing some steric strain from the metal center. The difference in the coordination modes between complexes **12** and **14** may be attributed to the relative hardness/softness of the Zn and Mg centers. The harder magnesium dication appears to prefer a higher coordination number (four) and so switches the more sterically encumbered six-membered coordination mode of ligand **11** to its four-membered chelate in order to reduce the steric environment around the metal, thus allowing for further coordination.

Conclusions

A novel chiral imino sulfinamidine ligand **LH** (**11**) has been synthesized from readily available reagents. The ligand was employed in the synthesis of mononuclear Zn(II) and Al(III) alkyl complexes, which were structurally characterized by X-ray crystallography. Complexes **12** and **13** contained **L** binding in a bidentate fashion through a six-membered chelate, potentially placing the metal within a highly chiral environment. Further coordination modes of **11** were observed in the binuclear Mg(II) complex **14** in which three molecules bound as bi- and tridentate ligands through both six-membered and four-membered chelates in a novel homoleptic/heteroleptic amide complex. Further investigation into complexes of other metals and the different coordination modes of ligand **11** is now in progress.

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Supporting Information Available: X-ray structure determination and details of the crystallographic data as CIF files, including additional structures of $\mathbf{(LH{\cdot}LiI{\cdot}thf)_2}$ and $\mathbf{L_2Zn}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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