

# Synthesis, structure, and properties of magnesium complexes containing cyclopentadienyl and amidinate ligand sets<sup>☆</sup>

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## Abstract

*N,N'*-Bis(2,6-diisopropylphenyl)(*tert*-butyl)amidine and *N,N'*-bis(2,4,6-trimethyl-phenyl)(*tert*-butyl)amidine were prepared and treated with  $[\text{CpMgMe}(\text{Et}_2\text{O})_2]$  in diethyl ether or tetrahydrofuran to afford the monomeric amidinate complexes  $[\text{CpMg}(\eta^2\text{-}^t\text{BuC}(\text{N}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3))_2)]$  (87%) and  $[\text{CpMg}(\eta^2\text{-}^t\text{BuC}(\text{N}(2,4,6\text{-}\text{Me}_3\text{C}_6\text{H}_2))_2)(\text{THF})]$  (76%). The solid-state structures of the amidines and resultant magnesium complexes were determined by X-ray diffraction methods. In the solid-state, the magnesium complexes are monomeric and contain one  $\eta^5$ -cyclopentadienyl ligand and one  $\eta^2$ -amidinate ligand, as well as one tetrahydrofuran ligand for the latter.  $[\text{CpMg}(\eta^2\text{-}^t\text{BuC}(\text{N}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3))_2)]$  can be sublimed unchanged with 80% recovery at 180 °C/0.05 torr, while  $[\text{CpMg}(\eta^2\text{-}^t\text{BuC}(\text{N}(2,4,6\text{-}\text{Me}_3\text{C}_6\text{H}_2))_2)(\text{THF})]$  decomposes to  $\text{Cp}_2\text{Mg}$  (77%) and  $[\text{Mg}(\eta^2\text{-}^t\text{BuC}(\text{N}(2,4,6\text{-}\text{Me}_3\text{C}_6\text{H}_2))_2)]$  (83%) under similar conditions.  $[\text{Mg}(\eta^2\text{-}^t\text{BuC}(\text{N}(2,4,6\text{-}\text{Me}_3\text{C}_6\text{H}_2))_2)]$  was prepared independently through treatment of dibutylmagnesium with two equivalents of *N,N'*-bis(2,4,6-trimethylphenyl)(*tert*-butyl)amidine in toluene at ambient temperature.

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**Keywords:** Magnesium; Cyclopentadienyl; Amidine; Amidinate; Chemical vapor deposition

## 1. Introduction

Amidinate ligands  $[\text{RC}(\text{NR}')_2]^-$  have been widely investigated in transition, lanthanide, and main group metal chemistry [1,2]. They are pseudo-allyl ligands and commonly act as bidentate ( $\eta^2$ ) or bridging monodentate ( $\mu\text{-}\eta^1\text{:}\eta^1$ ) four-electron donors through metal–nitrogen  $\sigma$ -bonds (Chart 1). Examples of  $\pi$ -bonded ( $\eta^3$ ) amidinate compounds [3] have been reported recently (Chart 1). Aside from these interesting structural features, amidinate ligands have been employed as important ancillary ligands in catalytic processes, often as cyclopentadienyl replacements. In recent years, Jordan has reported aluminum and gallium amidinate complexes that are catalytically active towards olefin polymerization [4]. Similar activities have also been found in transition metal amidinate complexes [5].

Additionally, Group 13 amidinate complexes have been investigated as potential chemical vapor deposition (CVD) precursors [6]. The versatility of the amidinate ligands is due to the fact that they can be modified at the nitrogen atoms and the carbon atom of the ligand core to achieve different steric and electronic demands.

In the past 20 years, bis(cyclopentadienyl)magnesium ( $\text{Cp}_2\text{Mg}$ ) has been the most widely used doping precursor for the growth of p-type semiconductor films by CVD techniques [7]. Despite the importance of  $\text{Cp}_2\text{Mg}$  in magnesium-doped Group 13 nitrides, virtually nothing is known about the chemical reaction path by which  $\text{Cp}_2\text{Mg}$  is converted to optically active defects. The study of the interaction of  $\text{Cp}_2\text{Mg}$  and nitrogen ligands may provide insight to the chemical intermediates during CVD processes. To this end, we have been exploring volatile magnesium compounds that may be used as CVD precursors and as models for study of chemical intermediates in CVD processes [8,9]. Our recent studies show that  $\text{Cp}_2\text{Mg}$  forms stable adduct with aliphatic amines, but undergoes slow protonation with anilines to form amido complexes [9]. In this paper, we report the synthesis, structure, and thermal proper-

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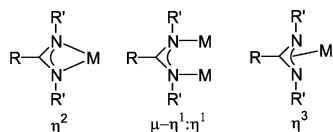


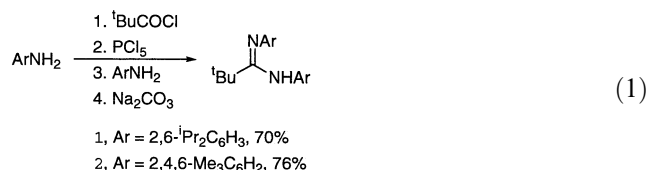
Chart 1. Coordination modes of amidinate ligands.

ties of two new bulky amidine ligands and some corresponding magnesium complexes that contain cyclopentadienyl and amidinate ligands. This study shows that the steric bulk of the amidinate ligand is a significant determinant of the thermal stability and volatility of the resultant complexes, and is therefore a critical issue in the design of advanced CVD precursors.

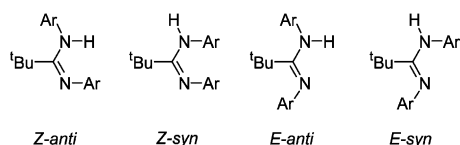
## 2. Results

### 2.1. Synthesis of amidines and CpMg amidinates

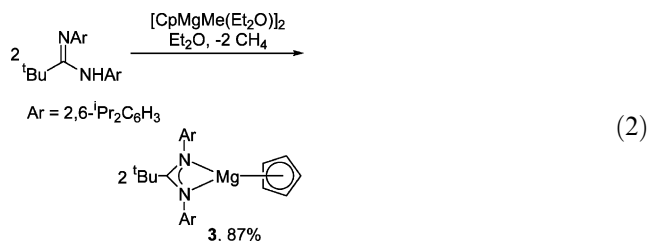
The amidines *N,N'*-bis(2,6-diisopropylphenyl)(*tert*-butyl)amidine (**1**) and *N,N'*-bis(2,4,6-trimethylphenyl)(*tert*-butyl)amidine (**2**) were prepared as white solids by adaptation of a route reported by Wolmershäuser [10], with the exception of the final step where sodium carbonate, instead of aqueous ammonia, was used to neutralize the hydrochloride salt (Eq. (1)). The structural assignments for **1** and **2** were based on spectral and analytical data and by X-ray crystal structure determinations as described below. The <sup>1</sup>H- and <sup>13</sup>C{<sup>1</sup>H}-NMR spectra of **1** and **2** in benzene-*d*<sub>6</sub> at ambient temperature contain broad resonances, and suggest an equilibrium in solution among different isomers (Chart 2). The identity of the isomers is not obvious from spectroscopic data. The solid-state structures of **1** and **2** are described below. The broad infrared absorptions of the nitrogen–hydrogen bonds range from 3416 to 3332 cm<sup>-1</sup>.



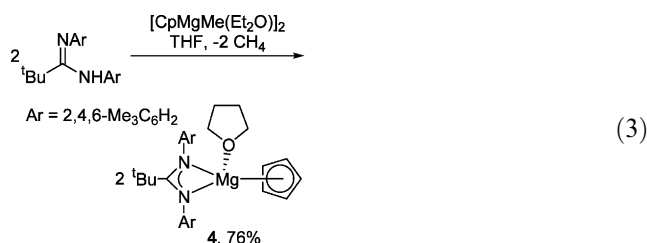
Neither **1** nor **2** reacted with Cp<sub>2</sub>Mg in toluene at ambient temperature after 72 h. Accordingly, the stronger nucleophile [CpMgMe(Et<sub>2</sub>O)]<sub>2</sub> [11] was used instead of Cp<sub>2</sub>Mg. [CpMgMe(Et<sub>2</sub>O)]<sub>2</sub>, which was prepared from redistribution of Cp<sub>2</sub>Mg and dimethylmagnesium in diethyl ether, reacted readily with **1** in diethyl

Chart 2. Possible isomers of amidines **1** and **2**.

ether at ambient temperature to afford [CpMg(η<sup>2</sup>-*t*BuC(N(2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>))<sub>2</sub>)] (**3**, 87%) upon removal of diethyl ether under reduced pressure (Eq. (2)). The structural assignment for **3** was based on spectral and analytical data, as well as X-ray diffraction methods. In the solid-state structure, **3** contains one η<sup>5</sup>-cyclopentadienyl ligand and one η<sup>2</sup>-amidinate ligand. Complex **3** did not form an isolable adduct upon treatment with tetrahydrofuran in toluene. Upon solvent removal and vacuum drying, only **3** was isolated.



Treatment of [CpMgMe(Et<sub>2</sub>O)]<sub>2</sub> with **2** in diethyl ether gave a product containing one diethyl ether ligand as indicated by <sup>1</sup>H-NMR spectroscopy. However, slow loss of the diethyl ether ligand prevented the isolation of a pure product. Similar dissolution in tetrahydrofuran, followed by workup, afforded [CpMg(η<sup>2</sup>-*t*BuC(N(Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>))<sub>2</sub>)(THF)] (**4**, 87%) as a white crystalline solid that was stable to loss of tetrahydrofuran at room temperature (Eq. (3)). The structural assignment of **4** was based on spectral and analytical data as well as X-ray diffraction methods. In the solid-state structure, **4** contains one η<sup>5</sup>-cyclopentadienyl ligand, one η<sup>2</sup>-amidinate ligand, and one tetrahydrofuran ligand.

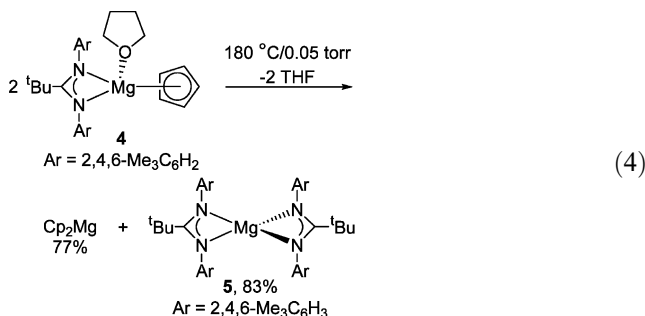


Complexes **3** and **4** are stable at ambient temperature and pressure under inert atmosphere. The <sup>1</sup>H-NMR spectra of **3** and **4** contain cyclopentadienyl resonances at δ 6.34 and 6.33, respectively, which are close to that of Cp<sub>2</sub>Mg (δ 5.97). The <sup>13</sup>C{<sup>1</sup>H}-NMR spectra contain cyclopentadienyl singlets at 106.70 and 105.47 ppm, respectively, which are again close to that of Cp<sub>2</sub>Mg (107.74 ppm).

### 2.2. Volatility studies and thermal reactivity

To assess their initial viability as CVD precursors, **3** and **4** were evaluated for their volatility and thermal stability. Complex **3** sublimed unchanged at 180 °C/0.05 torr, and was recovered in 80% yield in a preparative

sublimation. However, **4** decomposed under similar sublimation conditions to afford  $\text{Cp}_2\text{Mg}$  (77%) and  $\text{Mg}(\eta^2\text{-}^t\text{BuC}(\text{N}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2))_2)_2$  (**5**, 83%; Eq. (4)).  $\text{Cp}_2\text{Mg}$  was collected at the cold end of the sublimation apparatus, while **5** remained at the heated end. Complex **5** can be prepared independently in 95% yield from dibutylmagnesium and **2** (two equivalents). The structural assignment for **5** was based on spectral and analytical data, as well as an X-ray crystal structure determination as described below. The structural assignment for  $\text{Cp}_2\text{Mg}$  was based upon comparison of its NMR spectral data with those of an authentic sample.



### 2.3. Crystal structures

In order to establish the solid-state geometries, the X-ray crystal structures of **1–5** were determined. Crystallographic data are summarized in Table 1. Selected bond distances and angles are given in Tables 2–6. Perspective views of **1–5** are presented in Figs. 1–5.

Compound **1** crystallizes in a *Z-anti* structure, with central carbon–nitrogen bond distances of 1.321(3) and

Table 2  
Selected bond lengths (Å) and angles (°) for **1**

Bond lengths			
N(1)–C(1)	1.321(3)	N(1)–C(6)	1.425(3)
N(2)–C(1)	1.352(3)	N(2)–C(18)	1.433(3)
C(1)–C(2)	1.515(4)		
Bond angles			
N(1)–C(1)–N(2)	119.1(2)	C(1)–N(1)–C(6)	121.8(2)
C(1)–N(2)–C(18)	133.3(3)	N(1)–C(1)–C(2)	115.8(2)
N(2)–C(1)–C(2)	125.1(3)		

Table 3  
Selected bond lengths (Å) and angles (°) for **2**

Bond lengths			
N(1)–C(1)	1.280(2)	N(1)–C(6)	1.404(3)
N(2)–C(1)	1.375(3)	N(2)–C(15)	1.436(3)
C(1)–C(2)	1.530(3)		
Bond angles			
N(1)–C(1)–N(2)	116.0(2)	C(1)–N(1)–C(6)	129.7(2)
C(1)–N(2)–C(15)	122.9(2)	N(1)–C(1)–C(2)	130.8(2)
N(2)–C(1)–C(2)	113.2(2)		

1.352(3) Å. The nitrogen–carbon–nitrogen angle of the central core is 119.1(2)°. The structure exhibited disorder in the pendant groups, especially in the central *tert*-butyl moiety where multiple partial atomic positions were assigned for C(3), C(4) and C(5). Despite the disorder, a reasonable hydrogen position on N(2) was observed from the difference map and refined, which fixed the tautomer as *Z-anti*. However, the similar carbon–nitrogen bond lengths involving N(1) and N(2) suggest that **1** exists as a mixture of *Z-anti* and

Table 1  
Crystal data and data collection parameters for **1–5**

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
Empirical formula	$\text{C}_{29}\text{H}_{44}\text{N}_2$	$\text{C}_{23}\text{H}_{32}\text{N}_2$	$\text{C}_{34}\text{H}_{48}\text{MgN}_2$	$\text{C}_{32}\text{H}_{44}\text{MgN}_2\text{O}$	$\text{C}_{46}\text{H}_{62}\text{MgN}_4$
Formula weight	420.66	336.51	509.05	497.00	695.31
Temperature (K)	295(2)	295(2)	295(2)	295(2)	295(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	14.227(2)	18.515(4)	16.981(7)	8.182(1)	11.108(2)
<i>b</i> (Å)	10.738(1)	13.173(2)	11.160(5)	12.111(1)	12.170(2)
<i>c</i> (Å)	18.235(2)	18.680(4)	18.269(7)	16.161(1)	17.007(3)
$\alpha$ (°)				101.382(2)	94.270(3)
$\beta$ (°)	103.523(3)	112.551(3)	111.456(10)	94.251(1)	96.301(4)
$\gamma$ (°)				102.525(2)	106.526(4)
<i>V</i> (Å <sup>3</sup> )	2708.6(5)	4207.5(13)	3222(2)	1521.1(2)	2177.1(6)
<i>Z</i>	4	8	4	2	2
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.032	1.062	1.049	1.085	1.061
$\mu$ (mm <sup>-1</sup> )	0.059	0.062	0.078	0.083	0.075
$R(F)$ <sup>a</sup> (%)	5.33	5.59	6.95	6.23	7.00
$R_w(F)$ <sup>b</sup> (%)	12.13	15.64	17.50	18.58	17.61

<sup>a</sup>  $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ .

<sup>b</sup>  $wR = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)]^{1/2}$  for  $I > 2\sigma(I)$ .

Table 4  
Selected bond lengths (Å) and angles (°) for **3**

Bond lengths			
Mg(1)–N(1)	2.013(4)	Mg(1)–N(2)	2.028(4)
N(1)–C(1)	1.432(5)	N(1)–C(13)	1.342(4)
N(2)–C(13)	1.334(5)	N(2)–C(18)	1.416(5)
C(13)–C(14)	1.550(5)	Mg(1)–Cent	2.012
Bond angles			
N(1)–Mg(1)–N(2)	65.9(1)	Mg(1)–N(1)–C(1)	136.7(2)
Mg(1)–N(1)–C(13)	92.1(3)	Mg(1)–N(2)–C(13)	91.7(2)
Mg(1)–N(2)–C(18)	138.0(3)	N(1)–C(13)–N(2)	110.3(4)
C(1)–N(1)–C(13)	129.9(3)	C(13)–N(2)–C(18)	130.2(3)
N(1)–C(13)–C(14)	124.3(4)	N(2)–C(13)–C(14)	125.1(4)
N(1)–Mg(1)–Cent	144.9	N(2)–Mg(1)–Cent	148.8

Table 5  
Selected bond lengths (Å) and angles (°) for **4**

Bond lengths			
Mg(1)–N(1)	2.090(2)	Mg(1)–N(2)	2.097(2)
Mg(1)–O(1)	2.080(2)	N(1)–C(1)	1.341(3)
N(1)–C(2)	1.417(3)	N(2)–C(1)	1.341(3)
N(2)–C(15)	1.423(3)	C(1)–C(11)	1.546(3)
Mg(1)–Cent	2.140		
Bond angles			
N(1)–Mg(1)–N(2)	63.3(1)	Mg(1)–N(1)–C(1)	93.4(1)
Mg(1)–N(1)–C(2)	135.8(1)	Mg(1)–N(2)–C(1)	93.1(1)
Mg(1)–N(2)–C(15)	135.2(1)	N(1)–C(1)–N(2)	110.1(2)
C(1)–N(1)–C(2)	130.7(2)	C(1)–N(2)–C(15)	129.6(2)
N(1)–C(1)–C(11)	125.4(2)	N(2)–C(1)–C(11)	124.4(2)
O(1)–Mg(1)–N(1)	101.6(1)	O(1)–Mg(1)–N(2)	108.02(8)
N(1)–Mg(1)–Cent	132.2	N(2)–Mg(1)–Cent	129.8

Table 6  
Selected bond lengths (Å) and angles (°) for **5**

Bond lengths			
Mg(1)–N(1)	2.039(3)	Mg(1)–N(2)	2.038(3)
Mg(1)–N(3)	2.044(3)	Mg(1)–N(4)	2.041(3)
N(1)–C(1)	1.348(4)	N(1)–C(2)	1.421(4)
N(2)–C(1)	1.340(4)	N(2)–C(15)	1.431(4)
N(3)–C(24)	1.333(4)	N(3)–C(25)	1.415(4)
N(4)–C(24)	1.328(4)	N(4)–C(38)	1.424(4)
C(1)–C(11)	1.528(5)	C(24)–C(34)	1.536(5)
Bond angles			
N(1)–Mg(1)–N(2)	64.9(1)	N(3)–Mg(1)–N(4)	64.6(1)
N(1)–Mg(1)–N(3)	131.8(1)	N(1)–Mg(1)–N(4)	139.3(1)
N(2)–Mg(1)–N(3)	139.9(1)	N(2)–Mg(1)–N(4)	131.5(1)
Mg(1)–N(1)–C(1)	92.9(2)	Mg(1)–N(1)–C(2)	135.6(2)
Mg(1)–N(2)–C(1)	93.1(2)	Mg(1)–N(2)–C(15)	136.8(2)
Mg(1)–N(3)–C(24)	92.4(2)	Mg(1)–N(3)–C(25)	136.8(2)
Mg(1)–N(4)–C(24)	92.7(2)	Mg(1)–N(4)–C(38)	135.1(2)
N(1)–C(1)–C(11)	125.7(3)	N(2)–C(1)–C(11)	125.0(3)
N(3)–C(24)–C(34)	123.8(3)	N(4)–C(24)–C(34)	125.8(3)
N(1)–C(1)–N(2)	109.0(3)	N(3)–C(24)–N(4)	110.2(3)

*E-syn* tautomeric forms in the solid-state. The *Z-anti* form probably predominates, due to the longer C(1)–N(2) bond length and the observation of a hydrogen

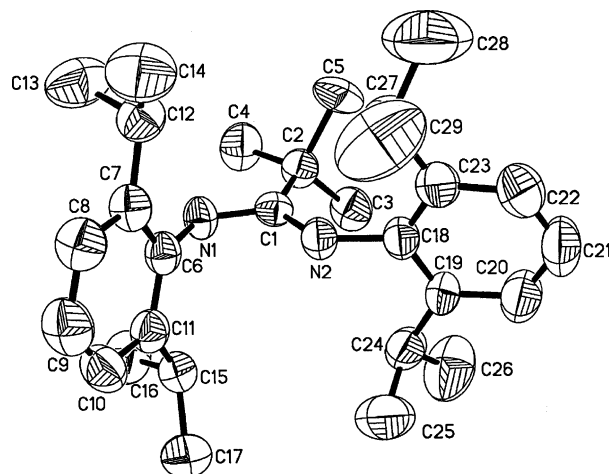


Fig. 1. Perspective view of **1** (50% probability ellipsoids; hydrogen atoms are omitted for clarity).

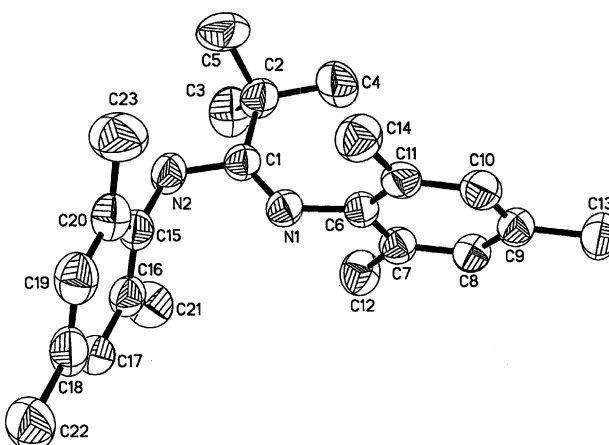


Fig. 2. Perspective view of **2** (50% probability ellipsoids; hydrogen atoms are omitted for clarity).

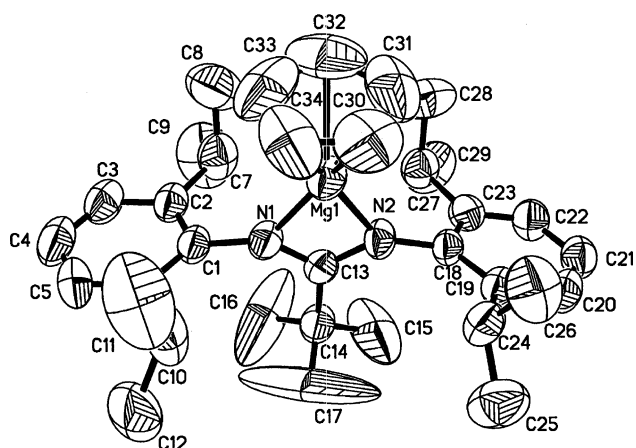


Fig. 3. Perspective view of **3** (50% probability ellipsoids; hydrogen atoms are omitted for clarity).

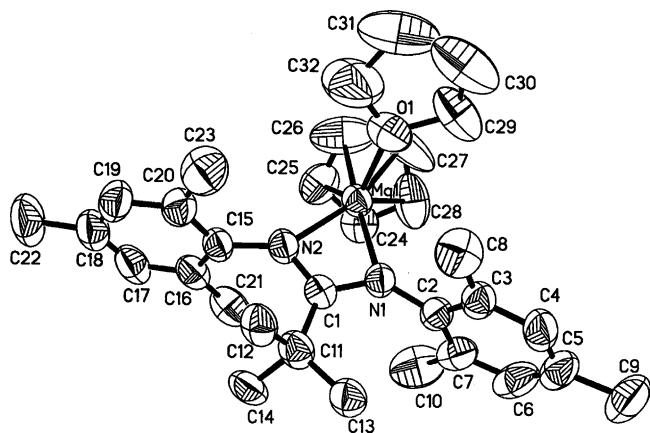


Fig. 4. Perspective view of **4** (50% probability ellipsoids; hydrogen atoms are omitted for clarity).

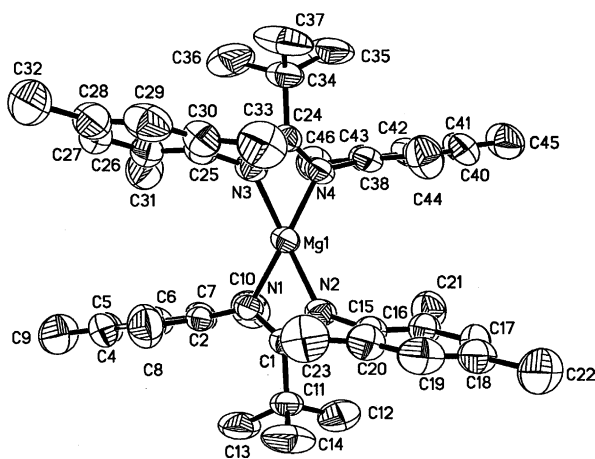


Fig. 5. Perspective view of **5** (50% probability ellipsoids; hydrogen atoms are omitted for clarity).

atom on N(2). However, the crystal data were not of high enough quality to provide a quantitative estimate of the tautomer distribution. Wolmershäuser [10] has observed a similar mixture of isomers in the solid-state structure of a bulky amidine. In **1**, the hydrogen atom bound to N(2) is aimed toward the  $\pi$ -system of the aromatic ring containing C(6)–C(11), raising the possibility of an intramolecular hydrogen bond. However, the distance between the hydrogen atom and the ring centroid is long (2.964 Å), suggesting that this interaction is weak.

Compound **2** crystallizes in a *Z-anti* structure, with central carbon–nitrogen bond lengths of 1.280(2) and 1.375(3) Å. The larger difference in carbon nitrogen bond lengths in **2**, as compared to **1**, suggests that **2** crystallizes solely as *Z-anti* structure. The nitrogen–carbon–nitrogen bond angle of the central core is 116.0(2)°. In **2**, there are no  $\pi$ -contacts involving the nitrogen-bound hydrogen atom.

Complex **3** crystallizes as a monomer, with one  $\eta^5$ -cyclopentadienyl ligand and one  $\eta^2$ -amidinate ligand

bonded to the magnesium center. The magnesium–carbon (C<sub>5</sub>H<sub>5</sub>) bond lengths range from 2.309(7) to 2.331(7) Å. The magnesium–cyclopentadienyl centroid distance is 2.012 Å. The magnesium–nitrogen bond lengths are 2.012(4) and 2.028(3) Å. The nitrogen–carbon bond lengths in the amidinate core are 1.342(4) and 1.334(5) Å, reflecting delocalized nitrogen–carbon bonding. The sum of the angles within the MgCN<sub>2</sub> metallacycle is 360.0°, indicating a planar structure. The dihedral angle of the planes of the amidinate and cyclopentadienyl ligands is 95.8°. Within the MgCN<sub>2</sub> metallacycle, the nitrogen–magnesium–nitrogen and nitrogen–carbon–nitrogen bite angles are 65.85(13) and 110.3(4)°, respectively.

Complex **4** crystallizes as a monomer, with one  $\eta^5$ -cyclopentadienyl ligand, one  $\eta^2$ -amidinate ligand, and one tetrahydrofuran ligand bonded to the magnesium ion. The magnesium–carbon (C<sub>5</sub>H<sub>5</sub>) bond lengths range from 2.413(3) to 2.461(3) Å. The magnesium–cyclopentadienyl centroid distance is 2.140 Å. The magnesium–nitrogen bond lengths are 2.090(2) and 2.097(2) Å, respectively. These distances are slightly longer than those in **3**, due to the increase in coordination number at magnesium in **4**. The nitrogen–carbon bond lengths within the amidinate core are both 1.341(1) Å, reflecting delocalized nitrogen–carbon bonding. The sum of the angles of the MgCN<sub>2</sub> metallacycle is 360.0°, indicating a planar structure. The dihedral angle of the planes of the amidinate and cyclopentadienyl ligands is 49.2°, which is smaller than the value in **3** due to accommodation of the tetrahydrofuran ligand. Within the MgCN<sub>2</sub> metallacycle, the nitrogen–magnesium–nitrogen and nitrogen–carbon–nitrogen bite angles are 63.34(7) and 110.1(2)°, respectively.

Compound **5** crystallizes as a monomer, with two  $\eta^2$ -amidinate ligands bonded to a tetrahedrally coordinated magnesium ion. The magnesium–nitrogen bond lengths range from 2.039(3) to 2.044(3) Å. The nitrogen–carbon bond lengths of the amidinate cores range from 1.328(4) to 1.348(4) Å, reflecting delocalized nitrogen–carbon bonding. The sums of the angles of the MgCN<sub>2</sub> metallacycles are both 359.9°, indicating virtually planar fragments. The nitrogen–magnesium–nitrogen and nitrogen–carbon–nitrogen bite angles are 64.9(1) and 109.0(3)°, 64.6(1) and 110.2(3)°, respectively.

### 3. Discussion

The bulky amidines **1** and **2** are new compounds that were prepared by modification of a procedure originally reported Wolmershäuser for the synthesis of *C*-aryl and *C*-methyl amidines with bulky aryl groups on the nitrogen atoms [10]. The synthetic procedures described herein proceed in high yield, and **1** and **2** can be prepared on large scales from commercially available



starting materials. Like the amidines reported by Wolmershäuser [10], **1** and **2** reveal complex NMR spectra between 20 and 70 °C due to the presence of isomers and tautomers in solution. In the solid-state, both **1** and **2** crystallize predominantly (**1**) or exclusively (**2**) in the *Z-anti* form. The *Z-anti* structure probably reflects minimization of steric interactions between the aryl groups and between the aryl groups and the *tert*-butyl groups. There is evidence for a weak intramolecular N–H···arene hydrogen bond in **1**, and no evidence for such a hydrogen bond in **2**. The weak to absent hydrogen bonding in **1** and **2** is reflected by the high nitrogen–hydrogen infrared stretch absorptions of 3416 and 3396 cm<sup>-1</sup>. By contrast, *N,N'*-bis(2,6-diisopropylphenyl)acetamide crystallizes as a dimer with a C<sub>2</sub>H<sub>2</sub>N<sub>4</sub> ring that is held together by two N–H···N hydrogen bonds [10]. The presence of the *tert*-butyl groups in **1** and **2** clearly increases the steric congestion, compared to *N,N'*-bis(2,6-diisopropylphenyl)acetamide, the methyl-substituted analog of **1**. While **1** and **2** are new compounds, Jordan has previously reported the synthesis of lithium *N,N'*-bis(2,6-diisopropylphenyl)-4-*tert*-butylamidinate, which was generated in situ from <sup>t</sup>BuLi and *N,N'*-bis(2,6-diisopropylphenyl)carbodiimide [4c].

Due to the bulky substituents on the amidinate core carbon and nitrogen atoms, only the η<sup>2</sup>-coordination mode was observed for the amidinate ligands in **3**–**5**. Jordan has previously proposed that bulky substituents on the nitrogen and carbon atoms forces a wider carbon–nitrogen–carbon angle at the core nitrogen atoms, which pushes the nitrogen lone pairs inward toward the ‘mouth’ of the amidinate ligand and favors η<sup>2</sup>-coordination [4d]. In **3**, the C(1)–N(1)–C(13) and C(18)–N(2)–C(13) angles are 129.9(3) and 130.2(3)°, while in **4** the C(2)–N(1)–C(1) and C(15)–N(2)–C(1) angles are 130.7(2) and 129.6(2)°, respectively. These angles are much larger than the ~120° angle that would be expected for a sterically uncongested imino moiety. The angular distortions in **3** and **4** are clearly due to crowding between the *tert*-butyl groups and the bulky aryl groups, and are consistent with Jordan’s model. Arnold has also reported extensively on amidinate complexes containing bulky nitrogen and carbon substituents [12].

Only a handful of bis(amidinate) complexes of magnesium have been structurally characterized [12a,13–21]. They are either monomeric (e.g. [Mg(η<sup>2</sup>-MeC(N<sup>t</sup>Bu)<sub>2</sub>)]<sub>2</sub>) or dimeric (e.g. [Mg(η<sup>2</sup>-MeC(N<sup>t</sup>Pr)<sub>2</sub>)]<sub>2</sub>), depending on the steric bulk of the substituents on the nitrogen atoms [14]. The magnesium–nitrogen bond lengths in magnesium amidinate complexes reported to date range from 2.01 to 2.14 Å, which are similar to the values observed in **3**–**5** (2.01–2.10 Å). The nitrogen–magnesium–nitrogen bite angles in known complexes range from 59.3 to 65.8°,

indicating that the steric bulk in **3** and **4** is at the high end of these complexes.

A major issue that is presented herein relates to the thermal stability and volatility of mixed cyclopentadienyl amidinate complexes of magnesium. Complex **3** can be sublimed at 180 °C/0.05 torr without any evidence for decomposition. By contrast, **4** decomposes completely to Cp<sub>2</sub>Mg and **5** under similar sublimation conditions. The reason for the contradictory thermal behavior may be related to the different steric demands of the aromatic substituents on the nitrogen atoms. In the solid-state structures, **3** has a large pocket that is formed by the four isopropyl groups. There is just enough room for the cyclopentadienyl to sit on top of the pocket, and the magnesium center is thus protected from interacting with neutral donor ligands. Consistent with this proposal, **3** does not form an isolable tetrahydrofuran adduct. However, **4** possesses smaller methyl substituents on the aryl groups and there is thus sufficient room left at the magnesium ion to allow coordination of tetrahydrofuran. The presence of an extra coordination site in **4** may also explain its decomposition to Cp<sub>2</sub>Mg and **5** upon attempted sublimation. The open coordination site obtained upon tetrahydrofuran loss may allow formation of species with bridged amidinate ligands, which could then decompose to the observed products. Since <sup>1</sup>H-NMR spectra of Cp<sub>2</sub>Mg and **5** show no evidence for an equilibrium with **4** in the absence of tetrahydrofuran, it is likely that **3** and **4** are stabilized kinetically relative to Cp<sub>2</sub>Mg and the bis(amidinate) complexes through the high activation energies required to achieve sterically congested dinuclear transition states or intermediates. Thus, the design of volatile, thermally stable magnesium complexes for use in CVD requires careful optimization of the steric parameters of both anionic species in complexes containing dissimilar ligands.

## 4. Experimental

### 4.1. General considerations

All reactions were performed under an inert atmosphere of argon using either glovebox or Schlenk line techniques. Toluene was distilled from sodium, THF and Et<sub>2</sub>O were distilled from purple solutions of sodium benzophenone ketyl, hexane was distilled from phosphorus pentoxide, and dichloromethane was distilled from calcium hydride. Cp<sub>2</sub>Mg was prepared according to a literature procedure [22].

<sup>1</sup>H-NMR spectra were obtained at 400 MHz while <sup>13</sup>C{<sup>1</sup>H}-NMR spectra were obtained at 100 MHz in benzene-*d*<sub>6</sub>. Infrared spectra were obtained using Nujol as the medium. Midwest Microlab, Indianapolis, IN, performed the elemental analyses. Melting points (m.p.)

were obtained on a Haake-Buchler HBI digital melting point apparatus and are uncorrected.

## 4.2. Synthesis of amidines

### 4.2.1. Preparation of ${}^t\text{BuC}(\text{NAr})(\text{NHAr})$ ( $\text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$ ) (**1**)

A 1000-ml flask was charged with 1-chloro-1-(2,6-diisopropylphenylimino)-2,2-dimethylpropane [23] (20.0 g, 71.6 mmol). Benzene (500 ml) and 2,6-diisopropylaniline (12.7 g, 71.6 mmol) were added. The resultant colorless solution was flushed with argon and then refluxed for 24 h. The solution was cooled to 0 °C and filtered through a coarse glass frit to afford **1**·HCl as a white solid. Crude **1**·HCl was dissolved in dichloromethane (500 ml) and was then treated with 0.1 M aqueous sodium carbonate (3.80 g, 35.8 mmol). The dichloromethane layer was separated from the aqueous layer, and removal of the dichloromethane afforded crude **1** as a white solid. Recrystallization of the crude material from EtOH afforded **1** as colorless crystals (21.1 g, 70%): m.p. 138–140 °C; IR (Nujol,  $\text{cm}^{-1}$ ) 3416 (m), 1656 (s), 1622 (m), 1607 (m), 1306 (m), 1230 (m), 1169 (m), 1127 (m), 1030 (m), 854 (m), 727 (s);  ${}^1\text{H-NMR}$  (benzene- $d_6$ ):  $\delta$  7.26–6.93 (m, 6H, Ph), 5.45 (s, 1H, NH), 3.48 (septet, 2H,  $(\text{CH}_3)_2\text{CH}$ ), 3.29 (septet, 2H,  $(\text{CH}_3)_2\text{CH}$ ), 1.39 (d,  $J = 6.4$  Hz, 6H,  $(\text{CH}_3)_2\text{CH}$ ), 1.23 (d,  $J = 6.4$  Hz, 6H,  $(\text{CH}_3)_2\text{CH}$ );  ${}^{13}\text{C-NMR}$  spectra revealed extremely broad resonances, both at 23 and 70 °C in benzene- $d_6$ , and are thus not reported. Anal. Calc. for  $\text{C}_{29}\text{H}_{44}\text{N}_2$ : C, 82.80; H, 10.54; N, 6.66. Found: C, 83.02; H, 10.29; N, 6.66%.

### 4.2.2. Preparation of ${}^t\text{BuC}(\text{NAr})(\text{NHAr})$ ( $\text{Ar} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ ) (**2**)

In a fashion similar to the preparation of **1**, treatment of 1-chloro-2,2-dimethyl-1-(2,4,6-trimethylphenylimino)propane [23] (32.0 g, 137.1 mmol) with 2,4,6-trimethylaniline (18.6 g, 137.1 mmol) in benzene (600 ml) afforded **2**·HCl. Subsequent treatment with sodium carbonate (7.27 g, 68.6 mmol), followed by recrystallization from EtOH, afforded **2** as white crystals (35.0 g, 76%): m.p. 159–160 °C; IR (Nujol,  $\text{cm}^{-1}$ ) 3396 (m), 3332 (m), 1655 (m), 1613 (s), 1583 (m), 1321 (m), 1256 (w), 1208 (w), 1169 (w), 1099 (w), 802 (w), 757 (m), 724 (m);  ${}^1\text{H-NMR}$  (benzene- $d_6$ ):  $\delta$  6.84 (bs, 2H, Ph), 6.62 (broad s, 2H, Ph), 4.94 (broad s, 1H, NH), 2.23, 2.08 (broad s, 9H,  $\text{CH}_3$ ), 1.17 (broad s, 9H,  $\text{C}(\text{CH}_3)_3$ );  ${}^{13}\text{C-NMR}$  spectra revealed extremely broad resonances, both at 23 and 70 °C in benzene- $d_6$ , and are thus not reported. Anal. Calc. for  $\text{C}_{26}\text{H}_{38}\text{N}_2$ : C, 82.09; H, 9.58; N, 8.32. Found: C, 81.92; H, 9.68; N, 8.24%.

## 4.3. Synthesis of magnesium cyclopentadienyl amidinate complexes

### 4.3.1. Preparation of $(\text{CpMg}(\eta^2\text{-}{}^t\text{BuC}(\text{NAr})_2))$ ( $\text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$ ) (**3**)

A 100-ml Schlenk flask was charged with  $\text{Cp}_2\text{Mg}$  (0.155 g, 1.00 mmol),  $\text{MgMe}_2$  (0.054 g, 1.0 mmol), and  $\text{Et}_2\text{O}$  (30 ml). The solution was stirred at ambient temperature for 1 h, and then **1** (0.840 g, 2.00 mmol) was added. The resultant mixture was stirred for an additional 18 h. Removal of the volatile components under reduced pressure afforded **3** as a white solid (0.860 g, 87%): m.p. 280–282 °C; IR (Nujol,  $\text{cm}^{-1}$ ) 1619 (w), 1583 (w), 1178 (m), 1006 (m), 968 (m), 778 (s), 762 (m), 727 (m);  ${}^1\text{H-NMR}$  (benzene- $d_6$ ):  $\delta$  7.02 (m, 6H,  $\text{C}_6\text{H}_3$ ), 6.34 (s, 5H,  $\text{C}_5\text{H}_5$ ), 3.23 (sept, 4H,  $(\text{CH}_3)_2\text{CH}$ ), 1.22 (d,  $J = 6.6$  Hz, 24H,  $(\text{CH}_3)_2\text{CH}$ ), 0.78 (s, 9H,  $(\text{CH}_3)_3\text{C}$ );  ${}^{13}\text{C}\{{}^1\text{H}\}$ -NMR (benzene- $d_6$ , ppm): 178.96 ( $\text{C}^t\text{-Bu}$ ), 142.94 ( $\text{C}_{ipso}$ ), 142.40 ( $\text{C}_{ortho}$ ), 124.49 ( $\text{C}_{para}$ ), 123.13 ( $\text{C}_{meta}$ ), 106.70 ( $\text{C}_5\text{H}_5$ ), 43.21 ( $(\text{CH}_3)_3\text{C}$ ), 30.03 ( $\text{CH}(\text{CH}_3)_2$ ), 28.92 ( $\text{CH}(\text{CH}_3)\text{CH}_3'$ ), 25.45 ( $\text{CH}(\text{CH}_3)(\text{CH}_3)''$ ), 22.00 ( $(\text{CH}_3)_3\text{C}$ ). Anal. Calc. for  $\text{C}_{34}\text{H}_{48}\text{MgN}_4$ : C, 80.22; H, 9.50; N, 5.50. Found: C, 80.10; H, 9.61; N, 5.47%.

### 4.3.2. Preparation of $(\text{CpMg}(\text{THF})(\eta^2\text{-}{}^t\text{BuC}(\text{NAr})_2))$ ( $\text{Ar} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ ) (**4**)

In a procedure similar to the preparation of **3**, treatment of  $\text{Cp}_2\text{Mg}$  (0.077 g, 0.50 mmol) and  $\text{MgMe}_2$  (0.027 g, 0.50 mmol) with **2** (0.336 g, 1.00 mmol) in THF (20 ml) afforded **4** as a white solid (0.380 g, 76%): m.p. 240 °C (dec); IR (Nujol,  $\text{cm}^{-1}$ ) 1660 (m), 1621 (m), 1607 (m), 1187 (m), 1009 (m), 854 (m), 764 (s), 727 (s);  ${}^1\text{H-NMR}$  (benzene- $d_6$ ):  $\delta$  6.88 (s, 4H,  $\text{C}_6\text{H}_2$ ), 6.33 (s, 5H,  $\text{C}_5\text{H}_5$ ), 3.15 (m, 4H, THF), 2.36 (s, 12H,  $o\text{-CH}_3$ ), 2.24 (s, 6H,  $p\text{-CH}_3$ ), 1.11 (m, 4H, THF), 0.94 (s, 9H,  $(\text{CH}_3)_3\text{C}$ );  ${}^{13}\text{C}\{{}^1\text{H}\}$ -NMR (benzene- $d_6$ , ppm): 175.81 ( $\text{C}^t\text{-Bu}$ ), 145.81 ( $\text{C}_{ipso}$ ), 131.74 ( $\text{C}_{ortho}$ ), 130.86 ( $\text{C}_{para}$ ), 128.99 ( $\text{C}_{meta}$ ), 105.47 ( $\text{C}_5\text{H}_5$ ), 68.62 (THF), 41.79 ( $(\text{CH}_3)_3\text{C}$ ), 29.39 ( $o\text{-CH}_3$ ), 24.67 ( $p\text{-CH}_3$ ), 20.90 (THF), 19.90 ( $(\text{CH}_3)_3\text{C}$ ). Anal. Calc. for  $\text{C}_{32}\text{H}_{44}\text{MgN}_2\text{O}$ : C, 77.33; H, 8.92; N, 5.64. Found: C, 76.91; H, 8.94; N, 5.67%.

### 4.3.3. Sublimation of **4**

Compound **4** (0.250 g) was slowly heated to 160 °C in a sublimation tube under reduced pressure (0.05 torr). After 1 h under these conditions, the heating was stopped and the tube was cooled to ambient temperature. The colorless crystals collected at the hot end were  $\text{Cp}_2\text{Mg}$  (0.030 g, 77%) as determined by  ${}^1\text{H-NMR}$  ( $\delta$  5.96) and  ${}^{13}\text{C-NMR}$  (107.7 ppm) analyses, while the residue in the cold end was  $\text{Mg}(\eta^2\text{-}{}^t\text{Bu}(\text{NAr})_2)$  ( $\text{Ar} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ ) (0.135 g, 77%, **5**). Complex **5** can also be prepared from  $\text{MgBu}_2$  (1.0 ml, 1.0 M in heptane) and **2** (0.673 g, 2.00 mmol) in hexane in 95% yield: m.p. 277–279 °C; IR (Nujol,  $\text{cm}^{-1}$ ) 1654 (w), 1621 (m), 1605 (m),

1222 (s), 1187 (s), 1030 (s), 799 (m), 726 (s);  $^1\text{H-NMR}$  (benzene- $d_6$ ):  $\delta$  6.80 (s, 8H,  $\text{C}_6\text{H}_2$ ), 2.20 (s, 24H,  $o\text{-CH}_3$ ), 2.10 (s, 12H,  $p\text{-CH}_3$ ), 0.87 (s, 18H,  $(\text{CH}_3)_3\text{C}$ );  $^{13}\text{C}\{^1\text{H}\}$ -NMR (benzene- $d_6$ , ppm): 180.07 ( $\text{C}^t\text{Bu}$ ), 144.69 ( $\text{C}_{\text{ipso}}$ ), 131.86 ( $\text{C}_{\text{ortho}}$ ), 131.56 ( $\text{C}_{\text{para}}$ ), 128.80 ( $\text{C}_{\text{meta}}$ ), 42.23 ( $\text{C}(\text{CH}_3)_3$ ), 28.92 ( $o\text{-CH}_3$ ), 20.95 ( $p\text{-CH}_3$ ), 19.46 ( $\text{C}(\text{CH}_3)_3$ ). Anal. Calc. for  $\text{C}_{46}\text{H}_{62}\text{MgN}_4$ : C, 79.46; H, 8.99; N, 8.06. Found: C, 79.64; H, 9.10; N, 8.09%.

#### 4.4. X-ray crystallographic structure determination for 1–5

Crystalline samples for X-ray structural determinations were mounted in thin-walled capillaries under a nitrogen atmosphere. Crystallographic data were collected at room temperature on a Bruker automated P4/CCD diffractometer with monochromated Mo radiation. A hemisphere of data was collected for each sample at 10 s/frame and integrated with the manufacturer's SMART and SAINT software, respectively. Absorption corrections were applied with Sheldrick's SADABS [24], and the structures were solved and refined using the programs of SHELXL-97 [25]. Compounds **1** and **2** crystallize from EtOH with no associated ions or solvent. Complexes **3** and **5** crystallize as neutral compounds from  $\text{CH}_2\text{Cl}_2$ –hexane with no associated ions or solvent. Complex **4** crystallizes from  $\text{CH}_2\text{Cl}_2$ –hexane and contains one THF ligand. Compound **1** crystallized as colorless rhomboids. Hydrogen atoms were placed in observed and calculated positions. The complex displayed typical disorder in the *tert*-butyl group and atoms C3, C4 and C5 were placed in two sets of partial positions. Compound **2** crystallized as colorless needles. Hydrogen atoms were placed in observed and calculated positions. Complex **3** crystallized as colorless irregular crystals. Hydrogen atoms were placed in calculated positions. The complex showed pendant group disorders as indicated by large thermal parameters. Complex **4** crystallized as colorless rhomboids. Hydrogen atoms were placed in calculated positions. Partial atoms were used to describe the *tert*-butyl disorder. Complex **5** crystallized as colorless tablets. Hydrogen atoms were placed in calculated positions. Large thermal parameters describe the disorder in the pendant methyl groups.

### 5. Supporting information available

X-ray crystallographic files reported in this paper in CIF format for the structure determinations of **1–5** have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 210459, 210460, 210461, 210462, 210463 for compounds **1**, **2**, **3**, **4**, and **5**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2

1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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