Synthesis and Characterization of Strontium Bis(*N*-isopropylanilide) and Comparison with the Lighter Magnesium and Calcium Congeners

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Dedicated to Professor Heinrich Nöth on the occasion of his 85th birthday

The metathesis reaction of strontium diiodide [(thf)$_5$SrI$_2$] with K[N(Ph)iPr] in THF yields [(thf)$_4$Sr{N(Ph)iPr}$_2$] (**1**). Ligand exchange reactions with 1,2-dimethoxyethane (DME), tetramethylethylenediamine (TMEDA), and pentamethyldiethylenetriamine (PMDETA) allow the isolation of the corresponding adducts [(dme)$_2$Sr{N(Ph)iPr}$_2$] (**2**), [(tmeda)(thf)Sr{N(Ph)iPr}$_2$] (**3**) and [(pmdeta)Sr{N(Ph)iPr}$_2$] (**4**), respectively. Magnesiation of *N*-isopropylaniline with dibutylmagnesium in THF leads to the formation of [(thf)$_2$Mg{N(Ph)iPr}$_2$] (**5**). A similar reaction in TMEDA gives nearly insoluble crystalline [(tmeda)Mg{N(Ph)iPr}$_2$] (**7**), whereas the mother liquor contains heteroleptic [(tmeda)(nBu)Mg{N(Ph)iPr}] (**6**). Magnesiation of *N*-isopropylaniline in 2,2,5,5-tetramethyltetrahydrofuran (Me$_4$thf) yields [(Me$_4$thf)Mg{N(Ph)iPr}$_2$] (**8**) with a three-coordinate metal center. In hydrocarbons this complex loses the bulky ether base, and the solvent-free dimer [Mg{N(Ph)iPr}$_2$]$_2$ (**9**) can be isolated. Reaction of this complex with 1,2-dimethoxyethane or metalation of *N*-isopropylaniline with dibutylmagnesium in DME yield the dme adduct, [(dme)Mg{N(Ph)iPr}$_2$] (**10**). The crystal structures show that the nitrogen atoms of the magnesium-bound *N*-isopropylanilide ions are in planar environments whereas strontium-bound *N*-isopropylanilide ions show rather short contacts between the alkaline earth metal and the *ipso*-carbon atoms of the phenyl groups leading to a pyramidalization of the coordination of the nitrogen atoms.

Key words: Amides, Anilides, Magnesium Amides, Strontium Amides, *N*-Isopropylanilides

Introduction

The number of amides of the alkaline earth metals was limited for a long time to diverse magnesium derivatives and very few calcium complexes [1]. The heavier congeners attracted some interest only a few years ago [2 – 5]. The need of highly reactive superbases initiated the development of a variety of concepts in order to enhance the reactivity of *s*-block organometallics [6, 7]. Based on magnesium amides, the "inverse crowns" of mixed *s*-block metal amides exhibit an intriguing reactivity [8 – 11] allowing isolation and characterization of doubly deprotonated and captured substrates. In general, synthesis of heterobimetallic organometallics such as *s*-block metal zincates or alkali metal calciates represents a valuable concept to alter the reactivity of organometallics [12]. Another strategy to enhance the reactivity is the use of heavier *s*-block metals thus enhancing the polarity of the metal-nitrogen bond and, hence, the nucleophilicity of the amide ion and the ionic nature of the complex. However, the very limited number of strontium and barium amides is in striking contrast to the comprehensive knowledge on magnesium and calcium amides.

Strontium bis[bis(trimethylsilyl)amide] complexes represent the first examples of strontium amides that are soluble in common organic solvents allowing homogeneous reaction conditions. These complexes were prepared *via* transmetalation from

M[N(SiMe$_3$)$_2$]$_2$ with M = Hg [13], Sn [14, 15]. Deprotonation of bis(trimethylsilyl)amine with pyrophoric strontium in tetrahydrofuran (THF) yielded [(thf)$_2$Sr{N(SiMe$_3$)$_2$}$_2$] which gave polymeric [(diox)Sr{N(SiMe$_3$)$_2$}$_2$]$_\infty$ after exchange of both thf ligands by one 1,4-dioxane molecule (diox) [16]. This metalation reaction of amine with strontium metal can also be catalyzed by BiPh$_3$ [17]. Recently, the synthesis of imidazol-2-ylidene adducts [(L)Sr{N(SiMe$_3$)$_2$}$_2$] allowed the stabilization of the unusual small coordination number of three at the strontium center [18].

Substitution of one trimethylsilyl group by a bulky aryl rest ensures solubility in ethers and leads to substituted strontium bis(*N*-trimethylsilylanilides) [19, 20]. Recently, related compounds Me$_2$Si(NDipp)$_2$*Ae*(thf)$_n$ (*Ae* = alkaline earth metal) were reported containing a bidentate bis(amido)silane backbone [21]. Decreasing steric demand of the anilido ligands leads from monomeric [(thf)$_4$Sr(NPh$_2$)$_2$] [22] and [(dme)$_2$(NH$_3$)Sr(*N*-carbazolyl)$_2$] [23] to dinuclear [(thf)$_3$Sr{μ-N(H)C$_6$H$_3$F$_2$}$_3$Sr(thf)$_3$I] [24] and finally to the one-dimensional polymer [(thf)$_2$Sr{μ-N(H)Ph}$_2$]$_\infty$ [25]. The alkaline earth metal amides M(NH$_2$)$_2$ are salt-like solids which are insoluble in common organic solvents [26, 27]; nevertheless, they recently regained considerable interest and were characterized by solid-state NMR techniques [28, 29]. Based on *ab initio* studies, Kaupp and Schleyer [30, 31] predicted a bent structure for mononuclear Sr(NH$_2$)$_2$ with a N–Sr–N bond angle of 131.7° whereas the homologous calcium bis(amide) was calculated as a linear molecule.

Silyl-free bidentate amido bases have also been known for several years. Pyrazolates bind *via* both nitrogen atoms to the large and soft heavy alkaline earth metals strontium and barium, Side-on coordination to the π systems was not observed in the solid state [32, 33]. Reduction of 1,4-diaryl-1,4-diaza-1,3-butadiene with strontium in THF yielded products with the corresponding bidentate 1,2-bis(amido)ethene base acting as a bidentate ligand [34]. In 2,5-bis(*N*-aryliminomethyl)pyrrolyl complexes of strontium this ligand acts as a tridentate base [35].
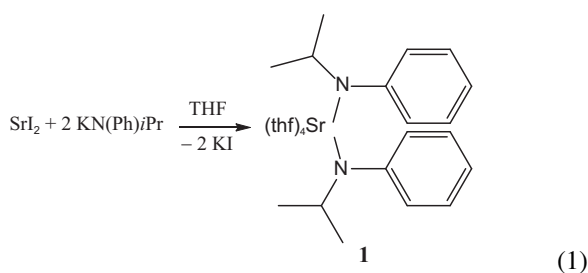
The interest in the amides of strontium has increased also due to the fact that these complexes showed catalytic activity [36, 37] in the Tishchenko reaction [38], intramolecular [39, 40] and intermolecular hydroamination of alkenes and alkynes [41], and hydrophanyla-

tion of carbodiimides [42]. For the calcium complexes we could show that the catalytic reactivity of *N*-alkyl substituted anilides is significantly enhanced compared to the diphenylamides (*N*-phenylanilides) [43] whereas the strontium bis[bis(trimethylsilyl)amide] exhibited a higher catalytic activity than the homologous calcium congener [39 – 41]. Therefore, we combined these strategies to prepare the extremely reactive strontium bis(*N*-isopropylanilides) and investigated the influence of the neutral Lewis bases (ethers and amines) on the solid-state structures. In order to understand the dependency between reactivity and size of the alkaline earth metal atoms we included studies on magnesium bis(*N*-isopropylanilides) and compared these complexes with the already well-known calcium derivative [44].
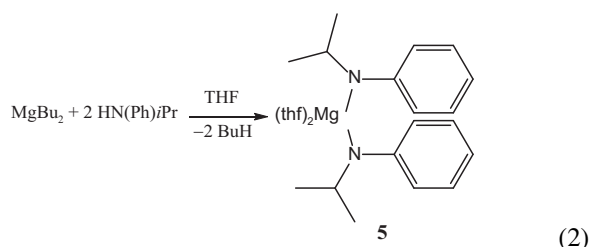
Results and Discussion

Synthesis

In a metathetical approach a THF solution of strontium diiodide [(thf)$_5$SrI$_2$] was added to K[N(Ph)*i*Pr] [45] also dissolved in THF yielding [(thf)$_4$Sr{N(Ph)*i*Pr}$_2$] (**1**). Due to the fact that potassium calciates and strontiates were observed in a similar reaction of K[N(Ph)*i*Pr] with calcium diiodide [44, 46] and strontium diiodide [46], respectively, we carefully followed the ideal stoichiometry shown in Eq. 1 in order to avoid the formation of these strontiates. The strontium bis(amide) **1** was formed quantitatively and precipitation of KI was observed. After removal of all solids by filtration and cooling of the solution crystalline **1** was isolated.

$$\text{SrI}_2 + 2 \text{ KN(Ph)}i\text{Pr} \xrightarrow[-2\text{ KI}]{\text{THF}} \text{(thf)}_4\text{Sr}$$
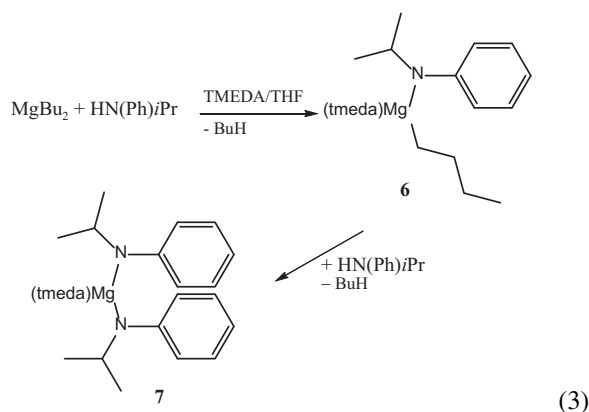
(1)

Ligand exchange reactions were successfully carried out after complete drying of **1** and addition of 1,2-dimethoxyethane (DME), tetramethylethylenediamine (TMEDA), and pentamethyldiethylenetriamine (PMDETA) yielding the corresponding Lewis base adducts [(dme)$_2$Sr{N(Ph)*i*Pr}$_2$] (**2**), [(tmeda)

(thf)Sr{N(Ph)*i*Pr}$_2$] (**3**) and [(pmdeta)Sr{N(Ph)*i*Pr}$_2$] (**4**), respectively. These complexes are soluble in THF, and in order to perform the ligand exchange reaction in a homogenous solution, THF had to be added to the reaction mixtures of TMEDA and PMDETA. The ether adducts contain hexacoordinate alkaline earth metal atoms whereas the bulkier amino bases tmeda and pmdeta stabilize a coordination number of five at the strontium centers.

For comparison reasons, the homologous magnesium derivatives were prepared *via* a magnesiation of *N*-isopropylaniline with dibutylmagnesium in THF according to Eq. 2 yielding [(thf)$_2$Mg{N(Ph)*i*Pr}$_2$] (**5**).

(2)

In order to prepare magnesium bis(*N*-isopropylanilide) with other coligands, the metalation reaction was performed in TMEDA. A precipitate formed immediately consisting of pure [(tmeda)Mg{N(Ph)*i*Pr}$_2$] (**7**) whereas the mother liquor contained heteroleptic [(tmeda)(*n*Bu)Mg{N(Ph)*i*Pr}] (**6**) and [(tmeda)Mg{N(Ph)*i*Pr}$_2$] (**7**). After cooling of the mother liquor, [(tmeda)(*n*Bu)Mg{N(Ph)*i*Pr}] (**6**) could be isolated. Such heteroleptic alkylmagnesium amides are well-known and were structurally characterized earlier [20, 49 – 58]. Prolonged reaction times allow a quantitative formation of the magnesium bis(amide) [(tmeda)Mg{N(Ph)*i*Pr}$_2$] (**7**) (Eq. 3).

(3)

In order to also test the coordination behavior of very bulky 2,2,5,5-tetramethyltetrahydrofuran (Me$_4$THF) the magnesiation of *N*-isopropylaniline was performed in this ether. Products isolated from this reaction mixture show the composition of [(Me$_4$thf)Mg{N(Ph)*i*Pr}$_2$] (**8**) with a tricoordinate metal center. Attempted recrystallization of this crystalline [(Me$_4$thf)Mg{N(Ph)*i*Pr}$_2$] (**8**) from a pentane solution yielded the solvent-free dimer [Mg{N(Ph)*i*Pr}$_2$]$_2$ (**9**). Reaction of this complex with 1,2-dimethoxyethane or metalation of *N*-isopropylaniline with dibutylmagnesium in DME yield the dme adduct, [(dme)Mg{N(Ph)*i*Pr}$_2$] (**10**).

NMR spectroscopy

With an increasing electronegativity difference between the metal and the nitrogen atoms, an increasing ionic nature of the M–N bond is expected [47]. This dependency has already been demonstrated for the alkali metal hydrides, methanides, cyclopentadienides, amides, fluorides, and hydroxides, and a similar relationship is true for the alkaline earth metal derivatives as was demonstrated for the alkaline earth metal bis(methanides). For such ionic molecules it can be envisioned that the influence of the neutral coligand and of the coordination number of the metal on the chemical ^{1}H (Table 1) and ^{13}C NMR shifts (Table 2) is negligible.

Table 1. ^{1}H NMR spectroscopic data of the *N*-isopropylanilide ions; spectra were acquired at 300 K in [D$_8$]THF solution.

Compound		Coligand	*o*-C*H*	*m*-C*H*	*p*-C*H*	C*H*	C*H*$_3$	Ref.
HN(Ph)*i*Pr		– ^{a}	6.53	7.04	6.52	3.59	1.17	
Mg	**5**	thf	6.28	6.79	6.02	3.51	1.20	
	7	tmeda ^{b}	6.33	6.84	6.06	3.55	1.25	
	8	Me$_4$thf ^{b}	6.33	6.84	6.07	3.55	1.25	
	10	dme	6.33	6.84	6.06	3.55	1.25	
Ca		thf	6.11	6.73	5.85	3.42	1.13	[44]
Sr	**1**	thf	6.11	6.80	5.86	3.48	1.14	
	2	dme	6.07	6.78	5.85	3.47	1.14	
	3	tmeda/thf	6.06	6.77	5.84	3.46	1.13	
	4	pmdeta	6.07	6.77	5.85	3.47	1.13	

^{a} δ(NH) = 4.41; chemical shifts in [D$_6$]benzene: 7.16 (*m*-H), 6.73 (*p*-H), 6.43 (*o*-H), 3.30 (CH$_{iPr}$), 2.94 (NH), 0.89 (CH$_3$, $^3J_{H,H}$ = 6.0 Hz); ^{b} due to solubility reasons the complexes were dissolved in [D$_8$]THF, and formation of the thf adducts can be assumed on the basis of identical NMR parameters; nevertheless, integration of these spectra verified the ratio of amide/coligand.

Compound		Coligand	*i*-C*H*	*o*-C*H*	*m*-C*H*	*p*-C*H*	C*H*	C*H*$_3$	Ref.
HN(Ph)*i*Pr		–	149.0	113.4	129.5	116.5	44.5	23.2	
Mg	**5**	thf	159.2	114.4	129.4	110.5	48.5	25.1	
	7	tmeda [a]	159.2	114.4	129.4	110.5	48.5	25.1	
	8	Me$_4$thf [a,b]	159.2	114.4	129.4	110.5	48.5	25.1	
	10	dme	159.2	114.4	129.4	110.5	48.5	25.1	
Ca		thf	157.1	109.6	126.6	104.9	44.8	21.4	[44]
Sr	**1**	thf	160.1	112.0	130.1	107.3	47.7	24.8	
	2	dme	160.1	111.9	130.1	107.3	47.7	24.8	
	3	tmeda/thf	160.1	111.9	130.4	107.4	47.8	24.8	
	4	pmdeta	160.2	111.9	130.3	107.4	47.8	24.8	

Table 2. ^{13}C{^{1}H} NMR spectroscopic data of *N*-isopropylanilide ions; spectra were acquired at 300 K in [D$_8$]THF solution.

[a] Due to solubility reasons the complexes were dissolved in [D$_8$]THF, and formation of the thf adducts can be assumed on the basis of identical NMR parameters; [b] in [D$_6$]benzene solution only the solvent-free dimer [Mg{N(Ph)*i*Pr}$_2$]$_2$ (**9**) and free Me$_4$THF were observed.

In order to evaluate the influence of the electronegativity difference ΔEN (and, hence, the ionicity of the M–N bond) on the chemical shifts we integrated also [(thf)$_3$Ca{N(Ph)*i*Pr}$_2$] [44] and [(thf)$_2$Mg{N(Ph)*i*Pr}$_2$] in Table 1 (Allred-Rochow electronegativities: Mg 1.23, Ca 1.04, Sr 0.99, N 3.07 [48]). 2,2,5,5-Tetramethyltetrahydrofuran (Me$_4$THF) represents a very bulky Lewis base, but it is easily pushed out of the coordination sphere of magnesium by stronger bases such as THF. Due to the fact that all NMR spectra were recorded from [D$_8$]THF solutions for solubility reasons, the NMR parameters of **5** and **6** are alike.

Molecular structures

The NMR data suggest a far-reaching similarity of the structural features of the *N*-isopropylanilide ions regardless of the central alkaline earth metal ion. Molecular structure and numbering scheme of [(thf)$_4$Sr{N(Ph)*i*Pr}$_2$] (**1**) are depicted in Fig. 1. Due to steric reasons the octahedral environment of the strontium center is heavily distorted. The thf ligands are squeezed together, and the bulky amido ligands are bent towards the thus formed gap. The mean Sr–N distance (257.1 pm) is slightly larger than observed in [(dme)$_2$Sr{N(SiMe$_3$)$_2$}$_2$] (Sr–N 253.8(7) pm, av. Sr–O 265.5 pm [59]) caused by enhanced steric repulsion between the thf ligands and the anilido ions. Contrary to this observation, the average Sr–O bond length of **1** (261.9 pm) is smaller; this finding hints toward steric requirements as dominating factors in the molecular structures of these ionic complexes.

The above mentioned delocalization of anionic charge within the anilido unit leads to a shortening of
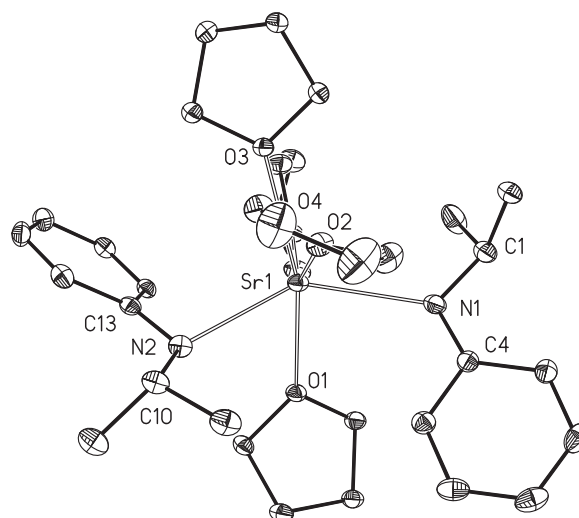

Fig. 1. Molecular structure and numbering scheme of [(thf)$_4$Sr{N(Ph)*i*Pr}$_2$] (**1**). The ellipsoids are drawn at a 40% probability level, H atoms are omitted.

the N–C$_{Ph}$ bond lengths (av. N–C$_{Ph}$ 135.9 pm) whereas the N–C$_{iPr}$ distances show a significantly larger average value of 147.5 pm. Due to the fact that electrostatic interactions dominate the molecular structure, the Sr–N distances play a much more significant role than the planar environments of the nitrogen atoms which allows adaption to steric requirements. Due to this fact also strongly deviating Sr–N–C$_{Ph}$ and Sr–N–C$_{iPr}$ bond angles are observed.

The molecular structure and numbering scheme of [(dme)$_2$Sr{N(Ph)*i*Pr}$_2$] (**2**) are shown in Fig. 2. Despite a rather similar composition, the molecular structures of **2** and [(dme)$_2$Sr{N(SiMe$_3$)$_2$}$_2$] [59] differ significantly. In the bis(trimethylsilyl)amido complex
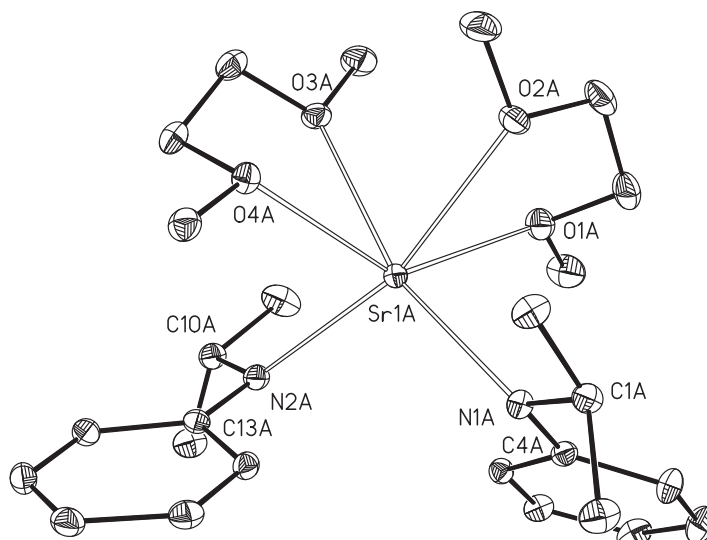
Fig. 2. Molecular structure and numbering scheme of [(dme)$_2$Sr{N(Ph)iPr}$_2$] (**2**). The ellipsoids represent a 40 % probability, H atoms are omitted. The asymmetric unit contains two molecules A and B, only molecule A is shown.
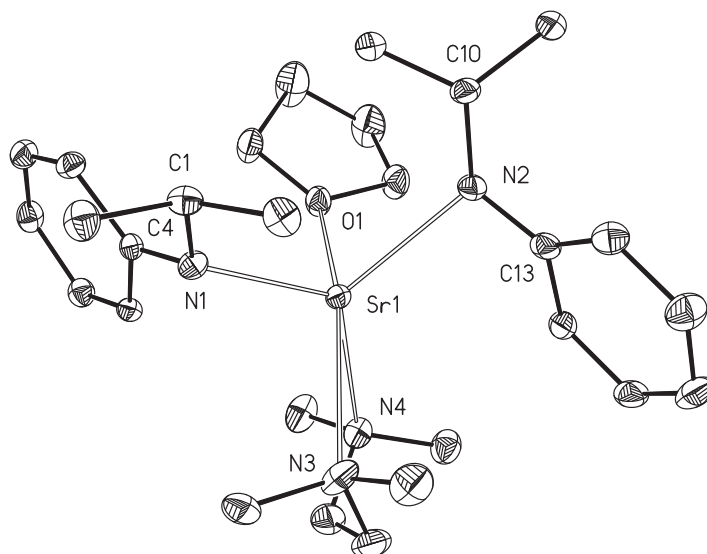

Fig. 3. Molecular structure and numbering scheme of [(tmeda)(thf)Sr{N(Ph)iPr}$_2$] (**3**). The ellidsoids represent a probability of 40 %, H atoms are omitted.

a strictly linear N–Sr–N moiety was found whereas in **2** a significantly bent N–Sr–N fragment (av. N–Sr–N 106.2°) is observed. The slightly released steric repulsion in **2** leads to shorter Sr–N and Sr–O bonds (av. Sr–N 252.6 pm, av. Sr–O 262.7 pm) in comparison to **1** (due to smaller ether ligands) and to [(dme)$_2$Sr{N(SiMe$_3$)$_2$}$_2$] [59] (due to smaller amido ligands).

In the amine adducts [(tmeda)(thf)Sr{N(Ph)iPr}$_2$] (**3**) and [(pmdeta)Sr{N(Ph)iPr}$_2$] (**4**) penta-coordinate strontium centers are found. These complexes are depicted in Figs. 3 and 4, respectively. In these compounds the Sr–N bonds to the anilido ions (av. Sr–N for **3**: 251.3, for **4**: 251.4 pm) are significantly shorter than those to the neutral amine ligands (av. Sr–N$_L$ for **3**: 276.7, for **4**: 275.9 pm). In both complexes bent N–
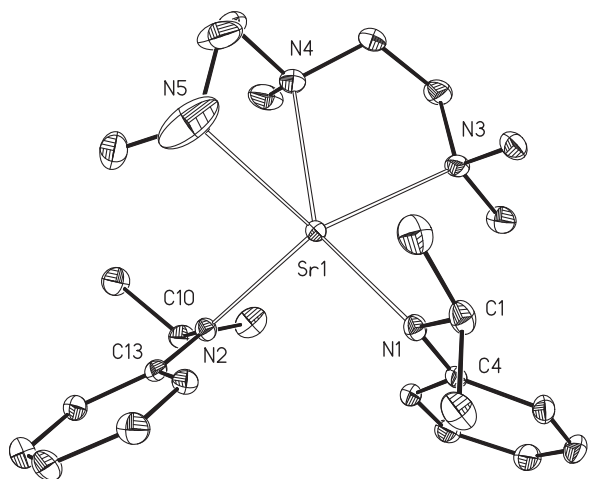
Fig. 4. Molecular structure and numbering scheme of [(pmdeta)Sr{N(Ph)*i*Pr}$_2$] (**4**). The ellipsoids are drawn at a 40 % probability level, H atoms are omitted.

Fig. 6. Molecular structure and numbering scheme of [(dme)Mg{N(Ph)*i*Pr}$_2$] (**10**). The asymmetric unit consists of two whole molecules, marked with the letters "A" and "B", and of two half molecules "C" and "D" that are completed by $(-x - 0.5, -y - 0.5, z)$. Only molecule A is displayed here. The ellipsoids represent a probability of 40 %, H atoms are omitted.

Sr–N bond angles (**3**: 108.8(1)°, **4**: 103.3(1)°) are observed.

The molecular structure and numbering scheme of [(thf)$_2$Mg{N(Ph)*i*Pr}$_2$] (**5**) are depicted in Fig. 5. The magnesium atom is in a distorted tetrahedral environment with a significantly widened N–Mg–N bond angle of 129.53(6)° due to steric and electrostatic repulsion between the bulky amide ions. Comparable values

were also observed for [(thf)$_2$Mg{N(SiMe$_3$)$_2$}$_2$] with bulky bis(trimethylsilyl)amide ions [13].

The molecular structure and numbering scheme of [(dme)Mg{N(Ph)*i*Pr}$_2$] (**10**) are shown in Fig. 6.

Fig. 5. Molecular structure and numbering scheme of [(thf)$_2$Mg{N(Ph)*i*Pr}$_2$] (**5**). The ellipsoids represent a 40 % probability, H atoms are omitted.

Compound	C. N.	M–N	M–O	M–N_L	N–M–N	Ref.
[Mg{N(SiMe$_3$)$_2$}$_2$]	2	191	–	–	180	[60]
[Mg{N(SiMePh$_2$)$_2$}$_2$]	2	196.6	–	–	162.8	[61]
[(μ-diox)$_{0.5}$Mg{N(SiMe$_3$)$_2$}$_2$]$_2$	3	194.6	205.3	–	142.9	[62]
[(2-Mepy)Mg{N(SiMe$_3$)$_2$}$_2$]	3	196.4	–	209.8	137.3	[63]
[(2,6-Me$_2$py)Mg{N(SiMe$_3$)$_2$}$_2$]	3	197.5	–	215.8	133.7	[63]
[(thf)$_2$Mg{N(SiMe$_3$)$_2$}$_2$]	4	202.1	209.4	–	127.9	[13]
[(4-Mepy)$_2$Mg{N(SiMe$_3$)$_2$}$_2$]	4	203.0	–	220.7	125.5	[63]
[(tmeda)(*n*Bu)Mg{N(Ph)*i*Pr}]	4	204.7	–	224.2	115.9 [a]	this work
[(thf)$_2$Mg{N(Ph)*i*Pr}$_2$]	4	202.9	204.6	–	129.5	this work
[(dme)Mg{N(Ph)*i*Pr}$_2$]	4	202.3	207.4	–	121.9	this work
[(thf)$_2$Ca{N(SiMe$_3$)$_2$}$_2$]	4	230.2	237.7	–	121.3	[14]
[(dme)Ca{N(SiMe$_3$)$_2$}$_2$]	4	227.1	239.7	–	123.6	[64]
[(thf)$_3$Ca{N(Ph)*i*Pr}$_2$]	5	234.5	241.7	–	115.8	[44]
[(thf)$_2$Sr{N(SiMe$_3$)$_2$}$_2$]	4	245.8	253.4	–	120.6	[14]
[(μ-diox)Sr{N(SiMe$_3$)$_2$}$_2$]$_\infty$	4	244.9	253.3	–	180	[10]
[(tmeda)(thf)Sr{N(Ph)*i*Pr}$_2$]	5	251.3	255.7	276.7	108.8	this work
[(pmdeta)Sr{N(Ph)*i*Pr}$_2$]	5	251.4	–	275.9	103.3	this work
[(dme)$_2$Sr{N(SiMe$_3$)$_2$}$_2$]	6	253.8	265.5	–	136.1	[59]
[(thf)$_4$Sr{N(Ph)*i*Pr}$_2$]	6	257.1	261.9	–	138.1	this work
[(dme)$_2$Sr{N(Ph)*i*Pr}$_2$]	6	252.6	262.7	–	106.2	this work

Table 3. Average values of selected bond lengths (pm) and angles (deg) of mononuclear magnesium, calcium and strontium *N*-isopropylanilides and, for comparison reasons, of the corresponding mononuclear alkaline earth metal bis[bis(trimethylsilyl)amides]. (C. N. coordination number of the alkaline earth metal; diox: 1,4-dioxane; dme: 1,2-dimethoxyethane; Mepy: methylpyridine; Me$_2$py: dimethylpyridine; N_L nitrogen atom of the neutral Lewis base tmeda or pmdeta or pyridine; pmdeta: pentamethyldiethylenetriamine; thf: tetrahydrofuran; tmeda: tetramethylethylenediamine).

[a] N–Mg–C bond angle.

This compound crystallized in the orthorhombic space group *Fdd*2 with 48 molecules in the unit cell with two whole molecules A and B and two half molecules C and D in the asymmetric unit. Only molecule A is depicted in Fig. 6.

As expected, the magnesium atom is in a distorted tetrahedral environment with the dme ligand acting as a bidentate Lewis base. As observed for the above mentioned magnesium anilides, a significant backdonation of charge from nitrogen atom with its planar coordination into the phenyl group leads to rather short N–C_{Ph} bonds whereas the N–C_{iPr} bond lengths are nearly 10 pm larger.

Selected structural parameters of these anilido complexes are compared in Table 3 with the data of the alkaline earth metal bis[bis(trimethylsilyl)amides]. Due to intramolecular steric and electrostatic repulsion a larger coordination number of the metal center leads to a lengthening of the M–N bonds. This strain also influences the distances between the metal ion and the neutral coligands. In distorted tetrahedral structures a widening of the N–M–N bond angles is observed. A remarkable difference is found for the complexes [(dme)$_2$Sr(NRR′)$_2$]: in the bis(trimethylsilyl)amide there is a *trans*-arrangement of the amide ions whereas for the *N*-isopropylanilide the *cis*-isomer is favored.

The substructures and coordination properties of the *N*-isopropylanilide ions are listed in Table 4. Magnesium-bound anilides show sums of angle at the nitrogen atoms close to 360° whereas for the heavier alkaline earth metals these values deviate from that for a planar arrangement. The C_{Ph}–N–C_{iPr} bond angles vary within a very small range and are slightly smaller than 120° due to the presence of a free electron pair (carrying the anionic charge) at the *sp*^{2}-hybridized nitrogen atom.

In general the M–N–C_{Ph} bond angles are significantly smaller than the angles to the isopropyl groups M–N–C_{iPr}. This finding is caused by electrostatic attraction between the metal ions and the *ipso*-carbon atoms C_{ipso} of the phenyl groups. The rather soft strontium atom can form strong bonds not only to rather hard Lewis bases such as ethers and amines, but also to the soft π systems of the phenyl groups, supported by back-donation of negative charge from the N atom into the phenyl ring leading to short N–C_{Ph} bonds and to rather small Sr–C_{ipso} distances. Whereas the magnesium derivatives are coordinatively saturated by the hard Lewis bases, the larger calcium atoms show an average Ca–C_{ipso} distance of 317.7 pm. In comparison to monomeric alkaline earth decamethyl metallocenes MCp*$_2$ (Mg–C 234.1, Ca–C 260.9, and Sr–C 275.0 pm [65]) the Ca–C_{ipso} values of [(thf)$_3$Ca{N(Ph)*i*Pr}$_2$] are 21.8 % larger than those of decamethylcalcocene. Despite a larger radius of Sr^{2+} (132 pm [48]) as compared to Ca^{2+} (114 pm [48]), smaller Sr–C_{ipso} distances are found, and a short contact is often also real-

Compound	M–N–C$_{Ph}$	M–N–C$_{iPr}$	C$_{Ph}$–N–C$_{iPr}$	ΣN	M–C$_{ipso}$	Ref.
[(thf)$_2$Mg{N(Ph)iPr}$_2$]	117.0(1)	126.0(1)	116.3(1)	359.3	–	this work
	122.8(1)	122.4(1)	114.8(1)	360.0	–	
[(tmeda)(nBu)Mg{N(Ph)iPr}]	120.9(1)	123.1(1)	115.8(2)	359.8	–	this work
[(dme)Mg{N(Ph)iPr}$_2$]	117.5(2)	126.6(2)	115.9(2)	360.0	–	this work
	116.7(2)	125.9(2)	116.1(2)	358.7	–	
	116.4(2)	126.8(2)	115.2(2)	358.4	–	
	114.4(2)	129.0(2)	116.5(2)	359.9	–	
	115.5(2)	128.8(2)	115.5(2)	359.8	–	
	116.6(2)	127.1(2)	116.0(2)	359.7	–	
[(thf)$_3$Ca{N(Ph)iPr}$_2$]	115.3(2)	123.1(2)	117.0(2)	355.4	318.4(3)	[44]
	115.8(2)	122.6(2)	116.7(2)	355.1	319.6(3)	
	115.1(2)	125.1(2)	116.8(2)	357.0	317.1(3)	
	113.7(2)	124.7(2)	117.3(3)	355.7	315.8(3)	
[(thf)$_4$Sr{N(Ph)iPr}$_2$]	122.1(2)	123.0(2)	114.2(3)	359.3	349.2(3)	this work
	101.7(2)	131.7(2)	116.7(3)	350.1	314.0(3)	
[(dme)$_2$Sr{N(Ph)iPr}$_2$]	106.4(2)	129.2(2)	116.9(2)	352.5	318.6(3)	this work
	107.5(2)	126.9(2)	118.0(3)	352.4	321.1(3)	
	109.2(2)	126.9(2)	117.2(3)	353.3	324.4(3)	
	106.0(2)	126.6(2)	117.1(2)	349.7	317.8(3)	
[(tmeda)(thf)Sr{N(Ph)iPr}$_2$]	98.4(2)	127.2(2)	117.4(3)	343.0	303.6(3)	this work
	104.3(2)	126.0(2)	117.6(3)	347.9	312.5(4)	
[(pmdeta)Sr{N(Ph)iPr}$_2$]	106.3(3)	131.7(3)	116.9(4)	354.9	317.5(4)	this work
	114.7(3)	127.9(3)	116.5(4)	359.1	332.6(5)	

Table 4. Coordination behavior of the *N*-isopropylanilide ions bound terminally to the alkaline earth metals magnesium, calcium, and strontium (abbreviations of coligands see Table 3).

ized to one *ortho*-carbon atom. The smallest value of 303.6 pm (observed in [(tmeda)(thf)Sr{N(Ph)iPr}$_2$]) is only 10.2 % larger than the Sr–C bond lengths in decamethylstrontocene. These additional interactions between the metal ions and the phenyl groups saturate the coordination spheres of the metals and stabilize monomeric complexes. The isoelectronic nature of N and CH justifies a comparison with benzylstrontium derivatives. A similar coordination behavior as observed for the anilides was also found for [(thf)$_2$Sr{CH(SiMe$_3$)C$_6$H$_4$-2-NMe$_2$}$_2$] with short Sr–C$_{ipso}$ and Sr–C$_{ortho}$ bond lengths between 286.2 and 301.9 pm [66].

Contrary to this coordination behavior the amide ions favor bridging positions with hard metal ions like Mg^{2+} (radius 86 pm [48]). Therefore, the tetramethyltetrahydrofuran ligand is liberated during recrystallization of [(Me$_4$thf)Mg{N(Ph)iPr}$_2$] (**8**) in hydrocarbons yielding dinuclear [iPr(Ph)N-Mg{μ-N(Ph)iPr}]$_2$ (**9**). The different coordination behavior of the terminal and bridging anilide ions clarifies the influence of the coordination number at the nitrogen atom on the M–N and N–C bond lengths. The molecular structure and numbering scheme of **9** is depicted in Fig. 7. Again this molecular structure is similar to that of the dimeric [(Me$_3$Si)$_2$N-Mg{μ-N(SiMe$_3$)$_2$}]$_2$ with mean Mg–N$_t$ and Mg–N$_{br}$ bond lengths of 197.5 and 215.1 pm, respectively [67]. Slightly smaller intramolecular strain

in **9** leads to marginally smaller bond lengths (average Mg–N$_t$ 197.0, Mg–N$_{br}$ 210.0 pm). In a covalent bonding model sp^3 hybridization of the bridging nitrogen atoms N1C and N1D can be assumed which hinders charge back-donation from the nitrogen atom into the phenyl ring. This situation causes a significant elongation of the N–C$_{Ph}$ bond (average N$_t$–C$_{Ph}$ 137.8, N$_t$–C$_{iPr}$ 146.4 pm; N$_{br}$–C$_{Ph}$ 143.5, N$_{br}$–C$_{iPr}$ 149.7 pm), but the N$_{br}$–C$_{iPr}$ distance also is lengthened due to increased steric strain at a tetracoordinate nitrogen atom leading to smaller C–N–C bond angles at the bridging N atoms (mean C–N$_t$–C 117.3°, C–N$_{br}$–C 113.9°).

The molecular structure and numbering scheme of [(tmeda)(nBu)Mg{N(Ph)iPr}] (**6**) is depicted in Fig. 8. The tetracoordinate magnesium center is in a distorted tetrahedral environment with Mg–N and Mg–C bond lengths in common ranges [68 – 71] (Mg1–C10 214.9(2), Mg1–N1 204.7(2), Mg1–N2 225.4(2), and Mg1–N3 222.9(2) pm). As expected, the Mg–N bonds to the negatively charged amide ions are much shorter than those to the neutral tmeda base.

In summary, the *N*-isopropylanilide ion contains a sp^2-hybridized nitrogen atom with significant charge delocalization from the N atom into the phenyl ring. If this amide ion is bound to a metal atom with a rather high electronegativity such as Mg, a significant covalent bond character leads to a planar environment of the nitrogen atom. The alkaline earth metal atom it-
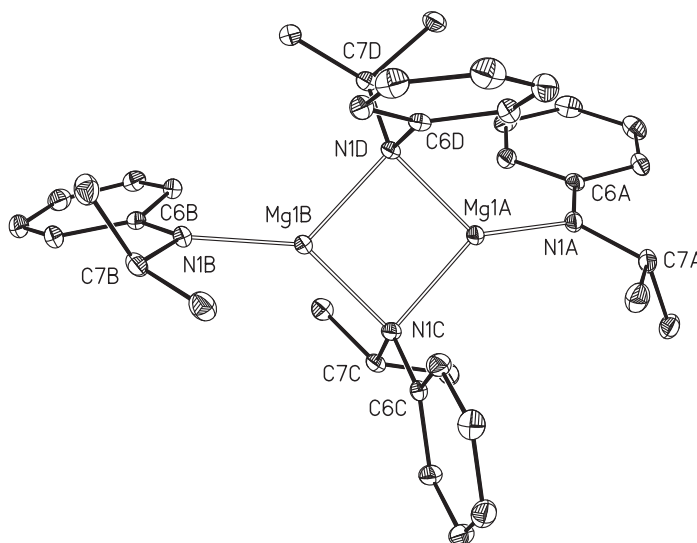
Fig. 7. Molecular structure and numbering scheme of dimeric [Mg{N(Ph)*i*Pr}$_2$]$_2$ (**9**). The asymmetric unit contains the whole molecule, the magnesium atoms are distinguished by the letters "A" and "B", the anilido substituents by the letters "A" and "B" for terminal and by "C" and "D" for bridging ions. H atoms are omitted.
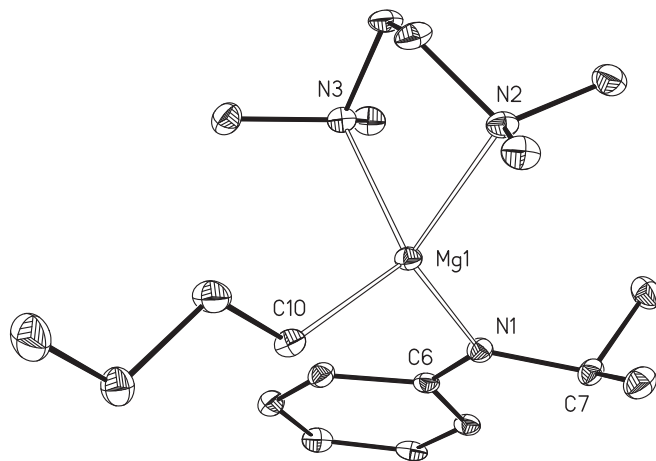

Fig. 8. Molecular structure and numbering scheme of heteroleptic [(tmeda)(*n*Bu)Mg{N(Ph)*i*Pr}] (**6**). The ellipsoids represent a probability of 40 %, H atoms are omitted.

self favors a (distorted) tetrahedral coordination sphere suggesting sp^3 hybridization. By contrast, in highly ionic complexes attractive electrostatic forces dominate the structures leading to small M–N distances, but the isopropyl groups turn towards coordination gaps thus yielding to steric requirements. In addition, the coordination number of the metal atoms in these ionic complexes usually exceeds four in order to maximize electrostatic attractions, limited only by intramolecular steric strain. Due to the fact that covalent bonding contributions can be neglected, any pyramidalization of the coordination geometry of the N atom is mainly a consequence of intramolecular steric repulsion between all ligands.

Conclusion

The *N*-isopropylanilides of magnesium are accessible with good yields *via* metalation of the secondary amine with commercially available dibutylmagnesium.

In the presence of TMEDA the heteroleptic intermediate [(tmeda)(*n*Bu)Mg{N(Ph)*i*Pr}] is obtained. In the presence of chelate bases such as 1,2-dimethoxyethane or TMEDA, the corresponding complexes are formed. Due to the lack of "simple" dialkyl- and diarylstrontium precursors [72 – 77] an alternative procedure had to be applied for the strontium analogs. In a metathetical approach, potassium *N*-isopropylanilide was reacted with strontium diiodide in THF because the KI by-product is extremely sparingly soluble in this ether. For this strategy it is mandatory to obey to the exact stoichiometry in order to avoid formation of strontiates such as $K_2Sr\{N(Ph)iPr\}_4$ (excess of potassium anilide) [46] or of iodide-containing products (excess of SrI_2). In a second reaction step the thf ligands can (at least partially) be exchanged by multidentate Lewis bases such as dme, tmeda, and pmdeta yielding monomeric complexes with penta- or hexacoordinate strontium centers.

From all these compounds, tetrahydrofuran complexes of the type $[(thf)_nM\{N(Ph)iPr\}_2]$ can be isolated with *n* depending on the size of the metal center (Mg: $n = 2$, Ca: $n = 3$, Sr: $n = 4$). The thf ligands can be exchanged by multidentate ligands such as dme, tmeda, and for strontium also by pmdeta. Upon dissolving the compounds in tetrahydrofuran, the thf complexes are reformed due to the large excess of the solvent molecules. For magnesium, 2,2,5,5-tetramethyltetrahydrofuran is an exception. This bulky ether forms a complex of the type $[(Me_4thf)Mg\{N(Ph)iPr\}_2]$ which loses this Lewis base already in hydrocarbon solvents yielding dimeric $[Mg\{N(Ph)iPr\}_2]_2$ with two terminal and two bridging anilide ions and three-coordinate alkaline earth metal atoms.

The magnesium-bound *N*-isopropylanilide ions show planar coordination at the nitrogen atom with significant back-bonding from the lone pair at N into the π system of the phenyl group. This fact leads to rather short N–C_{Ph} bonds. Due to the fact that the magnesium atoms are located in the anilido plane, no direct interaction between this alkaline earth metal atom and the π system of the phenyl ring is possible. In the *N*-isopropylanilides of strontium the interaction of the heavy alkaline earth metal with the *ipso*- and *ortho*-carbon atoms of the phenyl fragment leads to significantly different proximal N–C_{Ph} and distal N–C_{iPr} bond angles. In addition, and as a consequence of these π interactions, a slight pyramidalization occurs at

the nitrogen atoms. These structural features are also observed in isoelectronic benzyl derivatives and are far less pronounced in the calcium derivatives. Thus, strontium ions exhibit characteristic properties of a soft Lewis acid whereas the hard magnesium ions are less electropositive favoring Mg–N bonds with significant covalent character. Calcium also represents a Lewis acidic metal ion with the tendency to interact with the π system of the anilide ion, but this behavior is less pronounced than for the heavier alkaline earth metal.

Experimental

General remarks

All manipulations were carried out under anaerobic conditions in an argon or nitrogen atmosphere using standard Schlenk techniques. The solvents were dried according to common procedures and distilled in an argon or nitrogen atmosphere; deuterated solvents were dried over sodium, degassed, and saturated with argon or nitrogen. The yields given are not optimized. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker AC 200, AC 400, or AC 600 spectrometers. Chemical shifts are reported in parts per million. The residual signals of [D$_8$]THF were used as internal standards for the ^1H and ^{13}C NMR spectra. All compounds were very sensitive towards moisture and air and therefore, we were unable to obtain reliable data from the elemental analysis. None of these alkaline earth metal complexes showed a sharp melting point due to loss of coligand and decomposition reactions upon heating.

Synthesis of [(thf)$_4$Sr{N(Ph)iPr}$_2$] (**1**)

Solid (thf)$_4$SrI$_2$ (2 g, 3.61 mmol, thf content controlled by potentiometric iodide determination) was dissolved in 34 mL of THF and added to a stirred solution of [KN(Ph)*i*Pr] (1.25 g, 7.21 mmol) in 10 mL of THF. After 3 h of stirring at ambient conditions, all solids (KI) were removed by filtration. 5 mL of this solution was decanted, the volume reduced to 2.5 mL and this mother liquor stored at –60 °C. This procedure yielded colorless crystals of [(thf)$_4$Sr{N(Ph)*i*Pr}$_2$]. – ^1H NMR ([D$_8$]THF): $\delta = 6.76$ (4H, t, b, *m*-H), 6.07 (4H, d, b, *o*-H), 5.82 (2H, t, b, *p*-H), 3.58 (m, THF), 3.45 (2H, hept, $^3J_{H,H} = 6$ Hz, CH), 1.72 (m, THF), 1.09 (12H, d, $^3J_{H,H} = 6.2$ Hz, CH$_3$). – $^{13}C\{^1H\}$ NMR ([D$_8$]THF): $\delta = 160.1$ (*i*-C), 130.1 (*m*-C), 111.9 (*o*-C), 107,3 (*p*-C), 68.2 (THF); 47.7 (CH), 26.3 (THF), 24.8 (CH$_3$).

Synthesis of [(dme)$_2$Sr{N(Ph)iPr}$_2$] (**2**)

Solid [(thf)$_4$Sr{N(Ph)*i*Pr}$_2$] (160 mg, 0.24 mmol) was dissolved in 1 mL of DME and stored at –20 °C. This procedure led to formation of crystalline colorless

[(dme)$_2$Sr{N(Ph)iPr}$_2$]. – ^{1}H NMR ([D$_8$]THF): δ = 6.78 (4H, t, $^3J_{H,H}$ = 7.2 Hz, *m*-H), 6.07 (4H, d, $^3J_{H,H}$ = 7.6 Hz, *o*-H), 5.85 (2H, t, $^3J_{H,H}$ = 6.4 Hz, *p*-H), 3.47 (2H, hept, $^3J_{H,H}$ = 6 Hz, CH), 3.44 (8H, s, CH$_2$ (dme)), 3.28 (12H, s, CH$_3$ (dme)), 1.14 (12H, d, $^3J_{H,H}$ = 6.2 Hz, CH$_3$). – ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 160.1 (*i*-C), 130.2 (*m*-C), 111.9 (*o*-C), 107.3 (*p*-C), 72.6 (CH$_2$ (dme)), 58.8 (CH$_3$ (dme)), 47.7 (CH), 24.8 (CH$_3$). – IR (cm^{-1}): ν = 1584 s, 1538 w, 1485 s, 1458 w, 1365 w, 1343 m, 1319 s, 1303 s, 1271 w, 1261 w, 1248 w, 1211 w, 1183 m, 1161 w, 1133 w, 1112 m, 1060 vs, 1024 s, 1010 m, 983 s, 958 s, 855 s, 805 m, 739 s, 697 s, 608 m, 561 w, 536 m, 487 s, 450 w, 407 w.

Synthesis of [(tmeda)(thf)Sr{N(Ph)iPr}$_2$] (3)

Solid [(thf)$_4$Sr{N(Ph)iPr}$_2$] (160 mg, 0.24 mmol) was mixed with 2 mL of TMEDA. Due to the fact that a turbid reaction mixture was formed, additional 0.5 mL of THF had to be added for full dissolution. Storage at –20 °C yielded colorless crystals of **3**. – ^{1}H NMR ([D$_8$]THF): δ = 6.77 (4H, t, $^3J_{H,H}$ = 7.4 Hz, *m*-H), 6.06 (4H, d, $^3J_{H,H}$ = 7.8 Hz, *o*-H), 5.84 (2H, t, $^3J_{H,H}$ = 6.6 Hz, *p*-H), 3.61 (m, THF), 3.46 (2H, hept, $^3J_{H,H}$ = 6 Hz, CH), 2.30 (4H, s, CH$_2$ (tmeda)), 2.15 (12H, s, CH$_3$ (tmeda)), 1.77 (m, THF), 1.13 (12H, d, $^3J_{H,H}$ = 6 Hz, CH$_3$). – ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 160.1 (*i*-C), 130.2 (*m*-C), 111.9 (*o*-C), 107.4 (*p*-C), 68.1 (THF), 58.8 (CH$_2$ (tmeda)), 47.8 (CH), 46 (CH$_3$ (tmeda)), 26.3 (THF), 24.8 (CH$_3$). – IR (cm^{-1}): ν = 1589 s, 1506 sh, 1482 vs, 1382 w, 1363 w, 1307 m, 1278 vs, 1180 m, 1160 m, 1131 m, 1075 w, 1030 m, 984 m, 958 m, 867 w, 831 w, 798 m, 748 vs, 709 sh, 693 vs, 605 m, 497 m, 461 w.

Synthesis of [(pmdeta)Sr{N(Ph)iPr}$_2$] (4)

Solid [(thf)$_4$Sr{N(Ph)iPr}$_2$] (160 mg, 0.24 mmol) was dissolved in 2 mL of PMDETA and 0.5 mL of THF and warmed to 60 °C until a clear solution was formed. During cooling to room temperature a colorless solid precipitated which was collected on a frit. Storage of the mother liquor at −20 °C gave another crop of crystals suitable for X-ray structure analysis. – ^{1}H NMR ([D$_8$]THF): δ = 6.77 (4H, t, $^3J_{H,H}$ = 7.6 Hz, *m*-H), 6.07 (4H, d, $^3J_{H,H}$ = 8 Hz, *o*-H), 5.85 (2H, t, $^3J_{H,H}$ = 7 Hz, *p*-H), 3.46 (2H, hept, $^3J_{H,H}$ = 6 Hz, CH), 2.37 (8H, m, CH$_2$ (pmdeta)), 2.19 (3H, s, CH$_3$ (pmdeta)), 2.16 (12H, s, CH$_3$ (pmdeta)), 1.13 (12H, d, $^3J_{H,H}$ = 6 Hz, CH$_3$). – ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 160 (*i*-C), 130 (*m*-C), 111.9 (*o*-C), 107.4 (*p*-C), 59 (CH$_2$ (pmdeta)), 57.5 (CH$_2$ (pmdeta)), 48.0 (CH), 46.4 (CH$_3$ (pmdeta)), 43.3 (CH$_3$ (pmdeta)), 24.8 (CH$_3$).

Synthesis of [(thf)$_2$Mg{N(Ph)iPr}$_2$] (5)

Mg(nBu)$_2$ (2.8 mmol, 2.8 mL of a 1 M *n*-pentane solution) was added to a solution of *N*-isopropylaniline (0.71 mL, 5.6 mmol) in 40 mL of THF at 0 °C. The solution was stirred and warmed to r. t. while evolution of a gas was observed. After stirring for 16 h at r. t. the volume of the solution was reduced to 6 mL. Colorless crystals precipitated overnight at r. t. yield: 881 mg (2.02 mmol, 72 %). – ^{1}H NMR ([D$_8$]THF): δ = 1.20 (s, 12H, -CH(C*H$_3$*)$_2$), 3.51 (m, 2H, -C*H*(CH$_3$)$_2$), 6.02 (d, 4H, *p*-C*H*), 6.28 (s, 4H, *o*-C*H*), 6.79 – 6.8 (d, 4H, *m*-C*H*). – ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 25.1 (-CH(*C*H$_3$)$_2$), 48.5 (-*C*H(CH$_3$)$_2$), 110.5 (*p*-C), 114.4 (*o*-C), 129.4 (*m*-C), 159.2 (*i*-C). – IR (cm^{-1}): ν = 1584 s, 1548 m, 1491 s, 1489 s, 1458 m, 1357 m, 1335 w, 1323 m, 1303 vs, 1277 s, 1190 m, 1167 s, 1146 m, 1120 w, 1083 w, 1030 sh, 1014 s, 988 m, 967 m, 919 w, 850 s, 839 m, 747 vs, 696 vs, 624 m, 580 w, 544 w, 531 w, 504 m, 430 sh, 418 m. – MS (Micro-ESI): *m/z*(%) = 587 (5) [M+H–2thf]$_2^+$, 343 (24) [M+H–Mg–thf]$^+$, 271 (100) [iPrPhN]$_2^+$, 136 (30) [iPrPhN]$^+$, 94 (13) [NPh]$^+$.

Synthesis of [(tmeda)(nBu)Mg{N(Ph)iPr}] (6) and [(tmeda)Mg{N(Ph)iPr}$_2$] (7)

N-Isopropylaniline (813 mg, 6 mmol) was added at r. t. to 3 mL of a 1 M solution of Mg(nBu)$_2$ in *n*-pentane containing 370 mg of TMEDA (3.2 mmol) and 5 mL of Et$_2$O. Formation of a gas, increase of temperature and formation of a colorless precipitate were observed. The mixture was stirred for 68 h at r. t. The solid material was collected and shown to consist of pure microcrystalline **7**, yield: 589 mg, 1.4 mmol, 48 %. The mother liquor contained heteroleptic **6**, and cooling of this mother liquor to 5 °C gave colorless crystals of **6**. Yield: 179 mg (0.54 mmol, 18 %).

*Physical data of **6***: ^{1}H NMR ([D$_8$]THF): δ = −0.53 (t, 2H, $^3J_{H,H}$ = 8.4 Hz, Mg-C*H$_2$*-), 0.85 (m, 3H, *n*Bu -C*H$_3$*), 1.16 (d, 6H, $^3J_{H,H}$ = 6.4 Hz, -CH(C*H$_3$*)$_2$), 1.27 (m, 2H, *n*Bu -C*H$_2$*-), 1.53 (m, 2H, *n*Bu -C*H$_2$*-) 2.16 (s, 12H, tmeda -C*H$_3$*), 2.32 (s, 4H, tmeda -C*H$_2$*-), 3.38 – 3.46 (m, 1H, -C*H*(CH$_3$)$_2$), 5.96 (t, 1H, $^3J_{H,H}$ = 7.0 Hz, *p*-C*H*), 6.24 (d, 2H, $^3J_{H,H}$ = 8.4 Hz, *o*-C*H*), 6.77 (t, 2H, $^3J_{H,H}$ = 7.8 Hz, *m*-C*H*). – ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 9.7 (Mg-*C*H$_2$-), 15.6 (t, *n*Bu -*C*H$_3$), 25.3 (-CH(*C*H$_3$)$_2$), 32,8 (*n*Bu -*C*H$_2$-), 34.0 (*n*Bu -*C*H$_2$-), 46.3 (tmeda -*C*H$_3$), 48.3 (-*C*H(CH$_3$)$_2$), 58.9 (tmeda -*C*H$_2$-), 109.5 (*p*-C), 113.7 (*o*-C), 129.3 (*m*-C), 160.0 (*i*-C). – IR (cm^{-1}): ν = 1597 s, 1547 w, 1488 s, 1463 s, 1360 w, 1350 w, 1311 vs, 1277 s, 1188 m, 1162 m, 1144 m, 1121 w, 1021 s, 995 m, 988 m, 966 m, 949 s, 830 m, 794 m, 744 vs, 693 s, 620 m, 584 m, 541 m, 532 sh, 502 m, 479 s, 441 m. – MS (DEI): *m/z*(%) = 584 (36) [M+H–tmeda]$_2^+$, 274 (55) [iPrPh*n*Bu]$^+$, 120 (53) [iPrPh]$^+$, 117 (100) [TMEDA]$^+$, 58 (83) [*n*Bu]$^+$, 42 (58) [iPr]$^+$.

*Physical data of **7***: ^{1}H NMR ([D$_8$]THF): δ = 1.25 (d, 12H, $^3J_{H,H}$ = 6.4 Hz, -CH(C*H$_3$*)$_2$), 2.15 (s, 12H, tmeda -C*H$_3$*), 2.31 (s, 4H, tmeda -C*H$_2$*-), 3.52 – 3.59 (m, 2H,

-C*H*(CH$_3$)$_2$), 6.06 (t, 2H, $^3J_{H,H}$ = 7 Hz, *p*-C*H*), 6.33 (d, 4H, $^3J_{H,H}$ = 8.4 Hz, *o*-C*H*), 6.84 (t, 4H, $^3J_{H,H}$ = 8 Hz, *m*-C*H*). – ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 25.1 (-CH(*C*H$_3$)$_2$), 46.3 (tmeda -*C*H$_3$), 48.5 (-*C*H(CH$_3$)$_2$), 59.0 (tmeda -*C*H$_2$-), 110.5 (*p*-C), 114.4 (*o*-C), 129.4 (*m*-C), 159.2 (*i*-C). – IR (cm^{-1}): ν = 1597 s, 1579 m, 1550 w, 1489 s, 1471 m, 1459 sh, 1376 w, 1359 w, 1353 w, 1300 vs, 1278 s, 1196 s, 1172 m, 1145 m, 1118 w, 1068 w, 1032 w, 1018 w, 999 sh, 989 m, 972 m, 941 m, 922 w, 832 s, 795 s, 742 s, 688 vs, 621 m, 594 w, 542 w, 497 s, 473 sh, 443 m. – MS (DEI): *m/z*(%) = 268 (16) [*i*PrPhN]$_2^+$, 135 (11) [*i*PrPhN]$^+$, 120 (42) [*i*PrPh]$^+$, 77 (23) [Ph]$^+$, 43 (100) [*i*Pr]$^+$, 29 (95) [Me]$_2^+$.

Synthesis of [(Me$_4$thf)Mg{N(Ph)iPr}$_2$] (*8*)

Mg(*n*Bu)$_2$ (2.45 mmol, 2.45 mL of a 1 M *n*-pentane solution) was added to a solution of *N*-isopropylaniline (675 mg, 4.95 mmol) in Me$_4$THF (632 mg, 4.9 mmol) at 0 °C. The pale-yellow solution was stirred and warmed to r. t. while formation of a gas and precipitation of solid **8** were observed. Cooling of this solution gave an additional crop of crystals of **8**. Yield: 740 mg (1.75 mmol, 71.5 %). – ^{1}H NMR ([D$_8$]THF): δ = 1.16 (s, 12H, Me$_4$THF -C*H$_3$*), 1.25 (d, 12H, $^3J_{H,H}$ = 6 Hz, -CH(C*H$_3$*)$_2$), 1.81 (s, 4H, Me$_4$THF -C*H$_2$*-), 3.52–3.59 (m, 2H, -C*H*(CH$_3$)$_2$), 6,07 (t, 2H, $^3J_{H,H}$ = 6.8 Hz, *p*-C*H*), 6.33 (d, 4H, $^3J_{H,H}$ = 8.4 Hz, *o*-C*H*), 6.84 (t, 4H, $^3J_{H,H}$ = 7.6 Hz, *m*-C*H*). – ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 25.1 (-CH(*C*H$_3$)$_2$), 30.2 (Me$_4$THF -*C*H$_3$), 39.6 (Me$_4$THF -*C*H$_2$-), 48.5 (-*C*H(CH$_3$)$_2$), 81.2 (Me$_4$THF (CH$_3$)$_2$ $-$ *C*), 110.5 (*p*-C), 114.4 (*o*-C), 129.4 (*m*-C), 159.2 (*i*-C). – ^{13}C{^{1}H} NMR ([D$_6$]benzene): δ = 24.5 and 25.3 (-CH(*C*H$_3$)$_2$), 30.2 (Me$_4$THF -*C*H$_3$), 39.6 (Me$_4$THF -*C*H$_2$-), 46.0 and 49.9 (-*C*H(CH$_3$)$_2$), 81.2 (Me$_4$THF (CH$_3$)$_2$ $-$ *C*), 113.1 and 114.4 (*o*-C), 123.1 and 123.9 (*p*-C), 130.4 and 131.1 (*m*-C), 150.1 and 157.4 (*i*-C) (complete loss of Me$_4$THF in [D$_6$]benzene and quantitative formation of [Mg{N(Ph)iPr}$_2$]$_2$ (**9**) is observed). – IR (cm^{-1}): ν = 1583 s, 1554 w, 1486 vs, 1459 m, 1374 w, 1345 w, 1302 vs, 1276 s, 1221 w, 1190 m, 1163 w, 1149 w, 1124 m, 1082 w, 1029 w, 987 w, 958 w, 924 w, 854 m, 829 sh, 813 s, 782 w, 745 vs, 688 vs, 638 m, 540 w, 499 m, 430 m, 412 m. – MS (DEI): *m/z*(%) = 585 (43) [M+H–Me$_4$thf]$_2^+$, 158 (27) [M+H–Me$_4$thf]$^+$, 135 (100) [*i*PrPhN]$^+$, 91 (9) [NPh]$^+$, 77 (16) [Ph]$^+$, 43 (38) [*i*Pr]$^+$.

Synthesis of [Mg{N(Ph)iPr}$_2$]$_2$ (*9*)

Recrystallization of **8** from *n*-heptane yielded quantitatively colorless **9**. – ^{1}H NMR ([D$_6$]benzene): δ = 0.99 (d, 12H, CH(C*H$_3$*)$_2$, $^3J_{H,H}$ = 6.0 Hz), 1.17 (d, 12H, $^3J_{H,H}$ = 5.4 Hz, -CH(C*H$_3$*)$_2$), 3.60 (m, 2H, -C*H*(CH$_3$)$_2$), 6.54 (d, 4H, $^3J_{H,H}$ = 7.8 Hz, *o*-C*H*), 6.67 (t, 2H, $^3J_{H,H}$ = 7.2 Hz, *p*-C*H*), 6.72 (d, 4H, $^3J_{H,H}$ = 7.2 Hz, *o*-C*H*), 6.74 (t, 2H,

$^3J_{H,H}$ = 7.2 Hz, *p*-C*H*), 6.95 (t, 4H, $^3J_{H,H}$ = 6.9 Hz, *m*-C*H*), 7.28 (t, 4H, $^3J_{H,H}$ = 7.2 Hz, *m*-C*H*). – ^{13}C{^{1}H} NMR ([D$_6$]benzene): δ = 157.4 and 150.1 (*i*-C), 131.1 and 130.4 (*m*-C), 123.9 and 123.2 (*p*-C), 114.5 and 113.2 (*o*-C), 49.9 and 46.1 (*C*HMe$_2$), 25.4 and 24.5 (CH(*C*H$_3$)$_2$). – IR (cm^{-1}): ν = 1585 s, 1558 m, 1486 vs, 1463 m, 1386 w, 1373 w, 1360 w, 1343 m, 1302 vs, 1277 s, 1261 m, 1224 s, 1185 s, 1162 s, 1144 m, 1129 m, 1114 s, 1079 m, 1030 s, 989 m, 970 s, 911 w, 855 s, 844 m, 812 vs, 759 s, 744 vs, 715 m, 691 vs, 641 m, 620 w, 576 w, 503 s, 453 w, 430 m.

Synthesis of [(dme)Mg{N(Ph)iPr}$_2$] (*10*)

Mg(*n*Bu)$_2$ (3 mmol, 3 mL of a 1 M *n*-pentane solution) was added to a solution of *N*-isopropylaniline (0.8 mL, 6 mmol) in 8 mL of DME at 0 °C. The solution was stirred and warmed to r. t. while evolution of a gas was observed. After stirring for 67 h at r. t. the volume of the solution was reduced to 6.5 mL. Colorless crystals precipitated overnight at 5 °C. Crystals were isolated by decanting the solution and removing all volatiles *in vacuo*. Yield: 953 mg (2.49 mmol, 83 %). – ^{1}H NMR ([D$_8$]THF): δ = 1.25 (d, 12H, $^3J_{H,H}$ = 6.4 Hz, -CH(C*H$_3$*)$_2$), 3.27 (s, 6H, dme -C*H$_3$*), 3.43 (s, 4H, dme -C*H$_2$*-), 3.55 (m, 2H, -C*H*(CH$_3$)$_2$), 6.06 (t, 2H, $^3J_{H,H}$ = 7 Hz, *p*-C*H*), 6.33 (d, 4H, $^3J_{H,H}$ = 8.0 Hz, *o*-C*H*), 6.84 (t, 4H, $^3J_{H,H}$ = 7.8 Hz, *m*-C*H*). – ^{13}C{^{1}H} NMR ([D$_8$]THF, 300 K): δ = 25.1 (-CH(*C*H$_3$)$_2$), 48.5 (-*C*H(CH$_3$)$_2$), 59.0 (dme -*C*H$_3$), 72,8 (dme -*C*H$_2$-), 110.5 (*p*-C), 114.4 (*o*-C), 129.4 (*m*-C), 159.2 (*i*-C). – IR (cm^{-1}): ν = 1598 s, 1581 s, 1550 m, 1488 vs, 1457 m, 1363 w, 1353 w, 1302 vs, 1278 s, 1261 sh, 1239 w, 1190 m, 1167 m, 1153 m, 1143 w, 1086 s, 1051 vs, 1032 sh, 1017 sh, 987 m, 968 s, 867 m, 836 s, 801 m, 742 vs, 687 s, 625 m, 539 w, 504 m, 411 m. – MS (DEI): *m/z* (%) = 584 (46) [2M–dme]$^+$, 450 (13) [2M–dme–N*i*PrPh]$^+$, 382 (2) [M]$^+$, 315 (8) [2M–dme–2*i*PrPhN]$^+$, 158 (48) [MgN*i*PrPh]$^+$, 135 (100) [*i*PrPhN]$^+$, 120 (100) [*i*PrPh]$^+$, 91 (58) [DME]$^+$, 77 (55) [Ph]$^+$, 45 (100) [*i*Pr]$^+$.

Crystal structure determinations

The intensity data for the compounds was collected on a Nonius KappaCCD diffractometer using graphite-monochromatized MoK_α radiation. Data were corrected for Lorentz and polarization effects but not for absorption [78, 79]. The structures were solved by Direct Methods (SHELXS [80]) and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97 [81]). All hydrogen atoms bound in compound **6** were located by difference Fourier syntheses and refined isotropically. The other hydrogen atoms were included at calculated positions with fixed displacement parameters. All non-hydrogen atoms were refined anisotropically. XP (Siemens Analytical X-ray Instru-

Compound	**1**	**2**	**3**	**4**
Formula	$C_{34}H_{56}N_2O_4Sr$	$C_{26}H_{44}N_2O_4Sr$	$C_{28}H_{48}N_4OSr$	$C_{27}H_{47}N_5Sr$
M_r	644.43	536.25	544.32	529.32
T, °C	−140(2)	−140(2)	−140(2)	−140(2)
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_12_12_1$	$P2_1/n$
a, Å	9.51850(10)	19.5832(3)	9.3081(2)	10.1354(2)
b, Å	18.6638(5)	17.0467(3)	14.8639(3)	19.0258(3)
c, Å	19.2891(4)	18.1278(2)	21.2496(5)	15.0031(4)
β, deg	98.570(1)	109.049(1)	90	93.261(1)
V, Å^3	3388.47(12)	5720.20(15)	2939.98(11)	2888.42(11)
Z	4	8	4	4
ρ, g cm^{-3}	1.26	1.25	1.23	1.22
μ, mm^{-1}	16.3	19.2	18.6	18.9
Measured data	19898	34524	17639	17482
Unique data / R_{int}	7738 / 0.0546	13108 / 0.0536	6690 / 0.0596	6610 / 0.0502
Data with $I > 2\sigma(I)$	5843	9615	5913	5127
R_1 [$I > 2\sigma(I)$]^a	0.0546	0.0500	0.0463	0.0636
wR_2 (on all F^2)^b	0.1071	0.0914	0.0936	0.1481
S^c	1.126	1.121	1.147	1.158
Res. dens., e Å^{-3}	0.637 / −0.737	0.372 / −0.349	0.488 / −0.484	1.383 / −0.799
Flack parameter x	–	–	−0.002(8)	–
CCDC No.	924051	924052	924053	924054

Table 5. Crystal data and refinement details for the X-ray structure determinations of compounds **1–6**, **9**, **10**.

Compound	**5**	**6**	**9**	**10**
Formula	$C_{26}H_{40}MgN_2O_2$	$C_{19}H_{37}MgN_3$	$C_{36}H_{48}Mg_2N_4$	$C_{22}H_{34}MgN_2O_2$
M_r	436.91	331.83	585.40	382.82
T, °C	−140(2)	−140(2)	−140(2)	−140(2)
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1$	$P2_1/c$	$P2_1$	$Fdd2$
a, Å	9.0167(2)	7.4197(2)	8.3784(2)	18.4746(6)
b, Å	13.4581(3)	16.0270(3)	17.1379(4)	92.395(3)
c, Å	10.4996(2)	17.7840(5)	11.4503(2)	15.5534(5)
β, deg	94.905(1)	101.051(1)	93.762(1)	90
V, Å^3	1269.44(5)	2075.58(9)	1640.59(6)	26549.1(15)
Z	2	4	2	48
ρ, g cm^{-3}	1.14	1.06	1.19	1.15
μ, mm^{-1}	0.9	0.9	1.0	1.0
Measured data	7911	12242	10083	25587
Unique data / R_{int}	5186 / 0.0179	4750 / 0.0552	6995 / 0.0190	12335 / 0.0318
Data with $I > 2\sigma(I)$	4975	3517	6733	11312
R_1 [$I > 2\sigma(I)$]^a	0.0377	0.0598	0.0346	0.0521
wR_2 (on all F^2)^b	0.0894	0.1285	0.0799	0.1151
S^c	1.083	1.087	1.082	1.153
Res. dens., e Å^{-3}	0.331 / −0.172	0.270 / −0.248	0.195 / −0.166	0.540 / −0.227
Flack parameter x	0.08(19)	–	0.13(14) (racemate)	0.45(18) (racemate)
CCDC No.	924055	924056	924057	924058

Table 5. contd.

^{a} $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$; ^{b} $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\text{Max}(F_o^2,0) + 2F_c^2)/3$; $S = \text{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

ments, Inc.) was used for structure representations. Crystallographic data as well as structure solution and refinement details are summarized in Table 5.

CCDC 924051 (**1**), CCDC 924052 (**2**), CCDC 924053 (**3**), CCDC 924054 (**4**), CCDC 924055 (**5**), CCDC 924056 (**6**), CCDC 924057 (**9**), and CCDC 924058 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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