Crystal structures and thermal properties of Ba(1,2,4-t-Bu$_3$C$_5$H$_2$)$_2$ and Sr(1,2,4-t-Bu$_3$C$_5$H$_2$)$_2$: Precursors for atomic layer deposition

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Abstract

Sterically hindered Lewis base free bis(1,2,4-tri-*tert*-butylcyclopentadienyl)strontium (**1**) and bis(1,2,4-tri-*tert*-butylcyclopentadie-nyl)barium (**2**) were synthesized using the common metathesis route and characterized with NMR, MS, TGA/SDTA and XRD. Compound **1** crystallized as a monomer with typical bent structure. Asymmetric unit contains two independent slightly different Sr(t-Bu$_3$C$_5$H$_2$)$_2$ molecules with Cp(centroid)–Sr–Cp(centroid) angles of 165.1° and 169.4°. Depending on the way of crystallization two polymorphs (**2a** and **2b**) were observed for Ba(t-Bu$_3$C$_5$H$_2$)$_2$. On sublimation Ba(t-Bu$_3$C$_5$H$_2$)$_2$ crystallizes as chains in which one methyl group of each Ba(t-Bu$_3$C$_5$H$_2$)$_2$ unit interacts with neighboring Ba(t-Bu$_3$C$_5$H$_2$)$_2$ unit's barium atom. Slow crystallization of waxy evaporation residue of toluene solution results in monoclinic crystals (**2b**) whose asymmetric unit contains four slightly different individual Ba(t-Bu$_3$C$_5$H$_2$)$_2$ molecules with Cp(centroid)–Ba–Cp(centroid) angles of 161.3–164.9°. Both compounds prepared are volatile, thermally stable and reactive and thus suitable precursors for atomic layer deposition of thin films.
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1. Introduction

Recently, metallocenes of the heavier alkaline-earth metals have found use as volatile precursors for thin film preparation by atomic layer deposition (ALD) [1–6]. Suitable ALD precursors are volatile and thermally stable compounds with high reactivity against the co-precursors like water, O$_3$ or H$_2$S. Some of the metallocenes meet these requirements well and indeed metallocenes of strontium and barium have been shown to be the first precursors that can be used to deposit oxides of these metals using water as an oxygen precursor [1]. While seeking for the most suitable precursors several cyclopentadienyl compounds of strontium and barium have been studied and tested in film deposition experiments. In these studies three well known strategies for making volatile metal complexes were utilized: (i) cyclopentadienyl ligands with sterically demand-ing substituents were used, (ii) coordination sphere of the cylopentadienyl complexes were filled using Lewis base ligands and (iii) donor functionalized cyclopentadienyl ligands were used. According to the studies [6,7] the best strategy is the first one *i.e.*, the best ALD precursors proved to be those with large sterically demanding bulky cyclopen-tadienyl ligands. Adducted cyclopentadienyl compounds tended to decompose or loose the adduct forming Lewis base when heated or sublimed. Compounds with donor functionalized cyclopentadienyl ligands showed good vac-uum sublimation behavior below some onset temperature at which they rapidly decomposed.

The first strategy has been tested with ligands like pen-tamethylcyclopentadienyl, tri-isopropylcyclopentadienyl and tri-*tert*-butylcyclopentadienyl. Among these ligands the largest ligand tri-*tert*-butylcyclopentadienyl was found to be the most suitable one. Complexes M(t-Bu$_3$C$_5$H$_2$)$_2$ (M = Sr, Ba) had the best thermal stability, and it was also noticed that this ligand can be prepared conveniently in one pot synthesis [8] with good yield. Some other recently

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reported strontocenes and barocenes with even more bulky ligands are $Ba(i\text{-}Pr_4C_5H_4)_2$ [9], $M(i\text{-}Pr_5C_5)_2$ [10], and $M((Me_3Si)_3C_5H_2)_2$ (M = Sr, Ba) [11]. These compounds have not been tested as possible ALD precursors. However, compared to $M(t\text{-}Bu_3C_5H_2)_2$ (M = Sr, Ba) lower overall synthesis yields (ligand + complex) and more complicated synthesis make $Ba(i\text{-}Pr_4C_5H_4)_2$ and $M(i\text{-}Pr_5C_5)_2$ (M = Sr, Ba) less attractive while $M((Me_3Si)_3C_5H_2)_2$ is unattractive because of the silicon which may contaminate the films deposited. $M(i\text{-}Pr_5C_5)_2$ (M = Sr, Ba) [10] may also be even too well shielded to have high reactivity against ALD co-precursors like water.

While our interest for the metallocenes of heavier alkaline earth metals originates from the possibility to use them as volatile precursors for thin film growth by ALD these compounds also have some interesting characteristic features. Most of the base free metallocenes of heavier alkaline-earth metals (Ca, Sr, Ba) have structures with non parallel rings in the solid state and as well in the gas phase [11–17]. The only reported exception, $Ba(i\text{-}Pr_5C_5)_2$ [10] with Cp(centroid)–M–Cp(centroid) angle of 180°, is a compound where the metal has sterically extremely crowded environment. In the light of previous studies in addition to steric factors Cp(centroid)–M–Cp(centroid) bending angles are also affected by electrostatic factors (electronic configuration) like polarization of the core electrons and d-orbital involvement [13,18,19]. Also attractive van der Waals forces between substituents has been proposed and studied [15,20,21]. Another feature of these metallocenes is the varying relative orientation of the cyclopentadienyl ligands [11,16] which is affected by both the ligands and the metals. Orientations with the lowest energy are of course evident but energy differences between different orientations are low.

In this paper, we are reporting crystal structures and thermal properties of two Lewis base free compounds, namely $Sr(t\text{-}Bu_3C_5H_2)_2$ and $Ba(t\text{-}Bu_3C_5H_2)_2$. These compounds and also Mg, Ca, Yb and Sm analogs were recently reported by Weber et al. [16] but structures for the base free compounds of Sr and Ba were not reported. Structures presented here are an addition to a series of bent structures observed for alkaline-earth metals. Depending on the way of crystallization two kinds of structures were observed for $Ba(t\text{-}Bu_3C_5H_2)_2$.

2. Results and discussion

Compounds were synthesized from anhydrous BaI_2 or $SrBr_2$ and $K(t\text{-}Bu_3C_5H_2)$ by using the common metathesis route. Synthesis resulted in THF solvated complexes $Sr(t\text{-}Bu_3C_5H_2)_2(THF)_x$ and $Ba(t\text{-}Bu_3C_5H_2)_2(THF)$. $Sr(t\text{-}Bu_3C_5H_2)_2(THF)_x$ lost THF under vacuum while desolvation of $Ba(t\text{-}Bu_3C_5H_2)_2(THF)$ was achieved by heating under vacuum, by sublimation of the complex or by refluxing the complex in toluene and slowly distilling the solvent off.

Mass spectra recorded for complexes **1**, **2a** and **2b** show molecular ions and peaks assigned for fragment ions.

Spectra are similar with spectra recorded for THF adducts [6,16]. Spectra stayed similar through the whole used temperature range of 50–370 °C and only small variation in the relative peak intensities was seen. These observations suggest that the compounds do not decompose at least not in large extent, and that their thermal stability is good. ^1H and ^{13}C NMR spectra for **1**, **2a** and **2b** in benzene-d_6 are like reported earlier [16].

$Sr(t\text{-}Bu_3C_5H_2)_2$, **1**, crystallizes in monoclinic space group $P2_1/c$ with cell dimensions of 19.428(4), 18.374(4), 19.706(4) Å with $\beta = 109.50(3)°$. Exactly the same crystals were obtained from sublimation and crystallization from hexane. The asymmetric unit of **1** has two independent molecules with slightly different angles and distances (Fig. 1). The two independent molecules have η^5-coordinated ligands and bent structure typical for alkaline-earth and rare-earth metallocenes [11–15]. Cyclopentadienyl rings in both molecules of the asymmetric unit are eclipsed (twist angles are in Table 1) and rotated approximately 72° compared to each other so that on the opening side of the sandwich wedge two t-butyl groups are parallel in the middle. All the above crystal and molecular characteristics of compound **1** are quite similar with previously characterized compounds $M(t\text{-}Bu_3C_5H_2)_2$ M = Mg, Ca, Sm, Yb [16], and Eu [22]. In fact the structure of **1** is an addition to this isostructural series.

Sr–Cp(centroid) distances are 2.522–2.523 Å and 2.526–2.533 Å, and Cp(centroid)-Sr–Cp(centroid) angles are
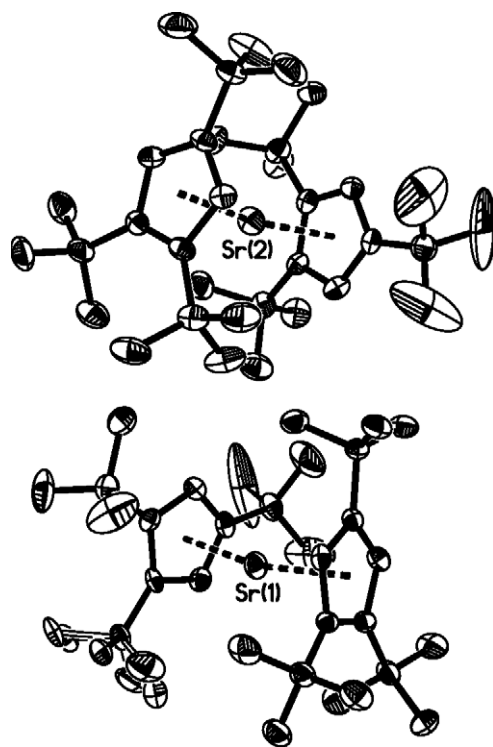

Fig. 1. Structure of $Sr(t\text{-}Bu_3C_5H_2)_2$ (**1**), asymmetric unit. Thermal ellipsoids are drawn on the 50% probability level. Hydrogen atoms are omitted for clarity. One t-butyl group is refined as disordered between two positions.

Table 1
Selected bond distances and angles for $Sr(t\text{-}Bu_3C_5H_2)_2$ and $Ba(t\text{-}Bu_3C_5H_2)_2$

| | 1 | | 2a | 2b | | | |
	Sr1	Sr2	Ba1	Ba1	Ba2	Ba3	Ba4
Ba–C(ring) (Å)	2.773(5)–2.829(5)	2.788(5)–2.816(5)	2.966(3)–3.046(3)	2.945(7)–2.984(7)	2.935(7)–2.997(7)	2.952(6)–2.995(6)	2.953(7)–2.981(7)
	2.777(5)–2.832(5)	2.797(5)–2.831(5)	2.977(3)–3.058(3)	2.934(7)–2.974(6)	2.938(7)–2.985(7)	2.923(7)–2.963(7)	2.948(7)–2.990(7)
Ba–Cp(centroid) (°)	2.522	2.526	2.749	2.707	2.716	2.710	2.714
	2.523	2.533	2.763	2.692	2.699	2.689	2.709
C(ring)–C(ring) (Å)	1.400(6)–1.460(6)	1.402(6)–1.433(6)	1.406(3)–1.450(4)	1.399(11)–1.448(11)	1.393(11)–1.432(10)	1.401(10)–1.437(11)	1.396(11)–1.433(10)
	1.396(6)–1.442(6)	1.402(6)–1.446(7)	1.409(4)–1.456(4)	1.403(10)–1.441(10)	1.400(10)–1.423(10)	1.383(10)–1.448(10)	1.402(10)–1.434(9)
C(ring)–C(CH$_3$)$_3$ (Å)	1.526(6)–1.546(7)	1.519(7)–1.566(6)	1.537(4)–1.554(4)	1.509(11)–1.539(10)	1.496(10)–1.553(11)	1.509(10)–1.542(11)	1.527(10)–1.567(10)
	1.538(6)–1.554(6)	1.531(6)–1.545(7)	1.534(4)–1.555(4)	1.508(11)–1.556(10)	1.502(11)–1.552(9)	1.521(10)–1.537(11)	1.512(10)–1.558(10)
Cp(centroid)–Ba–Cp(centroid) (°)	165.1	169.4	159.7	164.9	162.8	164.3	161.3
Twist angle (°)	0.8	1.7	4.1	6.3	1.9	5.8	3.1
Shortest M to CH$_3$ distance (Å)	3.325 (C13B)	3.417 (C47)	3.352 (C33)	3.443 (C133)	3.471 (C233)	3.451 (C334)	3.476 (C432)

The twist angle is measured as described by Weber et al. [16].

165.1° and 169.4°. Compared to the only other known structure of base free strontocene $Sr[(Me_3Si)_3C_5H_2)]_2$ (2.54 Å, 159.4°) [11] and also the barium analog these distances are shorter and the angles are larger. Compared to the Mg, Ca and Yb analogs [16] the opposite is true. Sm [16] and Eu [22] analogs have similar distances and angles with 1. These observations are as expected and are due to the ionic radius of strontium (1.18 Å at 6 coordination) [23] which falls between Yb^{2+} and Ba^{2+} and is about the same with Eu^{2+} and Sm^{2+}. Displacements of the t-butyl groups from the cyclopentadienyl ring planes are between 0.006 Å and 0.205 Å (=0.21–7.36°). The only obvious trend in the displacements seems to be that t-butyl groups on the sides of the sandwich wedge are least displaced. Three t-butyl groups in the asymmetric unit are clearly disordered but only one of these groups could be refined as disordered between two positions.

In contrast with $Sr(t\text{-}Bu_3C_5H_2)_2$, $Ba(t\text{-}Bu_3C_5H_2)_2$ crystallizes either in orthorhombic Pbca (2a) or in monoclinic $P\,2_1/c$ (2b) space group (Table 2) depending on the way of crystallization. Orthorhombic crystals, 2a, were obtained by sublimation of the compound while the monoclinic pseudo orthorhombic crystals, 2b, grew slowly from waxy evaporation residue of toluene solution. In 2a molecules have different conformation compared to the molecules in 2b. Asymmetric unit of the orthorhombic crystal, 2a, is only one molecule (Fig. 2) while the asymmetric unit of the monoclinic crystal, 2b, contains 4 individual molecules (Fig. 3) which have minor differences in their structures (see Table 1).

In the orthorhombic crystal, 2a, separate molecules are interacting with each other forming chains. One terminal methyl carbon (C33) of tri-tert-butylcyclopentadienyl ligand in each complex stretches to distance of 3.352(3) Å from barium ion of the adjacent molecule as shown in Fig. 4.

Similar interactions have been found in structures of $Ba(Me_5C_5)_2$ [24] and $Ba[(Me_3Si)_3C_5H_2)]_2$ [11] where methyl carbons reach to distances of 3.35–3.36 Å and 3.275(6) Å from neighboring barium atoms, respectively. It is likely that the larger ionic radius of barium compared to Sr^{2+}, Ca^{2+}, Mg^{2+} and +2 rare earth metal ions makes such an interaction possible. Ba–Cp(centroid) distances in 2a are 2.749 and 2.763 Å while Ba–C(ring) distances are 2.966–3.058 Å. Cp(centroid)–Ba–Cp(centroid) angle is 159.7°. Ba ion is formally 7 coordinated and compared to other known 7-coordinate barium cyclopentadienyl compounds, $Ba(t\text{-}Bu_3C_5H_2)_2(THF)$ [6], $Ba((Me_3Si)_2C_5H_2)_2$ [11], $Ba(t\text{-}BuC_5Me_4)_2(CN_2\text{-}i\text{-}Pr_2C_2Me_2)$ [25], $Ba(Me_5C_5)_2(CN_2Me_2\text{-}C_2Me_2)$ [26], and $[Ba(Me_5C_5)_2]_2(N_2C_4H_4)$ [27] (average Ba–Cp(centroid) distances of 2.77, 2.75, 2.77, 2.74, 2.73 Å and Cp(centroid)–Ba–Cp(centroid) angles of 148.1, 162.2, 148.0, 137.0, 137.7°, respectively), the distances are average while the angle is quite large. Cp-rings are almost eclipsed and rotated approximately 140° compared to each other so that on the opening side of the sandwich wedge two hydrogen atoms are parallel in the middle and on both sides of the hydrogen atoms there are t-butyl groups. Similar

Table 2
Crystal data and structure refinement for Sr(*t*-Bu₃C₅H₂)₂ (**1**) and Ba(*t*-Bu₃C₅H₂)₂ (**2a,b**)

Crystal data and structure refinement for Sr(t-Bu$_3$C$_5$H$_2$)$_2$ (**1**) and Ba(t-Bu$_3$C$_5$H$_2$)$_2$ (**2a,b**)

Compound	**1**	**2a**	**2b**
Empirical formula	$C_{34}H_{58}Sr$	$C_{34}H_{58}Ba$	$C_{34}H_{58}Ba$
Formula weight (g mol⁻¹)	554.42	604.14	604.14
Temperature (K)	173(2)		
Wavelength (Å)	0.71073 (Mo Kα)		
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$ (no. 14)	*Pbca* (no. 61)	$P2_1/c$ (no. 14)
Unit cell dimensions (Å), (°)	$a = 19.428(4)$	$a = 11.536(2)$	$a = 21.322(4)$
	$b = 18.374(4)$	$b = 20.730(4)$	$b = 36.699(7)$
	$\beta = 109.50(3)$		$\beta = 90.00(3)$
	$c = 19.706(4)$	$c = 27.622(6)$	$c = 16.812(3)$
Volume (Å³)	6631(3)	6606(2)	13 155(4)
Z	8	8	16
D_{calc} (Mg m⁻³)	1.111	1.215	1.220
Absorption coefficient (mm⁻¹)	1.644	1.220	1.226
$F(000)$	2400	2544	5088
Crystal size (mm)	$0.26 \times 0.24 \times 0.20$	$0.24 \times 0.13 \times 0.10$	$0.30 \times 0.20 \times 0.20$
θ Range for data collection (°)	5.0–25.0	5.0–27.6	5.03–26.00
Index ranges	$-19 \leqslant h \leqslant 23$,	$-13 \leqslant h \leqslant 14$,	$-26 \leqslant h \leqslant 26$,
	$-16 \leqslant k \leqslant 21$,	$-26 \leqslant k \leqslant 26$,	$-45 \leqslant k \leqslant 45$,
	$-22 \leqslant l \leqslant 23$	$-35 \leqslant l \leqslant 35$	$-20 \leqslant l \leqslant 20$
Reflections collected	25 125	70 628	102 457
Independent reflections	11 049	7501	24 111
Reflections with $I > 2\sigma(I)$	6094	4916	12 835
Completeness to θ [°]	$25.00° = 94.6\%$	$27.57° = 98.3\%$	$26.00° = 92.9\%$
Refinement method	Full-matrix least-squares on F^2		
Data/restraints/parameters	11 049/0/699	7501/0/333	24 111/0/1334
Goodness-of-fit on F^2	0.983	1.002	0.996
R_1 indices [$I > 2\sigma(I)$][a]	0.0631	0.0350	0.0712
wR_2 indices [$I > 2\sigma(I)$][b]	0.1098	0.0610	0.1626
R_1 indices (all data)[a]	0.1510	0.0764	0.1456
wR_2 indices (all data)[b]	0.1305	0.0698	0.1958
Largest difference in hole and peak [e Å⁻³]	−0.47 and 0.82	−0.59 and 0.55	−0.95 and 2.64

[a] $R_1 = \sum ||F_o| - |F_c||/|F_o|$.
[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

relative orientation of the ligands was observed for 7-coordinated Ba[[(Me₃Si)₃C₅H₂)]₂ [11]. *t*-Butyl groups are displaced from the cyclopentadienyl ring planes by 0.003–0.218 Å (=0.11–8.08°). The bridging *t*-butyl group is 6.54° from the cyclopentadienyl ring plane and largest displacement (8.08°) is involving C(27).

In monoclinic structure **2b** there is no intermolecular bonding but close intramolecular contacts. In each individual molecule one methyl carbon is 3.443–3.476 Å from barium centre (see Table 1). These weak contacts arise from the different ring orientation in **2b** relative to **2a**. In **2b** the ring orientation in each molecule is like in **1** and most of the known complexes MCp′₂ with 1,2,4-substituted Cp-rings, *i.e.*, the Cp-rings are approximately eclipsed (twist angle = 1.9–6.3°) and rotated 72° so that on the opening side of the sandwich wedge two *t*-butyl groups are approximately parallel in the middle. Ba–Cp(centroid) distances are 2.689–2.716 Å and Ba–C(ring) distances 2.923(7)–2.997(7) Å. Despite the intramolecular contacts these smaller values compared to those observed for the molecule in orthorhombic crystal **2a** suggest lower coordination number. For comparison Ba–Cp(centroid) distances in 6-coordinate barocenes like Ba(*i*-Pr₄C₅H₄)₂ [9] and

Ba(*i*-Pr₅C₅)₂ [10] are 2.677–2.679 Å and 2.749 Å (elongated by steric hindrance), respectively. The Cp(centroid)–Ba–Cp(centroid) angles in **2b** are different for each 4 molecules in the asymmetric unit and vary between 161.3° and 164.9° (Table 1). Larger angles compared to those observed for **2a** with one methyl carbon coordinated to barium are expected. Other known base free barocene structures with 6-coordinated barium, Ba(*i*-Pr₄C₅H₂)₂ [9], and Ba(*i*-Pr₅C₅)₂ [10] have bending angles of 154° and 180°, respectively. *t*-Butyl groups are displaced from the cyclopentadienyl ring planes by 0.003–0.153 Å (=0.11–5.82°). Similarly to **1**, *t*-butyl groups on the sides of the sandwich wedge are mostly the least displaced groups.

TGA under N₂ atmosphere (1 atm) revealed that both Sr(*t*-Bu₃C₅H₂)₂ and Ba(*t*-Bu₃C₅H₂)₂ evaporated in a single step and left <10% residue (Fig. 5). Both compounds give very similar curves with weight loss taking place at exactly the same temperature range. The samples for TGA were loaded in air and this is most likely affected the residue. No differences in thermal behavior between barocene crystallized from toluene (monoclinic crystals, **2b**) and barocene from sublimation (orthorhombic crystals **2a** with molecules having interactions with each other) were
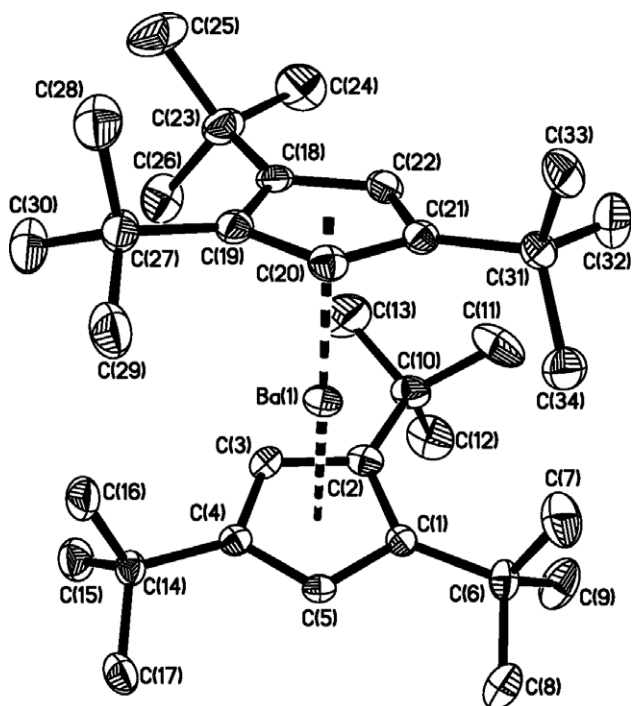
Fig. 2. Structure of Ba(t-Bu₃C₅H₂)₂, **2a**, asymmetric unit in orthorhombic crystals. Thermal ellipsoids are drawn on the 50% probability level. Hydrogen atoms are omitted for clarity.
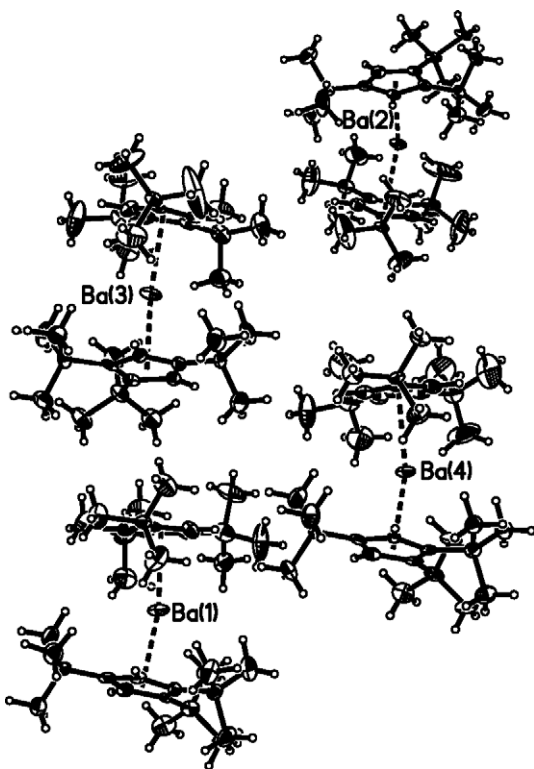

Fig. 3. Structure of Ba(t-Bu₃C₅H₂)₂, **2b**, asymmetric unit in monoclinic crystals. Thermal ellipsoids are drawn on the 50% probability level.

observed. This is as expected because the samples melt before evaporation. Compound **2a** melts at 155 °C. Waxy solid **2b** turns into liquid without sharp observable melting

point below 160 °C. Vacuum sublimation of Ba(t-Bu₃-C₅H₂)₂ took place at 160–220 °C/0.05 mbar. The sublimation yield was over 90%. Sr(t-Bu₃C₅H₂)₂ sublimed at 120–180 °C/0.05 mbar also with over 90% sublimation yield.

3. Conclusion

Sterically hindered Lewis base free Sr(t-Bu₃C₅H₂)₂ and Ba(t-Bu₃C₅H₂)₂ were structurally and thermally characterized. Structures presented are an addition to series of bent metallocenes of main group and lanthanoid elements. Results of the study follow the idea that balance between steric repulsions and van der Waals attractive forces direct the relative ring orientations and the bonding angles. Conformational flexibility of these compounds is also further emphasized by the fact that Ba(t-Bu₃C₅H₂)₂ crystallizes in two different forms depending on the way of crystallization. It seems that base-free barocenes with smaller ligands than i-Pr₄C₅H or i-Pr₅C₅ are very eager to find ways to extend their coordination sphere as shown by the two structures of Ba(t-Bu₃C₅H₂)₂ having methyl to barium close contacts. Volatility, thermal stability and reactivity of these compounds make them suitable precursors for atomic layer deposition of thin films.

4. Experimental

All complex preparations and manipulations were done under rigorous exclusion of air and moisture using standard Schlenk and glove box techniques. Ligand 1,2,4-tri-*tert*-butylcyclopentadiene [8] was prepared according to the literature methods. Sr(t-Bu₃C₅H₂)₂(THF)ₓ and Ba(t-Bu₃C₅H₂)₂(THF) were prepared as described in the literature [6,16]. Desolvation of Sr(t-Bu₃C₅H₂)₂(THF)ₓ was achieved by heating the THF-adduct under vacuum. Desolvation of Ba(t-Bu₃C₅H₂)₂(THF) was achieved by heating under vacuum, sublimation or by toluene reflux method [28].

¹H (200 MHz) and ¹³C NMR (50 MHz) spectra were recorded with a Varian Gemini 2000 instrument at ambient temperature. Chemical shifts were referenced to SiMe₄ and are given in ppm. Thermogravimetric analyses were carried out on a Mettler Toledo Starᵉ system equipped with a TGA 850 thermobalance using a flowing nitrogen atmosphere at 1 atm. The heating rate was 10 °C/min and the weights of the samples prepared to 70 µl pans with lids were between 10 and 11 mg. Melting points were taken from the SDTA data measured by the thermobalance. Mass spectra were recorded with a JEOL JMS-SX102 operating in electron impact mode (70 eV) using a direct insertion probe and sublimation temperature range of 50–370 °C. Elemental analyses (CHN) were tried but satisfactory results were not obtained because of the high air and moisture sensitivity of the samples.

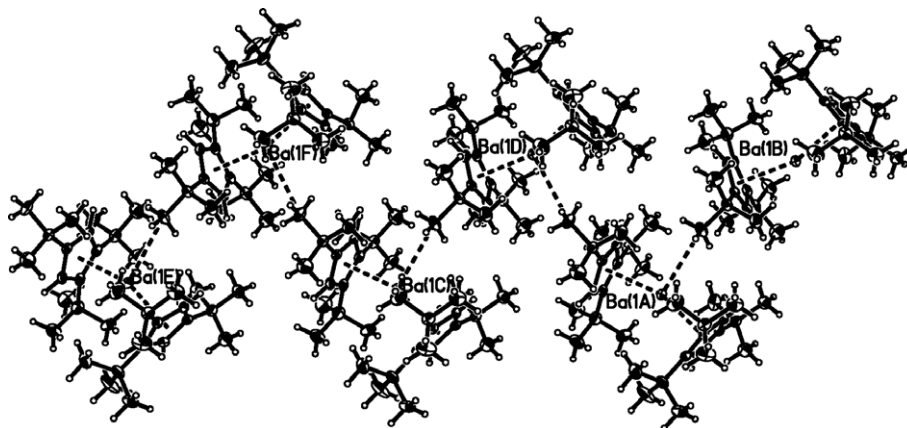*Sr(t-Bu₃C₅H₂)₂* (**1**). Mp 136 °C, ¹H NMR (C₆D₆) 1.39 (s, 18 H, C*H₃*), 1.43 (s, 36 H, C*H₃*), 5.96 (s, 2H, C*H*);

Fig. 4. Interaction between Ba(t-Bu$_3$C$_5$H$_2$)$_2$ units in **2a**. Chains running through the crystal structure are formed.
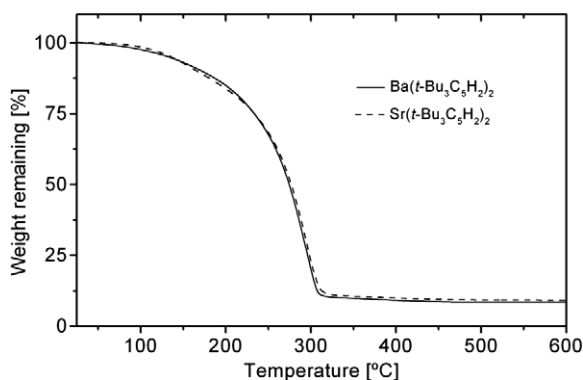

Fig. 5. TG curves of Sr(t-Bu$_3$C$_5$H$_2$)$_2$ and Ba(t-Bu$_3$C$_5$H$_2$)$_2$.

^{13}C{^{1}H} NMR (C$_6$D$_6$) 32.08 (C(CH$_3$)$_3$), 33.24 (CH$_3$), 33.66 (C(CH$_3$)$_3$), 34.53 (CH$_3$), 107.16 (ring CH), 129.89, 133.06 (ring C's). MS (EI, 70 eV) m/z 554 [Sr(t-Bu$_3$C$_5$H$_2$)$_2$]$^+$, 321 [Sr(t-Bu$_3$C$_5$H$_2$)]$^+$, 234 [t-Bu$_3$C$_5$H$_3$]$^+$, each with correct isotope pattern.

Ba(t-Bu$_3$C$_5$H$_2$)$_2$. Mp of orthorhombic crystals (**2a**) 155 °C, Mp of monoclinic crystals (**2b**) was not observed. ^{1}H NMR (C$_6$D$_6$) 1.36 (s, 18H, CH_3), 1.44 (s, 36H, CH_3), 5.87 (s, 2H, CH); ^{13}C{^{1}H} NMR (C$_6$D$_6$) 32.07 (C(CH$_3$)$_3$), 33.07 (CH$_3$), 33.55 (C(CH$_3$)$_3$), 34.56 (CH$_3$), 108.57 (ring CH), 130.43,132.88 (ring C's). MS (EI, 70 eV) m/z 604 [Ba(t-Bu$_3$C$_5$H$_2$)$_2$]$^+$, 371 [Ba(t-Bu$_3$C$_5$H$_2$)]$^+$, 234 [t-Bu$_3$-C$_5$H$_3$]$^+$, each with correct isotope pattern.

Crystal structure determination. Crystals suitable for XRD were found straight from sublimates (**1** and **2a**). In addition different crystals of Ba(t-Bu$_3$C$_5$H$_2$)$_2$ (**2b**) were found from waxy evaporation residue of toluene solution. Crystals were measured with a Bruker Nonius KappaCCD diffractometer (graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation). Area-detector scaling and absorption corrections were done with program SADABS [29].

Structures were solved with the SIR97 program [30] and further refinements were carried out using the SHELXL-97 [31] software package. All non-hydrogen atoms were refined anisotropically; H atoms were calculated according to the ideal geometry. Illustrations were produced by the SHELXTL program [32]. Crystal data for compounds **1**, **2a** and **2b** are presented in Table 2. In structure **1** there is some disorder in the t-butyl groups. One t-butyl group in asymmetric unit was refined as disordered between two positions. Both conformations were refined anisotropically with freely refining site occupancies. Crystals **2b** were of low quality and the crystal measured also contained a small twin component (twin matrix: 100 0-10 00-1, BASF = 0.10214).

Appendix A. Supplementary material

CCDC 631446, 631446 and 631448 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.08.008.

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