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Synthesis and characterization of Ti(IV), Zr(IV) and Al(III) salen-based complexes

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ABSTRACT

New Ti(IV), Zr(IV) and Al(III) salen-based complexes of formulae $[(L)TiCl_2]$, **2**, $[(L)ZrCl_2]$, **3**, and $[(L)\{Al(CH_2CH(CH_3)_2)_2\}_2]$, **4**, where L = *meso*-(*R*,*S*)-diphenylethylene-salen, were synthesized in high yields. $[(L)\{Al(CH_2CH(CH_3)_2)_2\}_2]$ is a bimetallic complex that results from the reaction of H_2L with either 1 or 2 equivalent of $Al(CH_2CH(CH_3)_2)_3$. The solid-state molecular structures of compounds **2** and **4·(C_7H_8)** were obtained by single-crystal X-ray diffraction. Crystal data for $C_{44}H_{54}Cl_2N_2O_2Ti$, (**2a**): monoclinic, space group *C*2/*c* (no. 15), a = 27.384(1) Å, b = 12.1436(8) Å, c = 28.773(2) Å, β = 112.644(2)°, V = 8830.6(9) Å^3, Z = 8, μ(MoKα) = 0.350 mm^{-1}, *Dcalc* = 1.146 g/cm^3, 26647 reflections measured (5.204° ≤ 2Θ ≤ 50.7°), 8072 unique (R_{int} = 0.0967, R_{sigma} = 0.1241) which were used in all calculations. The final R_1 was 0.0640 (I > 2σ(I)) and wR_2 was 0.1907 (all data). Crystal data for $C_{62}H_{72}Cl_2N_2O_2Ti$ (**2b**): monoclinic, space group $P2_1/c$ (no. 14), a = 19.606(1) Å, b = 12.793(1) Å, c = 23.189(2) Å, β = 105.710(4)°, V = 5599.0(7) Å^3, Z = 4, μ(MoKα) = 0.291 mm^{-1}, *Dcalc* = 1.182 g/cm^3, 37593 reflections measured (3.65° ≤ 2Θ ≤ 50.928°), 10304 unique (R_{int} = 0.0866, R_{sigma} = 0.1032) which were used in all calculations. The final R_1 was 0.0593 (I > 2σ(I)) and wR_2 was 0.1501 (all data). Crystal data for $C_{67}H_{97}Al_2N_2O_2$ (**4·(C_7H_8)**): triclinic, space group *P*-1 (no. 2), a = 10.0619(9) Å, b = 16.612(2) Å, c = 21.308(2) Å, α = 67.193(5)°, β = 78.157(6)°, γ = 77.576(5)°, V = 3176.8(6) Å^3, Z = 2, μ(MoKα) = 0.088 mm^{-1}, *Dcalc* = 1.063 g/cm^3, 42107 reflections measured (5.382° ≤ 2Θ ≤ 51.624°), 12111 unique (R_{int} = 0.0624, R_{sigma} = 0.0706) which were used in all calculations. The final R_1 was 0.0568 (I > 2σ(I)) and wR_2 was 0.1611 (all data). The solid-state molecular structure of $[(L)\{Al(CH_2CH(CH_3)_2)_2\}_2]$ reveals that both metal centres display a slightly distorted tetrahedral geometry bridged by the salen ligand. Both $[(L)TiCl_2]$ and $[(L)ZrCl_2]$ complexes display octahedral geometry with *trans*-chlorido ligands.

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1. Introduction

Salan- and salen-type compounds have been largely explored in coordination chemistry but the latter present various advantages [1]. Due to their rigid structure, salen-type ligands are ideal for equatorial coordination to transition metals, leaving two axial sites available for the coordination of ancillary ligands. Depending on the chemical nature of the N and O donor atoms, salen-type ligands may offer thermodynamic and kinetic stability to a large variety of metal centers [2-6]. The presence of bulky substituents in the phenolate rings may provide additional stereochemical protection [7-9]. Moreover, the incorporation of chiral centers within the salen backbone reveals an important role in enantioselective catalysis [9-12]. Most of the catalytic studies have been focused on middle and late *d*-block transition metal-salen complexes as catalysts for olefin epoxidation [13-14], cyclopropanation [15-17], aziridination [18-20], sulfoxidation [21-23], ring-opening polymerization of cyclic esters [24-29] and copolymerization of CO_2 and epoxides [30-32]. Early transition metal complexes supported by salen ligands are relatively less reported [33-37]. Nevertheless, vanadium derivatives have been widely explored for diverse applications [38-41]. Despite a large variety of mononuclear aluminum complexes supported by salen-type ligands have been reported mainly as catalysts for the ring-opening polymerization of cyclic esters [26-28], bimetallic derivatives have not been well studied [42-44]. In this work, we present the synthesis and structural characterization of new Ti(IV), Zr(IV) and Al(III) complexes based on *meso*-(*R*,*S*)-diphenylethylene-salen ligand.

2. Experimental

2.1. General considerations

meso-(*R*,*S*)-diphenylethylene-salen (H_2L, **1**) was prepared according to a described procedure [45].

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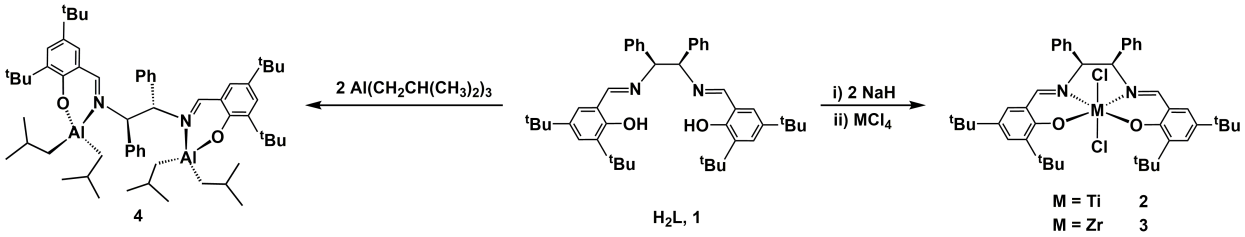


Scheme 1. Synthesis of the salen-based complexes **2**, **3**, and **4**.

Commercial NaH (60% dispersion in mineral oil) was washed several times with *n*-hexane and dried under vacuum. All other reagents were commercial grade and used without further purification. All manipulations were performed under an atmosphere of dry oxygen-free nitrogen by means of standard Schlenk and glovebox techniques. Solvents were pre-dried using 4 Å molecular sieves and refluxed over sodium-benzophenone (diethyl ether, THF and toluene) or CaH_2 (*n*-hexane) under an atmosphere of N_2 and collected by distillation. C_6D_6 was dried with 4 Å molecular sieves and freeze-pump-thaw degassed prior to use. NMR spectra were recorded in a Bruker AVANCE II 300 MHz spectrometer, at 296 K, referenced internally to residual proton-solvent (^{1}H) or solvent (^{13}C) resonances, and reported relative to tetramethylsilane (0 ppm). 2D NMR experiments such as ^{1}H-^{13}C{^{1}H} HSQC, and ^{1}H-^{1}H COSY were performed to make all assignments. Elemental analyses were carried out in Laboratório de Análises do IST using a EA110CE automatic analyzer Instrument.

2.2. Synthesis and characterization

2.2.1. [(meso-(R,S)-Diphenylethylene-salen)$TiCl_2$], 2

A THF solution of compound **1** (0.45 g, 0.70 mmol) was added to a suspension of NaH (0.04 mg, 1.7 mmol) in the same solvent at -30 °C. The temperature was allowed to rise slowly to room temperature and the mixture was further stirred for 3 h at 50 °C. The solution was filtered and added to 1.5 mL of a $TiCl_4$ solution (0.5 M in toluene). The mixture was further stirred for 16 h at room temperature. The red/orange solution obtained was evaporated to dryness and the residue was extracted with toluene. Evaporation of the solvent to dryness afforded a reddish crystalline solid (Scheme 1). Color: Red. Yield: 78%. ^{1}H NMR (300 MHz, C_6D_6, δ, ppm): 1.22 (s, 18H, $\mathrm{C}(\mathrm{C}H_3)_3$), 1.91 (s, 18H, $\mathrm{C}(\mathrm{C}H_3)_3$), 5.85 (s, 2H, $\mathrm{C_{Ph}}(\mathrm{C}H)\mathrm{N}$), 7.27-6.95 (overlapping, 12H total, $\mathrm{C}H_{\mathrm{Ph}}$ and $\mathrm{C}H_{\mathrm{PhO}}$), 7.85 (s, 2H, $\mathrm{C}H_{\mathrm{PhO}}$), 8.24 (s, 2H, $\mathrm{N{=}C}H$). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, δ, ppm): 30.0 ($\mathrm{C}(C\mathrm{H}_3)_3$), 30.9 ($\mathrm{C}(C\mathrm{H}_3)_3$), 33.9 ($C(\mathrm{CH}_3)_3$), 35.6 ($C(\mathrm{CH}_3)_3$), 76.7 ($\mathrm{C_{Ph}}(C\mathrm{H})\mathrm{N}$), 125.7 ($\mathrm{NCH}C_{\mathrm{PhO}}$), 128.1 ($C\mathrm{H_{PhO}}$), 128.2 (*o*-$C\mathrm{H_{Ph}}$), 129.7 (*p*-$C\mathrm{H_{Ph}}$), 130.7 (*m*-$C\mathrm{H_{Ph}}$), 131.6 ($C\mathrm{H_{PhO}}$), 136.9 ($C_{\mathrm{Ph}}(\mathrm{CH})\mathrm{N}$), 137.1 ($^t\mathrm{Bu}C_{\mathrm{PhO}}$), 143.7 ($^t\mathrm{Bu}C_{\mathrm{PhO}}$), 160.9 ($\mathrm{O}C_{\mathrm{PhO}}$), 166.8 ($\mathrm{N{=}}C\mathrm{H}$). Anal. calcd. for $C_{44}H_{54}Cl_2N_2O_2Ti$: C, 69.36; H, 7.15; N, 3.68. Found: C, 69.67; H, 7.65; N, 4.02%.

2.2.2. [(meso-(R,S)-Diphenylethylene-salen)$ZrCl_2$], 3

A THF solution of compound **1** (0.33 g, 0.41 mmol) was added to a suspension of NaH (0.02 g, 0.90 mmol) in the same solvent at -30 °C. The temperature was allowed to rise slowly to room temperature and the mixture was further stirred for 3 h at 50 °C. The solution was filtered and added to a THF solution of $ZrCl_4$ (0.09 g, 0.4 mmol). The yellow solution formed was stirred for 16 hours at room temperature. The solvent was evaporated to dryness and the residue was extracted with toluene. Evaporation of the solvent to dryness afforded a yellow crystalline solid (Scheme 1). Color: Yellow. Yield: 88%. ^{1}H NMR (300 MHz, C_6D_6, δ, ppm): 1.20 (s, 18H, $\mathrm{C}(\mathrm{C}H_3)$)), 1.87 (s, 18H, $\mathrm{C}(\mathrm{C}H_3)$)), 6.17 (s, 2H, $\mathrm{C_{Ph}}(\mathrm{C}H)\mathrm{N}$), 7.25-6.72 (overlapping, 14H total, $\mathrm{C}H_{\mathrm{PhO}}$ and $\mathrm{C}H_{\mathrm{Ph}}$), 8.02 (s, 2H, $\mathrm{N{=}C}H$). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, δ, ppm): 30.3 ($\mathrm{C}(C\mathrm{H}_3)_3$), 31.3 ($\mathrm{C}(C\mathrm{H}_3)_3$), 34.3 ($C(\mathrm{CH}_3)_3$), 35.9 ($C(\mathrm{CH}_3)_3$), 75.5 ($\mathrm{C_{Ph}}(C\mathrm{H})\mathrm{N}$), 123.4 ($\mathrm{NCH}C_{\mathrm{PhO}}$), 128.2 ($\mathrm{C}H_{\mathrm{PhO}}$), 128.8 ($\mathrm{C}H_{\mathrm{Ph}}$), 129.2 ($\mathrm{C}H_{\mathrm{Ph}}$), 130.7 ($\mathrm{C}H_{\mathrm{Ph}}$), 132.2 ($\mathrm{C}H_{\mathrm{PhO}}$), 135.4 ($C_{\mathrm{Ph}}(\mathrm{CH})\mathrm{N}$), 135.5 ($^t\mathrm{Bu}C_{\mathrm{PhO}}$), 139.4 ($^t\mathrm{Bu}C_{\mathrm{PhO}}$), 158.7 ($\mathrm{O}C_{\mathrm{PhO}}$), 169.2 ($\mathrm{N{=}}C\mathrm{H}$). Anal. calcd. for $C_{44}H_{54}N_2O_2Zr.(C_7H_8)_{0.5}$: C, 67.03; H, 6.87; N, 3.29; Found: C, 67.01; H, 7.12; N, 2.81%.

2.2.3. [(meso-(R,S)-Diphenylethylene-salen){$Al(CH_2CH(CH_3)_2)_2$}$_2$], 4

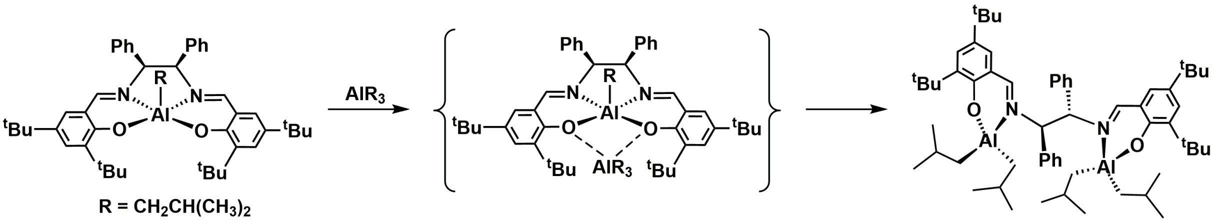
To a toluene solution of compound **1** (0.31 g, 0.48 mmol) cooled at -80 °C was slowly added 1.0 mL of a triisobutyl aluminum solution (1.1 M in toluene). The mixture was allowed to come to room temperature, and it was left stirring overnight. After filtration, the solvent was evaporated to dryness affording a white solid that was washed with Et_2O (Scheme 1). Color: White. Yield: 81%. ^{1}H NMR (300 MHz, C_6D_6, δ, ppm): 1.11-1.25 (overlapping, 32H total, 8H, $\mathrm{C}H_2\mathrm{CH(CH_3)_2}$ and 24H, $\mathrm{CH_2CH}(\mathrm{C}H_3)_2$), 1.25 (s, 18H, $\mathrm{C}(\mathrm{C}H_3)_3$), 1.54 (s, 18H, $\mathrm{C}(\mathrm{C}H_3)_3$), 2.00 (m, 4H, $\mathrm{CH_2\ C}H(\mathrm{CH_3})_2$), 5.21 (s, 2H, $\mathrm{C_{Ph}}(\mathrm{C}H)\mathrm{N}$), 6.67 (d, $^4J_{\mathrm{H\text{-}H}}$ = 2Hz, 2H, $\mathrm{C}H_{\mathrm{PhO}}$), 6.88 (d, $^3J_{\mathrm{H\text{-}H}}$ = 8Hz, 2H, $\mathrm{C}H_{\mathrm{Ph}}$), 6.98 (t, $^3J_{\mathrm{H\text{-}H}}$ = 8Hz, 4H, $\mathrm{C}H_{\mathrm{Ph}}$), 7.31 (d, $^3J_{\mathrm{H\text{-}H}}$ = 8Hz, 4H, $\mathrm{C}H_{\mathrm{Ph}}$), 7.44 (s, 2H, $\mathrm{N{=}C}H$), 7.63 (d, $^4J_{\mathrm{H\text{-}H}}$ = 2Hz, 2H, $\mathrm{C}H_{\mathrm{PhO}}$). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, δ, ppm): 26.5 ($\mathrm{CH_2}C\mathrm{H(CH_3)_2}$), 26.6 ($\mathrm{CH_2}C\mathrm{H(CH_3)_2}$), 28.6 ($C\mathrm{H_2CH(CH_3)_2}$), 28.7 ($C\mathrm{H_2CH(CH_3)_2}$), 28.8 ($\mathrm{CH_2CH}(C\mathrm{H_3})_2$), 28.9 ($\mathrm{CH_2CH}(C\mathrm{H_3})_2$), 29.7 ($\mathrm{C}(C\mathrm{H}_3)_3$), 31.4 ($\mathrm{C}(C\mathrm{H}_3)_3$), 34.0 ($C(\mathrm{CH}_3)_3$), 35.5 ($C(\mathrm{CH}_3)_3$), 72.6 ($\mathrm{C_{Ph}}(C\mathrm{H})\mathrm{N}$), 118.6 ($\mathrm{NCH}C_{\mathrm{PhO}}$), 128.3 ($C\mathrm{H_{PhO}}$), 129.1 ($C\mathrm{H_{Ph}}$), 129.5 ($C\mathrm{H_{Ph}}$), 129.6 ($C\mathrm{H_{Ph}}$), 133.0 ($C\mathrm{H_{PhO}}$), 134.8 ($C_{\mathrm{Ph}}(C\mathrm{H})\mathrm{N}$), 139.0 ($^t\mathrm{Bu}C_{\mathrm{PhO}}$), 141.2 ($^t\mathrm{Bu}C_{\mathrm{PhO}}$), 162.6 ($\mathrm{O}C_{\mathrm{PhO}}$), 172.6 ($\mathrm{N{=}}C\mathrm{H}$). Anal. calcd. for $C_{60}H_{90}Al_2N_2O_2\cdot(Et_2O)_3$: C, 75.35; H, 10.54; N, 2.44. Found: C, 75.22; H, 9.63; N, 2.47%.

2.3. General procedure for X-ray crystallography

Suitable crystals of compounds **2** (**2a** and **2b**) and **4·(C_7H_8)** were coated and selected in Fomblin® oil under an inert atmosphere of nitrogen. Crystals were then mounted on a loop external to the glovebox environment and data collected using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Bruker AXS-KAPPA APEX II diffractometer equipped with an Oxford Cryosystem open-flow nitrogen cryostat. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all observed reflections [46]. Absorption corrections were applied using SADABS [47]. The structures were solved by direct methods using SIR97[48] and SIR2004 [49]. Structure refinement was done using SHELXL [50]. These programs are part of the WinGX software package version 1.80.05 [51]. The hydrogen atoms were inserted in fixed positions and allowed to refine riding on the parent carbon atom. Compound **2a** also crystalized with half-molecules of toluene in the asymmetric unit. As all attempts to model the disordered solvent molecule did not lead to acceptable solutions, the Squeeze/PLATON [52] sequence was applied.

Table 1. Crystal data and details of structure refinement for compounds **2a**, **2b**, and **4·(C_7H_8)**.

Parameters	**2a**	**2b**	**4·(C_7H_8)**
Empirical formula	$C_{44}H_{54}Cl_2N_2O_2Ti$	$C_{62}H_{72}Cl_2N_2O_2Ti$	$C_{67}H_{97}Al_2N_2O_2$
Formula weight	761.66	995.99	1016.42
Temperature (K)	150(2)	150(2)	150(2)
Crystal system, space group	Monoclinic, C2/c	Monoclinic, $P2_1/c$	Triclinic, P-1
a, (Å)	27.384(1)	19.606(1)	10.0619(9)
b, (Å)	12.1436(8)	12.793(1)	16.612(2)
c, (Å)	28.773(2)	23.189(2)	21.308(2)
α, (°)	90	90	67.193(5)
β, (°)	112.644(2)	105.710(4)	78.157(6)
γ, (°)	90	90	77.576(5)
Volume ($Å^3$)	8830.6(9)	5599.0(7)	3176.8(6)
Z	8	4	2
ρ_{calc} (g/cm^3)	1.146	1.182	1.063
μ (mm^{-1})	0.350	0.291	0.088
F(000)	3232	2120	1110
Crystal size (mm^3)	0.18 x 0.08 x 0.08	0.12 x 0.10 x 0.10	0.26 × 0.24 × 0.20
Θ range for data collection (°)	2.602 to 25.350	1.825 x 25.464	2.691 to 25.812
Index ranges	$-32 \leq h \leq 31$	$-22 \leq h \leq 23$	$-10 \leq h \leq 12$
	$-14 \leq k \leq 14$	$-15 \leq k \leq 15$	$-20 \leq k \leq 2$
	$-32 \leq l \leq 34$	$-28 \leq l \leq 28$	$-26 \leq l \leq 25$
Reflections collected	26647	37593	42107
Independent reflections	8072 [R_{int} = 0.0967, R_{sigma} = 0.1241]	10304 [R_{int} = 0.0866, R_{sigma} = 0.1032]	12111 [R_{int} = 0.0624, R_{sigma} = 0.0706]
Data/restraints/parameters	8072/0/472	10304/0/634	12111/0/679
Goodness-of-fit on F^2	0.969	0.996	1.055
Final R indexes [I≥2σ(I)]	R_1 = 0.0640, wR_2 = 0.1688	R_1 = 0.0593, wR_2 = 0.1336	R_1 = 0.0568, wR_2 = 0.1468
Final R indexes [all data]	R_1 = 0.1095, wR_2 = 0.1907	R_1 = 0.1147, wR_2 = 0.1501	R_1 = 0.0922, wR_2 = 0.1611
Largest diff. peak/hole (e $Å^{-3}$)	0.539/-0.387	0.668/-0.283	0.723/-0.366



Scheme 2. Proposed structure for the intermediate species of the conversion of mononuclear to bimetallic salen complex of aluminum, **4**.

Crystallographic and experimental details of data collection and crystal structure determinations are available in Table 1. Illustrations of the molecular structures were made with ORTEP-3 [53] for Windows.

3. Results and discussion

Treatment of $TiCl_4$ or $ZrCl_4$ with the sodium salt of *meso*-(*R*,*S*)-diphenylethylene-salen (Na_2L), prepared by reaction of 2 equiv. of NaH with H_2L, **1**, afforded complexes [(L)$TiCl_2$], **2**, and [(L)$ZrCl_2$], **3**, respectively, in high yields. The reaction of compound **1** with 2 equiv. of triisobutylaluminum led to the formation of the bimetallic complex [(L){$Al(CH_2CH(CH_3)_2)_2$}$_2$], **2**, in 81% yield. The reaction of compound **1** with 1 equiv. of triisobutylaluminum also gave complex **2** as the unique product but in low yield due to the unbalanced stoichiometry. The synthetic procedures that led to the formation of the salen-based complexes **2**, **3** and **4** are shown in Scheme 1.

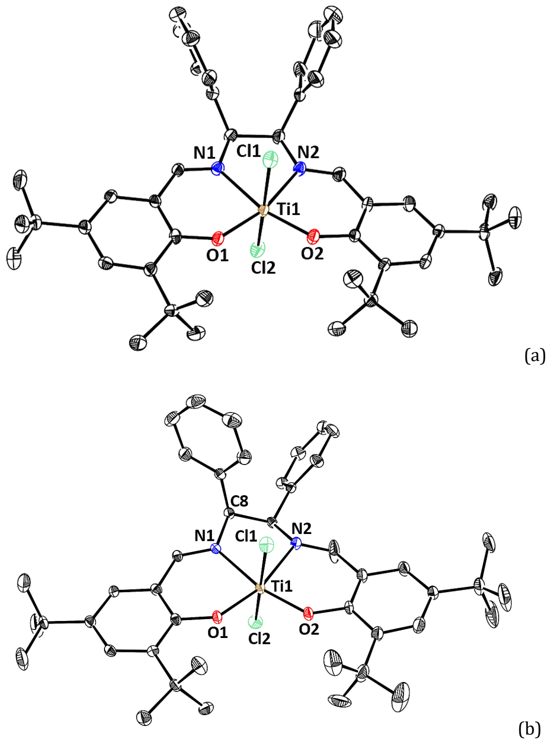
The structures of salen derivatives of Al(III) described in the literature reveal that these ligands may coordinate in a κ_4-N_2O_2 fashion, leading to mononuclear square pyramidal geometry complexes or bridge two metal centers, leading to tetrahedral coordinated Al. The mononuclear compounds are the kinetic products and are preferentially formed when the reactions are carried out at room temperature in a 1:1 stoichiometry. When the reactions are carried out above room temperature, typically in the range 70-110 °C, the products obtained are predominantly bimetallic species that correspond to the thermodynamic products [26,44]. The dimerization reactions also take place upon addition of 1 equiv. of AlR_3 to a solution of [(L)Al(R)] (R = alkyl), which suggests the formation of a phenolate bridged intermediate between [(L)Al(R)] and AlR_3, tentatively shown in Scheme 2. This type of bridge has been structurally characterized for diamino-bis(phenolate) Sc(III) complexes when the *ortho*-substituents of the phenolate rings are not bulky enough to prevent dimerization [54]. The strong ionic nature of the interaction between the N,O moiety of the salen ligand and Al(III), the high oxophilicity of Al(III) and the high acidity of AlR_3 are, altogether, the driving force for the extra stability of bimetallic mononuclear complexes.

The ^1H NMR spectra of compounds **2**-**4** are compatible with C_i symmetric species showing two singlets for the *tert*-butyl groups, one singlet for the two protons of the C2 bridge between the nitrogen atoms, one singlet assigned to the N=C*H* protons, and several resonances for the aromatic phenolate and phenyl moieties. The protons of the isobutyl groups in compound **4** appear as a multiplet at 2.00 ppm and between 1.24 and 1.13 ppm. The $^{13}C\{^1H\}$ NMR spectra display two sets of signals assigned to the ^{t}Bu groups, while the imine carbons and the carbons of the C2 bridge give rise to one signal each. The other carbon atoms of the phenolate and phenyl moieties show up in the aromatic region and the carbons of the isobutyl groups attached to the aluminum appear in the high field region of the spectrum. The NMR spectra of complexes **2**-**4** are presented as Supplementary Information.

Single crystals of compound **2** suitable for X-ray diffraction were obtained from a concentrated toluene solution, **2a**, and from a concentrated deuterated benzene solution in the NMR tube, **2b**. In the first case, the complex crystallized in the monoclinic system, space group C2/c, while in the NMR tube it crystallized in the monoclinic system, space group $P2_1/c$ with three molecules of benzene in the asymmetric unit.

Table 2. Selected bond lengths (Å) and angles (°) of **2a**, **2b**, and **4·(C_7H_8)**.

Bond	**2a**	**2b**	**4·(C_7H_8)**
	Distances (Å)		
M-O(1)	1.831(2)	1.807(2)	1.767(2)
M-O(2)	1.826(3)	1.812(2)	1.768(2)
M-N(1)	2.137(3)	2.133(2)	1.985(2)
M-N(2)	2.127(3)	2.175(2)	1.966(2)
M-Cl(1)	2.342(1)	2.330(1)	-
M-Cl(2)	2.382(1)	2.378(1)	-
Al(1)-C(45)	-	-	1.960(2)
Al(1)-C(49)	-	-	1.975(2)
Al(2)-C(53)	-	-	1.970(2)
Al(2)-C(57)	-	-	1.969(3)
	Angles (°)		
O(1)-M-O(2)	110.1(1)	110.52(9)	-
O(1)-M-N(1)	86.3(1)	86.09(9)	-
N(1)-M-N(2)	76.3(1)	76.72(9)	-
N(2)-M-O(2)	87.3(1)	86.55(9)	-
X(1)-M-X(2)	169.95(5)	172.57(4)	-
N(1)-Al(1)-C(45)	-	-	108.51(9)
N(1)-Al(1)-C(49)	-	-	112.76(8)
O(1)-Al(1)-C(45)	-	-	113.27(9)
O(1)-Al(1)-C(49)	-	-	107.61(9)
O(1)-Al(1)-N(1)	-	-	93.87(7)
C(45)-Al(1)-C(49)	-	-	118.2(1)
N(2)-Al(2)-C(53)	-	-	102.44(8)
N(2)-Al(2)-C(57)	-	-	110.37(9)
O(2)-Al(2)-C(53)	-	-	109.53(9)
O(2)-Al(2)-C(57)	-	-	107.0(1)
O(2)-Al(2)-N(2)	-	-	94.63(7)
C(53)-Al(2)-C(57)	-	-	127.9(1)



(a)

(b)

Figure 1. ORTEP diagram of **2a** (a) and **2b** (b) showing thermal ellipsoids at 40% probability level. Co-crystallized molecules of benzene and hydrogen atoms are omitted for clarity.

ORTEP views of the molecular structures of compound **2** are depicted in Figure 1. In both, the titanium atoms are hexacoordinated in distorted octahedral environments, with the donor atoms of the salen ligand in the equatorial plane (O1, O2, N1 and N2) and the two chlorido ligands, Cl1 and Cl2, occupying the axial sites. The metric parameters that characterize the two molecules are very similar, with exception of the dihedral angles between the phenyl rings bonded to the carbons of the C2 bridge that link the imine nitrogens that are 47.04 and 79.96°, respectively, for **2a** and **2b** and the dihedral angles between the mean equatorial planes and the phenolate ring planes (5.18 and 6.72° for **2a** and 5.88° and 8.43° for **2b**). A slight deviation of 0.503(2) Å of the C8 atom to the mean equatorial plane is also observed in **2b** as shown in Figure 2. The overall bond distances and angles are within the ranges reported for other dichloro titanium (IV) complexes supported by salen-type ligands (Table 2) [34, 55].

Crystals of compound **4** suitable for single crystal X-ray diffraction were obtained from a concentrated toluene solution at -20 °C.

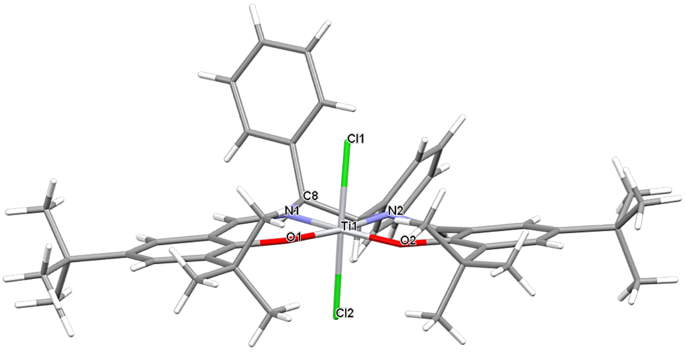


Figure 2. View along the equatorial plane of **2b**.

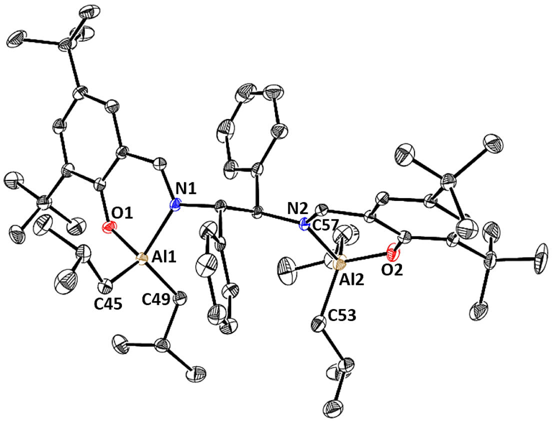


Figure 3. ORTEP diagram of compound **4** showing thermal ellipsoids at 40% probability level. A co-crystallized molecule of toluene and hydrogen atoms are omitted for clarity.

The compound crystallized in the triclinic *P*-1 space group with one molecule of toluene in the asymmetric unit. The ORTEP view of the molecular structure of compound **4** depicted in Figure 3 shows a bimetallic complex with the Al centers displaying slightly distorted tetrahedral geometries. Each aluminum atom is coordinated to one oxygen and one nitrogen atom of the salen ligand and to two isobutyl groups. The two metal centers are almost coplanar with the planes of the phenolate groups directly attached to them with deviations of 0.322 and 0.338 Å from those planes that define a dihedral angle of 56.15°. The overall bond distances and angles are within the ranges reported for other tetrahedral Al(III) complexes supported by salen-type ligands (Table 2) [26,42-44].

The comparison of the $M-O-C_{Ph}$ ($M = Ti, Al$) with the $H-O-C_{Ph}$ angles suggests that the *sp*^{2} character of the oxygen is higher in the complexes (139.6(2)-140.5(2)° in Ti and 130.9(1)-132.2(1)° in Al vs 101.7(16)° in H_2L) [45]. These differences may be the result of an extended conjugation in metal complexes in view to the neutral salen precursor. The slightly wider angle in the Ti complexes may reflect a higher covalent nature of the Ti-O bonds, as expected for a transition metal versus a main block metal.

4. Conclusion

New Ti(IV), Zr(IV) and Al(III) salen-based complexes of formulae $[(L)TiCl_2]$, $[(L)ZrCl_2]$ and $[(L)\{Al(CH_2CH(CH_3)_2)_2\}_2]$ (L = *meso*-(*R*,*S*)-diphenylethylene-salen) were synthesized and fully characterized. The solid-state molecular structure of $[(L)\{Al(CH_2CH(CH_3)_2)_2\}_2]$ reveals that both metal centers display a slightly distorted tetrahedral geometry. Both $[(L)TiCl_2]$ and $[(L)ZrCl_2]$ complexes display octahedral geometries around the metal centers.

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Supporting information S

CCDC 2058281-2058283 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement DS

Conflict of interests: The authors declare that they have no conflict of interest.
Author contributions: L.G.A. and J.H. performed the synthesis and characterization of the compounds; L.G.A. and A.M.M. supervised the experiments and wrote the manuscript.
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References

[1]. Pessoa, J. C.; Correia, I. *Coord. Chem. Rev.* **2019**, *388*, 227–247.
[2]. Motevalli, M.; Oduwole, A. D.; Parkin, B. C.; Ramnauth, R.; Sullivan, A. C.; Kaltsoyannis, N. *Dalton Trans.* **2003**, 3591–3598.
[3]. Rotsch, D. A.; Reinig, K. M.; Weis, E. M.; Taylor, A. B.; Barnes, C. L.; Jurisson, S. S. *Dalton Trans.* **2013**, *42*, 11614–11625.
[4]. Xie, J.; Lo, P.-K.; Lam, W. W. Y.; Man, W.-L.; Ma, L.; Yiu, S.-M.; Lau, K.-C.; Lau, T.-C. *Chem. Commun. (Camb.)* **2016**, *52*, 11430–11433.
[5]. Chiang, L.; Allan, L. E. N.; Alcantara, J.; Wang, M. C. P.; Storr, T.; Shaver, M. P. *Dalton Trans.* **2014**, *43*, 4295–4304.
[6]. Akbari, A.; Ahmadi, M.; Takjoo, R.; Heinemann, F. W. *J. Coord. Chem.* **2012**, *65*, 4115–4124.
[7]. Dyers, L., Jr; Que, S. Y.; VanDerveer, D.; Bu, X. R. *Inorg. Chim. Acta* **2006**, *359*, 197–203.
[8]. Mirkhani, V.; Moghadam, M.; Tangestaninejad, S.; Bahramian, B. *J. Iran. Chem. Soc.* **2008**, *5*, 375–383.
[9]. Lee, C. L.; Chen, D.; Chang, X.-Y.; Tang, Z.; Che, C.-M. *Organometallics* **2020**, *39*, 2642–2652.
[10]. Shaw, S.; White, J. D. *Chem. Rev.* **2019**, *119*, 9381–9426.
[11]. Hutson, G. E.; Türkmen, Y. E.; Rawal, V. H. *J. Am. Chem. Soc.* **2013**, *135*, 4988–4991.
[12]. White, J. D.; Shaw, S. *Org. Lett.* **2011**, *13*, 2488–2491.
[13]. Egami, H.; Irie, R.; Sakai, K.; Katsuki, T. *Chem. Lett.* **2007**, *36*, 46–47.
[14]. McGarrigle, E. M.; Gilheany, D. G. *Chem. Rev.* **2005**, *105*, 1563–1602.
[15]. Xu, Z.-J.; Fang, R.; Zhao, C.; Huang, J.-S.; Li, G.-Y.; Zhu, N.; Che, C.-M. *J. Am. Chem. Soc.* **2009**, *131*, 4405–4417.
[16]. Tai, S.; Maskrey, T. S.; Nyalapatla, P. R.; Wipf, P. *Chirality* **2019**, *31*, 1014–1027.
[17]. White, J. D.; Shaw, S. *Org. Lett.* **2014**, *16*, 3880–3883.
[18]. Man, W.-L.; Lam, W. W. Y.; Yiu, S.-M.; Lau, T.-C.; Peng, S.-M. *J. Am. Chem. Soc.* **2004**, *126*, 15336–15337.
[19]. Kawabata, H.; Omura, K.; Katsuki, T. *Tetrahedron Lett.* **2006**, *47*, 1571–1574.
[20]. Sun, W.; Herdtweck, E.; Kühn, F. E. *New J Chem* **2005**, *29*, 1577–1580.
[21]. Kim, S. S.; Rajagopal, G. *Synthesis (Mass.)* **2003**, 2461–2463.
[22]. Bismuto, A.; Cucciolito, M. E.; Ruffo, F.; Vitagliano, A.; Curcio, M. *Phosphorus Sulfur Silicon Relat. Elem.* **2015**, *190*, 1021–1028.
[23]. Katsuki, T.; Miyazaki, T. *Synlett* **2003**, 1046–1048.
[24]. Yang, Z.; Hu, C.; Duan, R.; Sun, Z.; Zhang, H.; Pang, X.; Li, L. *Asian J. Org. Chem.* **2019**, *8*, 376–384.
[25]. Duan, R.; Hu, C.; Li, X.; Pang, X.; Sun, Z.; Chen, X.; Wang, X. *Macromolecules* **2017**, *50*, 9188–9195.
[26]. Chen, H.-L.; Dutta, S.; Huang, P.-Y.; Lin, C.-C. *Organometallics* **2012**, *31*, 2016–2025.
[27]. Cui, Y.; Li, D.; Gao, B.; Zhou, Y.; Chen, L.; Qiu, B.; Li, Y.; Duan, Q.; Hu, N. *J. Coord. Chem.* **2016**, *69*, 656–667.
[28]. Gaston, A. J.; Navickaite, G.; Nichol, G. S.; Shaver, M. P.; Garden, J. A. *Eur. Polym. J.* **2019**, *119*, 507–513.
[29]. Yu, Y.; Yuan, D.; Wang, Y.; Yao, Y. *J. Organomet. Chem.* **2016**, *819*, 37–45.
[30]. Darensbourg, D. J. *Chem. Rev.* **2007**, *107*, 2388–2410.
[31]. Decortes, A.; Haak, R. M.; Martín, C.; Belmonte, M. M.; Martin, E.; Benet-Buchholz, J.; Kleij, A. W. *Macromolecules* **2015**, *48*, 8197–8207.
[32]. Ambrose, K.; Murphy, J. N.; Kozak, C. M. *Inorg. Chem.* **2020**, *59*, 15375–15383.
[33]. Davis, A.; Kilner, C. A.; Kee, T. P. *Inorg. Chim. Acta* **2004**, *357*, 3493–3502.
[34]. Kim, I.; Ha, Y. S.; Zhang, D. F.; Ha, C.-S.; Lee, U. *Macromol. Rapid Commun.* **2004**, *25*, 1319–1323.
[35]. Gurung, R. K.; McMillen, C. D.; Jarrett, W. L.; Holder, A. A. *Inorg. Chim. Acta* **2020**, *505*, 119496.
[36]. Gu, W.; Xu, P.; Wang, Y.; Yao, Y.; Yuan, D.; Shen, Q. *Organometallics* **2015**, *34*, 2907–2916.
[37]. Saha, T. K.; Ramkumar, V.; Chakraborty, D. *Inorg. Chem.* **2011**, *50*, 2720–2722.
[38]. Taheri, O.; Behzad, M.; Ghaffari, A.; Kubicki, M.; Dutkiewicz, G.; Bezaatpour, A.; Nazari, H.; Khaleghian, A.; Mohammadi, A.; Salehi, M. *Transit. Met. Chem.* **2014**, *39*, 253–259.
[39]. Balakrishnan, C.; Neelakantan, M. A. *Inorg. Chim. Acta* **2018**, *469*, 503–514.
[40]. Ghaffari, A.; Behzad, M.; Dutkiewicz, G.; Kubicki, M.; Salehi, M. *J. Coord. Chem.* **2012**, *65*, 840–855.
[41]. Białek, M.; Leksza, A.; Piechota, A.; Kurzak, K.; Koprek, K. *J. Polym. Res.* **2014**, *21*, 389.
[42]. Van Aelstyn, M. A.; Keizer, T. S.; Klopotek, D. L.; Liu, S.; Munoz-Hernandez, M.-A.; Wei, P.; Atwood, D. A. *Organometallics* **2000**, *19*, 1796–1801.
[43]. Clegg, W.; Harrington, R. W.; North, M.; Villuendas, P. *J. Org. Chem.* **2010**, *75*, 6201–6207.
[44]. Alaaeddine, A.; Roisnel, T.; Thomas, C. M.; Carpentier, J.-F. *Adv. Synth. Catal.* **2008**, *350*, 731–740.
[45]. Maru, M. S.; Barroso, S.; Adão, P.; Alves, L. G.; Martins, A. M. *J. Organomet. Chem.* **2018**, *870*, 136–144.
[46]. SAINT. Bruker AXS Inc. Madison. Wisconsin, USA, 1997-2003.
[47]. SADABS. Bruker AXS Inc. Madison. Wisconsin, USA, 1997-2003.
[48]. Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115–119.
[49]. Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **2005**, *38*, 381–388.
[50]. Sheldrick, G. M. *Acta Crystallogr. C Struct. Chem.* **2015**, *71*, 3–8.
[51]. Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.
[52]. Spek, A. L. *Acta Crystallogr. D Biol. Crystallogr.* **2009**, *65*, 148–155.
[53]. Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565–565.
[54]. Boyd, C. L.; Toupance, T.; Tyrrell, B. R.; Ward, B. D.; Wilson, C. R.; Cowley, A. R.; Mountford, P. *Organometallics* **2005**, *24*, 309–330.
[55]. Repo, T.; Klinga, M.; Leskelä, M.; Pietikäinen, P.; Brunow, G. *Acta Crystallogr. C* **1996**, *52*, 2742–2745.