

Scandium SALEN Complexes Bearing Chloro, Aryloxo, and Hydroxo Ligands

Christian Meermann,[†] Karl W. Törnroos,[†] and Reiner Anwander^{*†‡}*Department of Chemistry, University of Bergen, Allégaten 41, 5007 Bergen, Norway, and Institut für Anorganische Chemie, Universität Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany*

Received October 31, 2008

Heteroleptic amide complexes (SALEN)Sc[N(SiHMe₂)₂] (SALEN = Salen^{tBu,tBu}, Salcyc^{tBu,tBu}, or Salpren^{tBu,tBu} if not stated differently) were examined as synthesis precursors according to silylamine elimination reactions. Treatment of (SALEN)Sc[N(SiHMe₂)₂] with H₂O or phenols (HOAr^{R,R'}; R = *t*Bu, *i*Pr) afforded complexes [(SALEN)Sc(μ -OH)]₂ and (SALEN)Sc(OAr^{R,R'}), while chloro exchange products were formed from the respective reactions with NH₄Cl or AlMe₂Cl. Such complexes [(SALEN)Sc(μ -Cl)]₂ and (SALEN)ScCl(thf) were also obtained by utilizing alternative synthesis protocols, allowing for controlled donor absence and presence. Heteroleptic amide precursors [Sc(N^{*i*}Pr)₂(μ -Cl)(thf)]₂ and [Sc[N(SiHMe₂)₂](μ -Cl)(thf)]₂ readily undergo amine elimination reactions with H₂SALEN derivatives to form the corresponding chloride complexes. Spectroscopic and X-ray structural data of the heteroleptic scandium complexes revealed an exclusive intramolecular tetradentate coordination mode of the SALEN ligands independent of the SALEN ligand bite angle and the nature of the “second” ligand (chloro, amido, aryloxo, hydroxo). The coordination of the SALEN ligands is rationalized on the basis of (a) the displacement *d* of the metal center from the [N₂O₂] least-squares plane, (b) the dihedral angle α between the phenyl rings of the salicylidene moieties, and (c) the angle β = Ct–Ln–Ct (Ct = centroid of the phenyl rings) in the case of strongly twisted ligands.

Introduction

Complexes of the general formula (SALEN)Ln(III)–X, where Ln is a rare-earth metal, that is, Sc, Y, and the lanthanides, and SALEN is a *N,N'*-bis(salicylidene)ethylenediamine, are successfully employed in homogeneous catalysis, particularly for enantioselective organic transformations.^{1–3} These heteroleptic rare-earth metal SALEN complexes can be synthesized by different approaches featuring alk(aryl)oxo, hydroxo, and amido groups as actor ligands X.⁴ Most common are, indeed, salt metathesis synthesis protocols utilizing LnCl₃(thf)_{*n*} and alkali metal salts of the corresponding SALEN ligand as starting materials to

yield complexes [(SALEN)Ln(Cl)]_{*n*}.^{5–8} Deprotonation of H₂SALEN is conveniently achieved by applying KN(SiMe₃)₂, sodium or potassium hydride, or lithium bases such as MeLi or BuLi. The remaining chloro ligand in [(SALEN)Ln(Cl)]_{*n*} can then easily be exchanged in a subsequent salt metathesis by various actor ligands.⁹ Alcoholysis, that is, treatment of Ln(OR)₃ (R = alkyl, aryl) with H₂SALEN to give (SALEN)Ln(OR), is an alternative synthesis route, which has also been exploited in d-transition metal SALEN chemistry.^{9–12} Similarly, rare-earth metal amide complexes engage in protonolysis reactions displaying versatile synthesis precursors for complexes with noncyclopentadienyl ancillary ligands. The routinely used amide precursor compound Ln[N(SiMe₃)₂]₃, however, does not afford monomeric com-

* To whom correspondence should be addressed. E-mail: reiner.anwander@uni-tuebingen.de.

[†] University of Bergen.

[‡] Universität Tübingen.

(1) Lin, M. H.; RajanBabu, T. V. *Org. Lett.* **2002**, *4*, 1607–1610.

(2) Saha, B.; Lin, M. H.; RajanBabu, T. V. *J. Org. Chem.* **2007**, *72*, 8648–8655.

(3) O'Shaughnessy, P. N.; Knight, P. D.; Morton, C.; Gillespie, K. M.; Scott, P. *Chem. Commun.* **2003**, 1770–1771.

(4) Cozzi, P. G. *Chem. Soc. Rev.* **2004**, *33*, 410–421.

(5) Evans, W. J.; Fujimoto, C. H.; Ziller, J. W. *Chem. Commun.* **1999**, 311–312.

(6) Dube, T.; Gambarotta, S.; Yap, G. *Organometallics* **1998**, *17*, 3967–3973.

(7) Deacon, G. B.; Feng, T.; Hockless, D. C. R.; Junk, P. C.; Skelton, B. W.; Smith, M. K.; White, A. H. *Inorg. Chim. Acta* **2007**, *360*, 1364–1369.

(8) Gottfriedsen, J.; Spoida, M.; Blaurock, S. Z. *Anorg. Allg. Chem.* **2008**, *634*, 514–518.

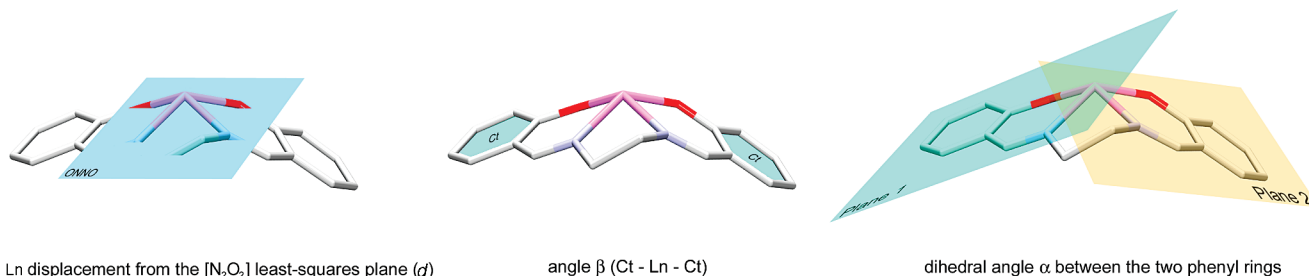
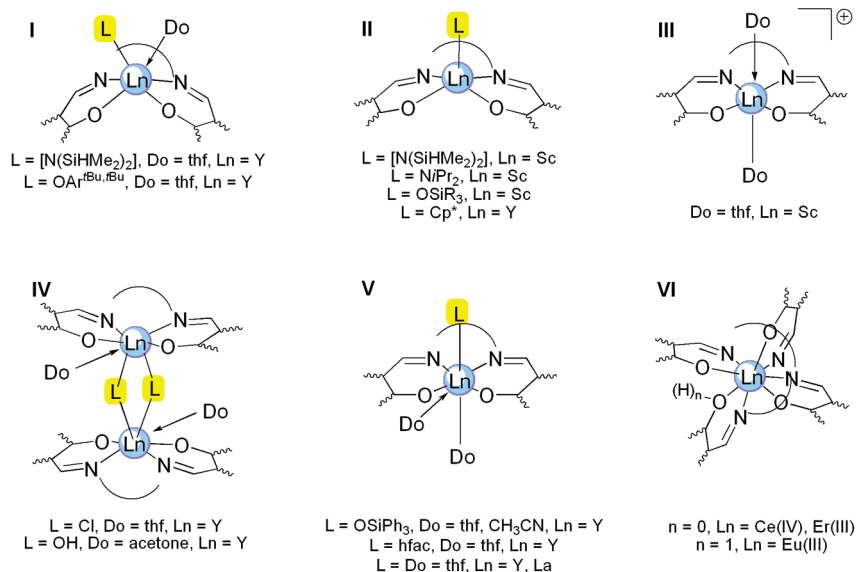


Figure 1. Coordination features of SALEN ligands.

Chart 1. Coordination Modes in Structurally Characterized Ln(III)/(IV)–SALEN Complexes (hfac = hexafluoroacetylacetonate)



plexes (SALEN)Ln(NR₂) due to steric constraints imparted by the bulky bis(trimethylsilyl)amido ligands.¹³ This problem can be dealt with by utilization of Ln[N(SiHMe₂)₂]₃(thf)_n according to the *extended silylamide route*.^{13,14} Contrary to aluminum SALEN chemistry, where AlR₃ and R₂AlCl feature repeatedly exploited starting materials, rare-earth metal alkyls have, to our knowledge, not yet been used as precursors for SALEN complexes.^{15,16} It is noteworthy that Piers et al. succeeded in synthesizing related scandium and yttrium salicylaldiminato complexes from Ln(CH₂SiMe₂-Ph)₃(thf)₂.¹⁷

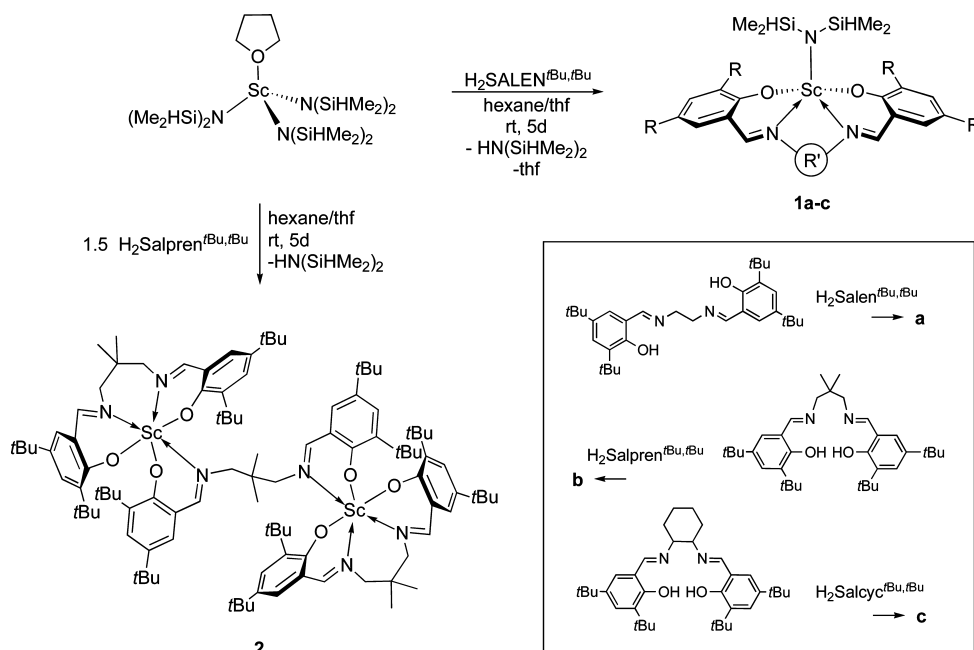
The large rare-earth metal(III) centers uniquely demonstrate the coordination flexibility of the dianionic SALEN ligand, which is strongly affected by the diimino

ligand backbone.¹⁸ Preferably, this dianionic tetradentate [ONNO] ligand chelates transition metals in an equatorial fashion, comparable to porphyrinato ligands. For the structurally characterized Ln(III)–SALEN complexes, the ancillary ligand coordination environment can be characterized by (i) the displacement d of the metal center from the $[N_2O_2]$ least-squares plane, (ii) the dihedral angle α between the phenyl rings of the salicylidene moieties, and (iii) the angle β (Ct–Ln–Ct) (Ct = centroid of the phenyl rings) in the case of strongly twisted ligands (Figure 1).

In rare-earth metal chemistry, the SALEN ligand adopts a variety of different coordination geometries (Chart 1). Cis coordination mode **I** has been found repeatedly, for example, in (SALEN)Y[N(SiHMe₂)₂](thf)^{1,13} or (Salen)Y(OAr^{tBu, tBu})(thf),⁹ and seems to be favored over the octahedral trans arrangement featured by cationic complex [(Salen)Sc(thf)₂][BPh₄]¹⁹ (**III**, Chart 1, cis and trans referring to the position of donor and actor ligands). Cationic complexes of the larger rare-earth metal centers [(Salpren)Ln(thf)₃][BPh₄] (Ln = Y, La) are seven-coordinate, and coordination of an additional donor molecule implies geometry **V**.¹⁹ A similar coordination geometry was detected in (Salen)Y(OSiPh₃)(thf)(CH₃CN).¹⁴

- (9) Evans, W. J.; Fujimoto, C. H.; Ziller, J. W. *Polyhedron* **2002**, *21*, 1683–1688.
- (10) Oviatt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 4072–4073.
- (11) Fukuzawa, S.; Komuro, Y.; Nakano, N.; Obara, S. *Tetrahedron Lett.* **2003**, *44*, 3671–3674.
- (12) Mascarenhas, C. M.; Miller, S. P.; White, P. S.; Morken, J. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 601–603.
- (13) Runte, O.; Priermeier, T.; Anwander, R. *Chem. Commun.* **1996**, 1385–1386.
- (14) Anwander, R.; Görlitzer, H. W.; Gerstberger, G.; Palm, C.; Runte, O.; Spiegler, M. *J. Chem. Soc., Dalton Trans.* **1999**, 3611–3615.
- (15) Evans, D. A.; Janey, J. M.; Magomedov, N.; Tedrow, J. S. *Angew. Chem., Int. Ed.* **2001**, *40*, 1884–1888.
- (16) Atwood, D. A.; Harvey, M. J. *Chem. Rev.* **2001**, *101*, 37–52.
- (17) Emslie, D. J. H.; Piers, W. E.; MacDonald, R. J. *Chem. Soc., Dalton Trans.* **2002**, 293–294.

- (18) Katsuki, T. *Chem. Soc. Rev.* **2004**, *33*, 437–444.
- (19) Liu, Q.; Meermann, C.; Görlitzer, H. W.; Herdtweck, E.; Sirsch, P.; Törnroos, K. W.; Anwander, R. *Dalton Trans.* **2008**, 6170–6178.

Scheme 1. Synthesis of Sc–SALEN Bis(dimethylsilyl)amide Complexes **1a–c** and Homoleptic Sc–Salpren Complex **2**

Heteroleptic Sc(III)–SALEN complexes appear sterically saturated in the absence of donor molecules favoring a square-pyramidal coordination, as in (*Salcyc*)Sc[N(SiHMe₂)₂] and (*Salpren*)Sc[NiPr₂] (**II**).²⁰ The same structural motif was found in (*Salen*)Y(Cp*).⁹ For small monoanionic actor ligands such as Cl[−] or OH[−], the coordination number at the yttrium metal center is increased to seven by dimerization, as found in [(*Salen*)Y(μ-Cl)(thf)]₂⁵ and [(*Salcyc*)Y(μ-OH)(acetone)]₂ (**IV**).¹² Tetravalent cerium can bind two SALEN ligands forming neutral complexes (SALEN^{R,R})₂Ce (SALEN^{R,R} = *Salen*^{tBu,tBu}, *Salen*^{H,Cl}, *Salcyc*^{H,H}, *Salcyc*^{Cl,Cl}; **VI**).^{8,21,22} The same geometry was also found for the anionic species in [(*Salen*^{H,H})₂Er][−][NH₂C₄H₁₀]⁺ and for (*Salen*^{H,H})Eu (*HSalen*^{H,H}).^{23,24}

In this article, we report on the versatility of scandium amide complexes for the synthesis of SALEN derivatives with additional chloro, aryloxo, and hydroxo ligands.

Results and Discussion

Synthesis of Sc–SALEN Amido Derivatives. The extended silylamide route gives easy access to heteroleptic complexes (SALEN)Ln[N(SiHMe₂)₂](thf)_x, as reported previously for Ln = Sc (**1a–c**, $x = 0$; Scheme 1), Y, and La ($x = 1$), with SALEN = *Salen*^{tBu,tBu}, *Salcyc*^{tBu,tBu}, and *Salpren*^{tBu,tBu}.^{19,20} The conformational mobility of the SALEN ligands is already expressed in the solid-state structures of their proligands, where ethylene-bridged H₂Salen adopts a

trans and H₂Salpren/H₂Salcyc a cis configuration (Scheme 1, inset).^{25,26} It is noteworthy that the highly flexible Salen ligand backbone or a mismatch of the chelate conformation and Ln³⁺ size can impede this silylamine elimination, as found for the system H₂Salen–La[N(SiHMe₂)₂]₃(thf)₂.¹⁹

H₂Salpren, on the other hand, featuring a substituted propylene link between the rigid cis-oriented salicylidene moieties, offers an ideal scaffold for the chelating coordination of Ln(III) centers, as shown for the synthesis of heteroleptic complex (*Salpren*)Sc[N(SiHMe₂)₂] (**1b**) (Scheme 1).^{20,27} However, recrystallization of complex **1b** at −35 °C from hexane caused ligand scrambling and formation of the homoleptic complex Sc₂(*Salpren*)₃ (**2**) in almost quantitative yield. The latter compound, **2**, can be also prepared by a protonolysis reaction according to the extended silylamide route when the proligand and Sc[N(SiHMe₂)₂]₃(thf) are used in a 3:2 ratio (Scheme 1). The composition of **2** could be confirmed by elemental analysis and IR spectroscopy. The IR spectrum revealed Salpren as the only coordinating ligand with a characteristic N=C stretching vibration at 1612 cm^{−1} ($\nu_{\text{C=N}}$ H₂Salpren = 1626–1631 cm^{−1}). The ¹H NMR spectrum of **2** was difficult to interpret due to two sets of magnetically different protons in the ligand backbones. A salt metathesis approach utilizing ScCl₃(thf)₃ and in situ generated K₂Salpren in a 2:3 ratio led to product mixtures which were not further investigated.

The solid-state structure of homoleptic **2** corroborates the high conformational flexibility of such ligand systems (Figure 2). Salpren not only adopts the common η⁴(O₂N₂) tetradentate coordination but can also act as a bridging ligand in a

(20) Meermann, C.; Sirsch, P.; Törnroos, K. W.; Anwender, R. *Dalton Trans.* **2006**, 1041–1050.

(21) Kubono, K.; Hirayama, N.; Kokusen, H.; Yokoi, K. *Anal. Sci.* **2001**, *17*, 193–197.

(22) Szlyk, E.; Wojtczak, A.; Dobrzanska, L.; Barwiolek, M. *Polyhedron* **2008**, *27*, 765–776.

(23) Mangani, S.; Takeuchi, A.; Yamada, S.; Orioli, P. *Inorg. Chim. Acta* **1989**, *155*, 149–152.

(24) Huang, L.; Huang, C.-H.; Xu, G.-X.; Han, Y.-Z.; Li, G.-P. *Chin. J. Struc. Chem.* **1990**, *9*, 100–104.

(25) Mucha, F.; Haberecht, J.; Bohme, U.; Roewer, G. *Monatsh. Chem.* **1999**, *130*, 117–132.

(26) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Fang, C. C.; Billodeaux, D. R.; Reibenspies, J. H. *Inorg. Chem.* **2004**, *43*, 6024–6034.

(27) Artus, G. R. J.; Rauch, M. U.; Herrmann, W. A. *Z. Kristallogr., New Cryst. Struct.* **1997**, *212*, 227–228.

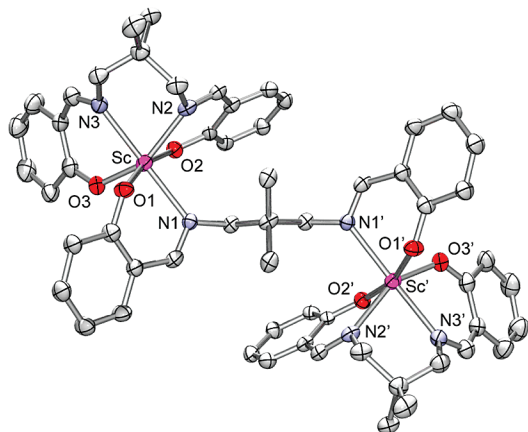


Figure 2. Solid-state structure of complex $\text{Sc}_2(\text{Salpren})_3$ (**2**). Heavy atoms are represented by atomic displacement ellipsoids at the 50% level. Hydrogen atoms and *t*Bu-substitution in the 3- and 5- positions are omitted for clarity.

μ_2 - $[\eta^2(\text{ON})]_2$ fashion between two scandium centers. Compound **2** crystallizes in the monoclinic space group $C2/c$. The scandium centers are six-coordinated, which is in contrast to previously investigated monomeric scandium SALEN complexes showing a square-pyramidal coordination geometry (coordination number = 5; **II**, Chart 1).²⁰

The $\eta^4(\text{O}_2\text{N}_2)$ coordinated Salpren ligand is bent about the scandium metal center with a dihedral angle α of 85.9° and an angle β (Ct–Sc–Ct) of 102.7° between the two phenyl rings (Table 1). This is a larger deviation than in monomeric (Salpren)Sc(NiPr₂) ($\alpha = 124.27(9)^\circ$).²⁰ The scandium oxygen and nitrogen distances ($\eta^4(\text{O}_2\text{N}_2)$: Sc–O2, 2.029(3) Å; Sc–O3, 1.980(3) Å; Sc–N2, 2.251(3) Å; Sc–N3, 2.278(3) Å. μ_2 - $[\eta^2(\text{ON})]_2$: Sc–O1, 2.025(2) Å; Sc–N1, 2.301(3) Å) match those found in (Salpren)Sc(NiPr₂) (Sc–O1, 1.994(2) Å; Sc–O2, 2.016(2) Å; Sc–N1, 2.277(2) Å; Sc–N2, 2.283(3) Å).²⁰

Synthesis of [(SALEN)Sc(OR)] Derivatives (R = H, OAr). It has been shown previously that (SALEN)Sc[N(SiHMe₂)₂] (**1a–c**) can easily be converted into siloxide complexes, for example, (Salen)Sc(OSi^{*t*}BuPh₂), and donor-stabilized monocationic species [(SALEN)Sc(thf)₂][BPh₄] by protonolysis reactions.^{19,20} As expected for rare-earth metal amide complexes, compounds **1a–c** are moisture-sensitive. However, hydrolysis comes to a halt at air-stable complexes [(SALEN)Sc(OH)] (**3a–c**) with the strongly chelating SALEN ligands counteracting extensive hydrolysis to Sc(OH)₃ and H₂SALEN (Scheme 2).

X-ray crystal structure analyses of compounds **3a–c** revealed dimeric complexes of the composition [(SALEN)Sc(μ -OH)]₂, with six-coordinated scandium metal centers (Figures 3–5; c.f., similar yttrium complexes are seven-coordinated and exhibit geometry **IV**, Chart 1). Complexes **3a** and **3c** crystallize in the orthorhombic space groups $Pba2$ and $P2_12_12_1$; however, **3b** crystallizes in the triclinic space group $P\bar{1}$.

For all three compounds, the hydrogen atoms on the μ -bridging O atoms could be located in the difference Fourier maps. The Sc–(μ -OH) bond lengths are similar and lie in the range of 2.0836(9)–2.1166(9) Å. Also, the Sc–O(SALEN) and Sc–N(SALEN) distances are consistent with each other

(Table 1; **3a**, av. Sc–O, 2.0054 Å; av. Sc–N, 2.2956 Å; **3b**, Sc–O1, 2.008(2) Å; Sc–O2, 2.009(2) Å; Sc–N1, 2.275(2) Å; Sc–N2, 2.277(2) Å; **3c**, av. Sc–O, 2.001 Å; av. Sc–N, 2.283 Å).

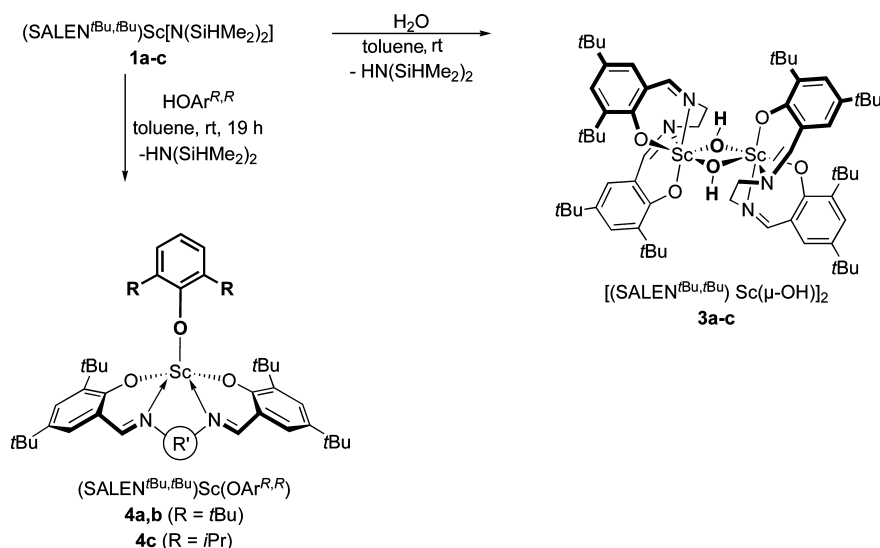
Because of the same core moiety [Sc(μ -OH)₂Sc], complexes **3a–c** allow for direct comparison of the intrinsic SALEN ancillary ligand coordination following the criteria introduced in Figure 1. The smallest angle β (Ct–Sc–Ct; largest bending) was found for the Salpren ligand in **3b** (94.6°), differing markedly from that of the Salcyc ligand (**3c**: 125.6° and 128.5° ; Table 1). Closest to planarity are the Salen ligands in compound **3a**, with angles of 136.5° and 137.0° . The only other structurally characterized SALEN lanthanide hydroxy complex [(Salcyc)Y(OCMe₂)(μ -OH)]₂ was obtained from Y₅O(O^{*i*}Pr)₁₃ and H₂Salcyc in dichloromethane and subsequent crystallization by allowing acetone to diffuse into the reaction mixture.¹² The presence of the hydroxo groups was explained by adventitious moisture. In the latter complex, the yttrium metal center is seven-coordinated and shows a geometry closer to **3b** than to the respective Salcyc complex **3c**. Clearly, the additional donor coordination and the larger metal ion size enforce this larger bending of the Salcyc ligand ($\beta = 112^\circ$). Partial hydrolysis of rare-earth metal alkyl complexes (Salan^{*t*Bu,R})Lu(CH₂SiMe₃)(thf) (Salan^{*t*Bu,R} = [2-O-3-*t*Bu-5-R-C₆H₂CH₂-N(CH₃)CH₂]₂, R = H, *t*Bu) by treatment with water-enriched N₂ gave mixed hydroxy/siloxy complexes (Salan^{*t*Bu,R})Lu(μ -OSiMe₃)(μ -OH)Lu(Salan^{*t*Bu,R}).²⁸ X-ray structure analysis of this Lu–Salan^{*t*Bu,tBu} complex revealed an asymmetric dimer with a geometry comparable to that of **3a**.²⁸

The feasibility of bulky ligand exchange reactions of rare-earth metal–SALEN amide complexes has been proven previously. Recently, we reported on the synthesis of (SALEN)Sc(OSiR₃) from complex **1** by protonolysis with the corresponding silanols and secondary ligand exchange of (Salen)Y[N(SiHMe₂)₂](thf) with HOAr^{*t*Bu,tBu}.^{13,20} Evans et al. investigated the accessibility of the latter aryloxide derivatives (Salen)Y(OAr^{*t*Bu,tBu})(thf) through different synthesis approaches.⁹ A salt metathesis approach utilizing [(Salen)Y(μ -Cl)(thf)]₂ and LiOAr^{*t*Bu,tBu} did not give a pure product; instead, the reaction of Y(OAr^{*t*Bu,tBu})₃ or (Salen)Y[N(SiMe₃)₂](thf) with the corresponding phenol formed the thf adduct (Salen)Y(OAr^{*t*Bu,tBu})(thf).⁹ According to a similar silylamine elimination reaction, **1a** and **1c** could be transformed quantitatively to (Salen)Sc(OAr^{*t*Bu,tBu}) (**4a**), (Salcyc)Sc(OAr^{*t*Bu,tBu}) (**4b**), and (Salcyc)Sc(OAr^{*t*Pr,iPr}) (**4c**), with HOAr^{*t*Bu,tBu} and HOAr^{*t*Pr,iPr} (Scheme 2). Additional donor coordination, as found for the yttrium complex, was not observed. The reactions were performed in hexane, the products crystallized from toluene solutions, and their composition confirmed by NMR and IR spectroscopy. Moreover, an X-ray crystallographic analysis of compound **4b** confirmed its mononuclear structure (Figure 6). The scandium center is five-coordinated in a square-pyramidal fashion (geometry **II**, Chart 1) by the ONNO+O coordinating atoms of the Salcyc and aryloxo ligands, reminiscent of the

Table 1. Selected Bond Distances (Å) and Bonding Features (deg/Å; according to Figure 1) for Compounds **2**, **3a–c**, **4b**, and **5b**^a

	2^b	3a	3b^b	3c	4b	5b	
						molecule 1	molecule 2
			SALEN Ligand $\eta^4(\text{O}_2\text{N}_2)$				
α [deg]	85.9	29.1	74.1	53.0	35.8	7.75	14.4
		36.6		52.2			
β [deg]	102.7	136.5	94.6	125.6	134.0	162.8	161.6
		137.0		128.5			
d [Å]	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c	0.73	0.20	0.20
Sc–O [Å]	2.029(3)	1.9943(9)	2.008(2)	1.998(2)	1.963(2)	1.973(5)	1.970(5)
	1.980(3)	2.0160(9)	2.009(2)	2.007(2)	1.993(2)	1.981(5)	1.976(5)
		1.9838(9) ^d		1.977(2) ^d			
		2.0275(9) ^d		2.022(2) ^d			
Sc–N [Å]	2.251(3)	2.315(1)	2.275(2)	2.286(3)	2.227(2)	2.237(6)	2.235(6)
	2.278(3)	2.286(1)	2.277(2)	2.297(3)	2.235(2)	2.245(6)	2.219(6)
		2.321(1) ^d		2.248(3) ^d			
		2.260(1) ^d		2.301(3) ^d			
			Actor Ligand E				
Sc1–E1 [Å]		2.1166(9)	2.089(2)	2.088(2)	1.946(2)	2.438(2)	2.440(2)
Sc1–E2 [Å]		2.0836(9)	2.093(2)	2.102(2)			

^a Actor ligand E = μ -OH (**3a–c**), $\text{OAr}^{\text{tBu,tBu}}$ (**4b**), Cl (**5b**). α = dihedral angle between the phenyl rings; β = angle Ct–Sc–Ct between the phenyl rings; d = displacement from the $[\text{N}_2\text{O}_2]$ least-squares plane (geometry I, Chart 1). ^b Intramolecular symmetry. ^c Not determined. ^d Second SALEN ligand.

Scheme 2. High-Yield Protonolysis Reactions of $(\text{SALEN}^{\text{tBu,tBu}}\text{Sc}[\text{N}(\text{SiHMe}_2)_2])$ (**1a–c**) with $\text{HOAr}^{\text{tBu,tBu}}$, $\text{HOAr}^{\text{tPr,tPr}}$, and H_2O 

ONNO+N coordination environment in precursor (Salcyc) $\text{Sc}[\text{N}(\text{SiHMe}_2)_2]$ (**1c**).²⁰ The distance of the scandium atom from the N_2O_2 least-squares plane (0.73 Å, Table 1) is comparable to the respective displacement in **1c** (molecule 1, 0.68 Å; molecule 2, 0.69 Å). The Sc–O(Salcyc) and Sc–N(Salcyc) bond distances are almost identical in **4b** (Sc–O1, 1.963(2) Å; Sc–O2, 1.993(2) Å; Sc–N1, 2.227(2) Å; Sc–N2, 2.235(2) Å) and **1c** (molecule 1, Sc1–O1, 1.985(3) Å; Sc1–O2, 1.976(3) Å; Sc1–N1, 2.254(3) Å; Sc1–N2, 2.227(3) Å; molecule 2, Sc2–O3, 1.981(3) Å; Sc2–O4, 1.977(3) Å; Sc2–N4, 2.268(3) Å; Sc2–N5, 2.215(3) Å). However, less steric crowding in **4b** is indicated by a larger angle β (Ct–Sc–Ct) of 134.0° compared to that for **1c** (molecule 1, 127.8°; molecule 2, 127.3°). The Sc– $\text{OAr}^{\text{tBu,tBu}}$ bond length of 1.946(2) Å is comparable to the Sc–O(siloxide) distance of 1.901(2) Å in five-coordinated complex (Salen)Sc(OSi^tBuPh₂).²⁰ The longer Y– $\text{OAr}^{\text{tBu,tBu}}$ distance in (Salen)Y($\text{OAr}^{\text{tBu,tBu}}$)(thf) (2.128(2) Å) follows the trend in ionic radii and the higher coordination number.⁹ Attempted further ligand exchange with

$\text{LiCH}_2\text{SiMe}_3$ toward putative (Salen)Sc(CH_2SiMe_3) was not successful, and the orange decomposition products were not further characterized. Furthermore, attempted synthesis of such alkyl complexes from homoleptic $\text{Sc}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2$ was also unsuccessful.

Synthesis of [(SALEN)Sc(Cl)] Derivatives. We have previously introduced heteroleptic amide/chloride complexes $[\text{Ln}(\text{NiPr}_2)_2(\mu\text{-Cl})(\text{thf})_2]$ (Ln = Sc, Y) as efficient precursors according to an amine elimination/salt metathesis reaction sequence.²⁰ According to synthesis protocol A (Scheme 3), the reaction of $[\text{Sc}(\text{NiPr}_2)_2(\mu\text{-Cl})(\text{thf})_2]$ with H_2Salen or H_2Salcyc gave the dinuclear chloro-bridged derivatives $[(\text{Salen})\text{Sc}(\mu\text{-Cl})_2]$ and $[(\text{Salcyc})\text{Sc}(\mu\text{-Cl})_2]$.²⁰ We also examined the reaction of $[\text{Sc}(\text{NiPr}_2)_2(\mu\text{-Cl})(\text{thf})_2]$ with $\text{H}_2\text{Salpren}$, producing several nonseparable products (**B**, Scheme 3). To further investigate the feasibility of amido/chloro ligand exchange under mild conditions, (SALEN)- $\text{Sc}[\text{N}(\text{SiHMe}_2)_2]$ (**1a**, **1b**) were treated with NH_4Cl and stirred until clear solutions formed (**C**, **E**, Scheme 3). While the only side products— NH_3 and $\text{HN}(\text{SiHMe}_2)_2$ —could be re-

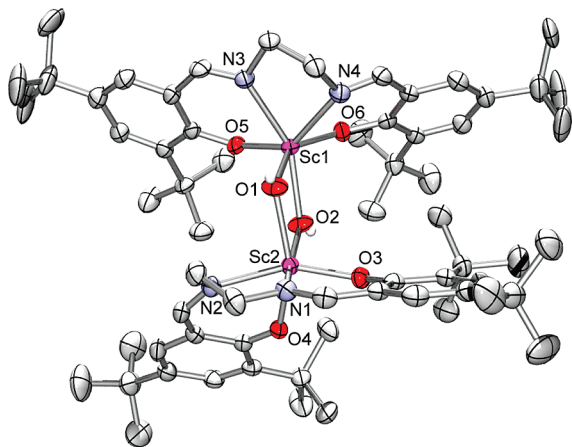


Figure 3. Solid-state structure of complex $[(\text{Salen})\text{Sc}(\mu\text{-OH})_2]$ (**3a**). Heavy atoms are represented by atomic displacement ellipsoids at the 50% level. Hydrogen atoms, except for H1O and H2O, and cocrystallized toluene are omitted for clarity.

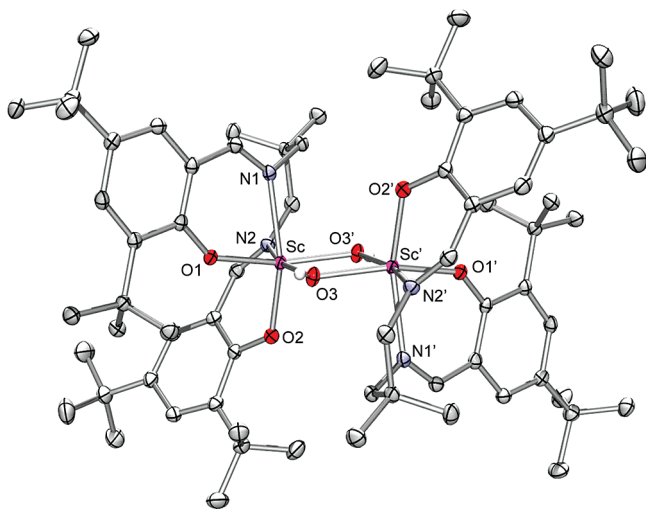


Figure 4. Solid-state structure of complex $[(\text{Salpren})\text{Sc}(\mu\text{-OH})_2]$ (**3b**). Heavy atoms are represented by atomic displacement ellipsoids at the 50% level. Hydrogen atoms, except for H1OH and H1OH', and cocrystallized C_6D_6 are omitted for clarity.

moved under reduced pressure, total consumption of the silylamido group was indicated by the complete disappearance of the Si–H band in the IR product spectra. If the reactions were performed in thf compounds, $(\text{Salen})\text{ScCl}(\text{thf})$ (**5a**) and $(\text{Salcyc})\text{ScCl}(\text{thf})$ (**5b**) could be isolated instead of $[(\text{SALEN})\text{Sc}(\mu\text{-Cl})_2]$ (**5**, Scheme 3).

Metal-coordinated thf was clearly revealed in the ^1H NMR spectrum of **5a** ($\delta = 1.29$ and 3.52 ppm; cf., noncoordinated thf in C_6D_6 , 1.40 and 3.57 ppm).²⁹ As reported previously, drying of the chloro exchange products under a vacuum was sufficient to completely remove any coordinated thf.²⁰ Removal of the coordinated donor solvent does, however, not markedly affect the magnetic environment of the SALEN ligand, resulting in almost identical ^1H NMR chemical shifts for the spectator ligands in **5** and $[(\text{SALEN})\text{Sc}(\mu\text{-Cl})_2]$. Formation of dimeric six-coordinate molecules after the removal of thf is plausible given the similar size of chloro and hydroxo ligands (cf., complexes **3a–c**). Complex **5** could

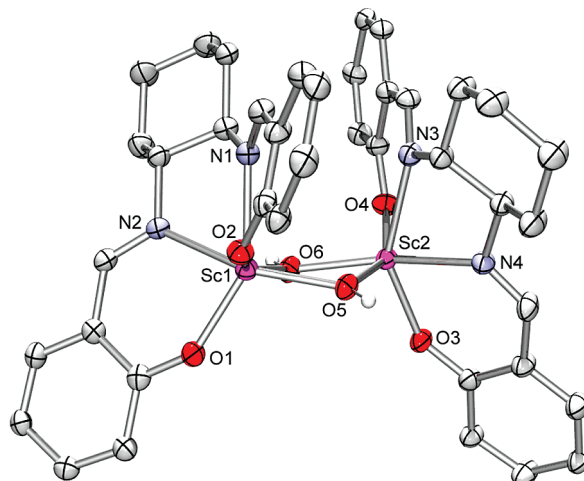


Figure 5. Solid-state structure of complex $[(\text{Salcyc})\text{Sc}(\mu\text{-OH})_2]$ (**3c**). Heavy atoms are represented by atomic displacement ellipsoids at the 50% level. Hydrogen atoms, except for H5O and H6O, *t*Bu-substitution in the 3- and 5- positions, and cocrystallized toluene are omitted for clarity.

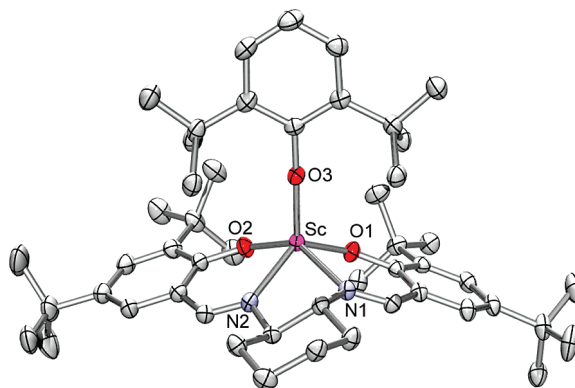
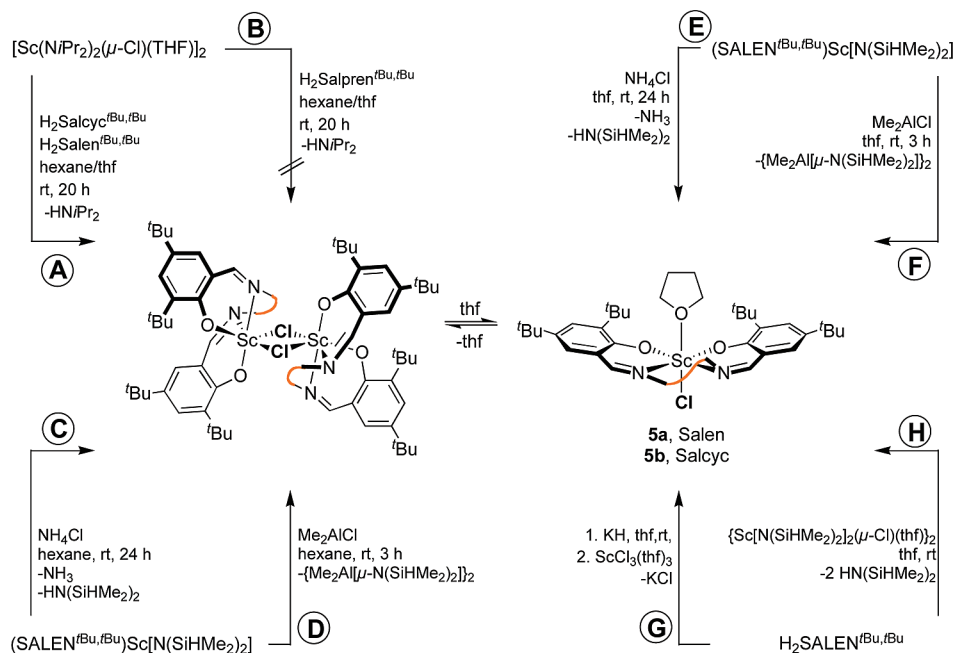


Figure 6. Solid-state structure of complex $(\text{Salcyc})\text{Sc}(\text{OAr}^{\text{tBu},\text{tBu}})$ (**4b**). Heavy atoms are represented by atomic displacement ellipsoids at the 50% level. Hydrogen atoms are omitted for clarity.

also be obtained according to approaches **D** and **F**, by reacting complexes **1a** and **1b** with Me_2AlCl , which also forms byproduct $\{\text{Me}_2\text{Al}[\mu\text{-N}(\text{SiHMe}_2)_2]\}_2$. Protocol **F** is less straightforward due to presence of thf and the formation of $\text{Me}_2\text{AlCl}(\text{thf})$; however, complete consumption of the $[\text{N}(\text{SiHMe}_2)_2]$ moieties was indicated by NMR spectroscopy. Synthesis approach **G** is certainly the fastest and easiest route toward **5a,b** and was exploited previously by Evans et al. and Gambarotta et al. for the synthesis of $[(\text{Salen})\text{Y}(\mu\text{-Cl})(\text{thf})_2]$ from YCl_3 and K_2Salen and $(\text{Salophen})\text{SmCl}(\text{OEt})$ ($\text{H}_2\text{Salophen} = N,N'$ -phenylenebis(3,5-di-*tert*-butyl-salicylideneimine)) from $\text{SmCl}_3(\text{thf})_3$ and the corresponding sodium salt, respectively.^{5,6} Unlike what was reported for yttrium, we used the thf adduct $\text{ScCl}_3(\text{thf})_3$ rather than the less soluble/reactive ScCl_3 . Such salt metathesis reactions potentially involve ate complexation. Deacon et al. reported on the reaction of anhydrous NdCl_3 with $\text{Na}_2(\text{Salpn})(\text{thf})$ ($\text{H}_2\text{Salpn} = N,N'$ -propylenebis(salicylideneimine)) yielding an insoluble precipitate of unknown composition. The same reaction with $\text{NdCl}_3 \times 2(\text{LiCl})$ gave complex $\{[\text{Nd}(\text{salpn})(\text{thf})\text{Cl}][\text{LiCl}(\text{thf})_2]\}_2$, which was structurally characterized.⁷

Contrary to $[\text{Sc}(\text{NiPr}_2)_2(\mu\text{-Cl})(\text{thf})_2]$, the analogous bis-(dimethylsilyl)amide complexes can only be obtained as mixtures of $[\text{Sc}[\text{N}(\text{SiHMe}_2)_2]_2(\mu\text{-Cl})(\text{thf})_2]$ and $\text{Sc}[\text{N}(\text{SiHMe}_2)_2]_2(\mu\text{-Cl})(\text{thf})_2$.

(29) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512–7515.

Scheme 3. Different Synthesis Protocols for Dimeric and Monomeric Sc–SALEN Chloride Complexes^a

^a Products $[(\text{Salen})\text{Sc}(\mu\text{-Cl})_2]$ and $(\text{Salen})\text{ScCl}(\text{thf})$ (**5a**) represent likely coordination geometries. Approaches C–H were only carried out for SALEN = Salen, Salcyc.

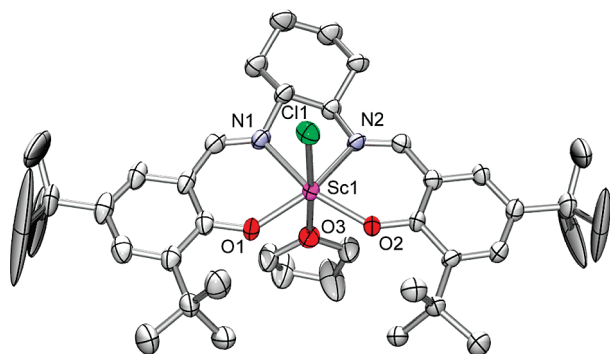


Figure 7. Solid-state structure of complex $(\text{Salcyc})\text{ScCl}(\text{thf})$ (**5b**, molecule one out of two). Heavy atoms are represented by atomic displacement ellipsoids at the 50% level. Hydrogen atoms and cocrystallized thf are omitted for clarity.

$\text{HMe}_2)_3(\text{thf})$.³⁰ The protonolysis reaction with H_2SALEN will therefore give a mixture of **1** and $(\text{SALEN})\text{ScCl}$, and we were fortunate to isolate the first monomeric scandium SALEN chloride complex, **5b**, from the reaction products. Admittedly, separation of **5b** from **1c** is only possible by fractional crystallization due to the high solubility of both complexes in noncoordinating solvents such as hexane. Compound **5b** could be fully characterized by NMR/IR spectroscopy and elemental analysis and crystallizes in the monoclinic space group $P2_1$ with two independent molecules in the unit cell (Figure 7). The scandium center in **5b** is octahedrally coordinated by one chloro ligand, one thf, and the Salcyc ligand (geometry **III**, Chart 1), reminiscent of the cationic fragment in $[(\text{Salen})\text{Sc}(\text{thf})_2][\text{BPh}_4]$.¹⁹ The scandium center in **5b** is well-embedded into the Salcyc ligand, as revealed by a metal center displacement of

0.20 Å from the N_2O_2 least-squares plane. However, the salicylidene groups are not coplanar, showing an angle β (Ct–Sc–Ct) of 162.8° (molecule 2: 161.6°), which compares to the aforementioned cationic complex ($\text{Sc}-\text{N}_2\text{O}_2 = 0.02$ Å, β (Ct–Sc–Ct) = 169.1°).¹⁹ Despite the different ligand imino backbone, the Sc–N and Sc–O distances in **5b** (molecule 1, Sc1–O1, 1.973(5) Å; Sc1–O2, 1.981(5) Å; Sc1–N1, 2.237(6) Å; Sc1–N2, 2.245(6) Å; molecule 2, Sc2–O4, 1.970(5) Å; Sc2–O5, 1.976(5) Å; Sc2–N3, 2.235(6) Å; Sc2–N4, 2.219(6) Å) match those in $[(\text{Salen})\text{Sc}(\text{thf})_2][\text{BPh}_4]$ (Sc1–O1, 1.973(2) Å; Sc1–O2, 1.967(2) Å; Sc1–N1, 2.233(2) Å; Sc1–N2, 2.222(2) Å). It is noteworthy that the Sc–O(thf) distances (Sc–O3, 2.177(2) Å; Sc–O4, 2.154(2) Å) in the latter cationic complex are shorter than in **5b** (molecule 1, Sc–O3, 2.287(5) Å; molecule 2, Sc–O6, 2.284(4) Å). The Sc–Cl bond distance of 2.438(2) Å (molecule 2, 2.440(2) Å) is comparable to the terminal Sc–Cl distance in monomeric complexes such as $\text{Sc}(\text{N}_2^{\text{TMS}}\text{Npy})\text{Cl}(\text{thf})$ (2.4426(7) Å; $\text{N}_2^{\text{TMS}}\text{Npy} = \text{MeC}(\text{C}_5\text{H}_4\text{N})(\text{CH}_2\text{NSiMe}_3)_2$) but, as expected, is shorter than in the dimeric precursor compound $[\text{Sc}[\text{N}(\text{SiHMe}_2)_2]_2(\mu\text{-Cl})(\text{thf})_2]$ (av. Sc–Cl, 2.56 Å).³⁰

Conclusions

Heteroleptic scandium SALEN amide complexes $(\text{SALEN})\text{Sc}[\text{N}(\text{SiHMe}_2)_2]$ can be easily converted into hydroxy, aryloxy, and chloride derivatives. In particular, protonolysis via treatment of $(\text{SALEN})\text{Sc}[\text{N}(\text{SiHMe}_2)_2]$ with NH_4Cl proved to be a viable route for the high-yield synthesis of discrete $(\text{SALEN})\text{ScCl}(\text{thf})_x$ complexes. The X-ray structural analyses of hydrolyzed complexes $[(\text{SALEN})\text{Sc}(\mu\text{-OH})_2]$ revealed a strong bonding of the chelating dianionic $[\text{ONNO}]$ ligands, which has important implications for their use as

(30) Meermann, C.; Törnroos, K. W.; Nerdal, W.; Anwander, R. *Angew. Chem., Int. Ed.* **2007**, *46*, 6508–6513.

versatile homogeneous Lewis acid catalysts. Moreover, distinct coordination features of the SALEN ligands are indicated in the solid state: the intrinsic SALEN bending increases (decreasing $\angle\beta$) in the order Salen < Salcyc < Salpren, depending on the nature of the ligand backbone. The formation of the homoleptic species $\text{Sc}_2(\text{Salpren})_3$ emphasizes ligand backbone conformational flexibility of the Salpren ligand, encouraging alternative ancillary ligand coordination such as intermolecular bridging and multiple coordination.

Experimental Section

General Considerations: Techniques and Reagents. All of the manipulations of metal complexes were performed under the rigorous exclusion of air and moisture in an argon-filled glovebox (MB Braun MB150B-G-II; <1 ppm O_2 , <1 ppm H_2O). Solvent pretreatment/purification was performed with Grubbs columns (MBraun SPS, solvent purification system). C_6D_6 was obtained from Aldrich, degassed, dried over Na for 24 h, filtered, and stored in a glovebox. $\text{Li}[\text{N}(\text{SiHMe}_2)_2]$ was prepared from $\text{HN}(\text{SiHMe}_2)_2$ (Aldrich) and *n*-butyllithium (Aldrich). Me_2AlCl , KH, 2,6-di-*tert*-butylphenol, and 2,6-diisopropylphenol were ordered from Aldrich and used as received. NH_4Cl (Aldrich) was sublimed before use. $\text{Sc}[\text{N}(\text{SiHMe}_2)_2]_3(\text{thf})^{31}$ and $(\text{SALEN})\text{Sc}[\text{N}(\text{SiHMe}_2)_2]^{20}$ were synthesized according to literature procedures. The SALEN ligand precursors were synthesized according to slightly modified literature procedures through a condensation reaction of salicylaldehyde derivative 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (Aldrich) with the corresponding diamines 1,2-ethylenediamine (Aldrich), 1,3-diamino-2,2-dimethylpropane (Aldrich), and (1*R*,2*R*)-(-)-1,2-diaminocyclohexane (Fluka).

NMR data were obtained in a C_6D_6 solution at 25 °C on a Bruker DMX-400 Avance (^1H , 400.13 MHz; ^{13}C , 100.61 MHz) and a Bruker-BIOSPIN-AV600 (5 mm cryo probe; ^1H , 600.13 MHz; ^{13}C , 150.91 MHz). ^1H and ^{13}C shifts are referenced to internal solvent resonances and reported relative to TMS. IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer using Nujol mulls sandwiched between CsI plates. Elemental analyses were performed on an Elementar Vario EL III.

$\text{Sc}_2(\text{Salpren})_3$ (2). $\text{Sc}[\text{N}(\text{SiHMe}_2)_2]_3(\text{thf})$ (115 mg, 0.22 mmol) was dissolved in 8 mL of hexane and 1.5 equiv of $\text{H}_2\text{Salpren}$ (179 mg, 0.34 mmol) in 3 mL of thf. The clear yellow solution was stirred for 6 days and the solvent removed under vacuum to give complex **2** as a dark yellow powder in almost quantitative yield (370 mg, 0.22 mmol, 98%). ^1H NMR (500 MHz, C_6D_6): 8.10 (s, 1H), 7.97 (s, 1H), 7.70 (m, 3H), 7.66 (m, 1H), 7.60 (s, 2H), 7.55 (m, 3H), 7.37 (s, 1H), 7.32 (s, 1H), 7.19 (d, 1H), 7.11 (s, 2H), 7.06 (s, 1H), 7.04 (s, 1H), 4.71 (d, 2H, $^2J_{\text{HH}} = 10.5$ Hz, N(CHH)), 4.13 (d, 1H, $^2J_{\text{HH}} = 12.5$ Hz, N(CHH)), 4.01 (d, 1H, $^2J_{\text{HH}} = 12.5$ Hz, N(CHH)), 3.75 (d, 1H, $^2J_{\text{HH}} = 10.5$ Hz, N(CHH)), 3.58 (d, 1H, $^2J_{\text{HH}} = 11.5$ Hz, N(CHH)), 2.86 (d, 2H, $^2J_{\text{HH}} = 12.5$ Hz, N(CHH)), 2.80 (d, 1H, $^2J_{\text{HH}} = 12.5$ Hz, N(CHH)), 2.65 (d, 1H, $^2J_{\text{HH}} = 12.5$ Hz, N(CHH)), 2.59 (d, 1H, $^2J_{\text{HH}} = 11.5$ Hz, N(CHH)), 2.28 (d, 1H, $^2J_{\text{HH}} = 10.5$ Hz, N(CHH)), 1.57 (s, 9H, *t*Bu), 1.52 (s, 27H, *t*Bu), 1.46 (s, 9H, *t*Bu), 1.45 (s, 9H, *t*Bu), 1.41 (s, 27H, *t*Bu), 1.34 (m, 9H, $\text{C}(\text{CH}_3)_2$), 1.31 (s, 18H, *t*Bu), 0.88 (m, 9H, $\text{C}(\text{CH}_3)_2$). IR (Nujol; cm^{-1}): 1612s (C=N), 1536m, 1317m, 1257m, 1170m,

1074w, 841w, 748w, 659w, 540w, 480w. Anal. calcd for $\text{C}_{105}\text{H}_{156}\text{N}_6\text{O}_6\text{Sc}_2$: C, 74.70; H, 9.31; N, 4.98. Found: C, 74.6; H, 9.3; N, 4.7.

$(\text{Salen})\text{Sc}(\mu\text{-OH})_2$ (3a). $(\text{Salen})\text{Sc}[\text{N}(\text{SiHMe}_2)_2]$ (30 mg, 0.04 mmol) was loaded into a Schlenk flask and dissolved in 2 mL of hexane. Outside the glovebox, excess H_2O was added to the yellow solution. Evaporation of the solvent under a vacuum gave a yellow powder, which was dissolved in toluene. Storage of the solution at ambient temperature produced single-crystalline complex **3a** as yellow cubes (7 mg, 0.006 mmol, 32%). ^1H NMR (600 MHz, C_6D_6): 7.65 (s, 4H, CH=N), 7.56 (s, 4H, CH_{Ar}), 6.99 (s, 4H, CH_{Ar}), 3.47 (dd, 4H, $^2J_{\text{HH}} = 12.6$ Hz, $^3J_{\text{HH}} = 6.6$ Hz, N(CHH) $_2$ N), 3.29 (s, 2H, OH), 2.71 (dd, 4H, $^2J_{\text{HH}} = 12.6$ Hz, $^3J_{\text{HH}} = 6.0$ Hz, N(CHH) $_2$ N), 1.68 (s, 36H, *t*Bu), 1.34 (s, 36H, *t*Bu). ^{13}C NMR (100.6 MHz, C_6D_6): 167.6 (CH=N), 163.7 (C-2), 139.1 (C_{Ar}), 136.4 (C_{Ar}), 129.0 (CH_{Ar}), 122.1 (C-1), 58.3 (N(CH $_2$) $_2$ N), 35.6 (*t*Bu), 33.9 (*t*Bu), 31.6 (*t*Bu), 29.9 (*t*Bu). IR (Nujol; cm^{-1}): 3690m (OH), 1621s (C=N), 1551m, 1533m, 1412m, 1336m, 1269vs, 1197m, 1057w, 866w, 793w, 744m, 550m, 483w. Anal. calcd for $\text{C}_{64}\text{H}_{94}\text{N}_4\text{O}_6\text{Sc}_2 \times \text{C}_{18}\text{H}_{24}$: C, 73.18; H, 8.84; N, 4.16. Found: C, 73.2; H, 8.5; N, 3.8.

$(\text{Salpren})\text{Sc}(\mu\text{-OH})_2$ (3b). A NMR sample of $(\text{Salpren})\text{Sc}[\text{N}(\text{SiHMe}_2)_2]$ (10 mg, 0.01 mmol) in 0.5 mL of C_6D_6 was stored outside the glovebox. After several days, single crystals could be harvested and identified as **3b**. ^1H NMR (400 MHz, CDCl_3): 7.92 (s, 4H), 7.34 (d, 4H, $^4J_{\text{HH}} = 2.8$ Hz, CH_{Ar}), 6.92 (d, 4H, $^4J_{\text{HH}} = 2.8$ Hz, CH_{Ar}), 4.30 (d, 4H, $^2J_{\text{HH}} = 12.0$ Hz, N(CHH)), 3.52 (s, 2H, OH), 3.08 (d, 4H, $^2J_{\text{HH}} = 12.0$ Hz, N(CHH)), 1.38 (s, 36H, *t*Bu), 1.24 (s, 36H, *t*Bu), 1.04 (s, 6H, $\text{C}(\text{CH}_3)_2$), 0.80 (s, 6H, $\text{C}(\text{CH}_3)_2$). ^{13}C NMR (100.6 MHz, CDCl_3): 168.7 (CH=N), 163.0 (C-2), 138.3 (C_{Ar}), 136.3 (C_{Ar}), 129.0 (CH_{Ar}), 128.2 (CH_{Ar}), 125.3, 121.0 (C-1), 74.3 (N(CHH)), 36.7 (*t*Bu), 35.4 (*t*Bu), 31.4 (*t*Bu), 29.8 (*t*Bu), 29.4 (*t*Bu), 27.1 ($\text{C}(\text{CH}_3)_2$), 22.8 ($\text{C}(\text{CH}_3)_2$). IR (Nujol; cm^{-1}): 3700w (OH), 1612vs (C=N), 1536m, 1412m, 1330m, 1317m, 1256s, 1201s, 1072m, 915w, 876w, 841m, 812w, 786m, 657s, 542s, 482s, 467s. Anal. calcd for $\text{C}_{70}\text{H}_{106}\text{N}_4\text{O}_6\text{Sc}_2 \times (\text{C}_7\text{H}_8)$: C, 72.16; H, 8.97; N, 4.37. Found: C, 72.5; H, 9.1; N, 4.2.

$(\text{Salcyc})\text{Sc}(\mu\text{-OH})_2$ (3c). Single crystals of **3c** were originally obtained when storing a reaction mixture of $[(\text{Salcyc})\text{ScCl}]$ and $\text{NaC}_5\text{Me}_4\text{H}$ in toluene/thf outside the glovebox, of course aiming at $(\text{Salcyc})\text{Sc}(\text{C}_5\text{Me}_4\text{H})$. ^1H NMR (600 MHz, C_6D_6): 7.81 (s, 2H, CH=N), 7.71–7.72 (m, 4H, CH=N, CH_{Ar}), 7.64 (d, 2H, $^4J_{\text{HH}} = 2.4$ Hz, CH_{Ar}), 7.22 (d, 2H, $^4J_{\text{HH}} = 2.4$ Hz, CH_{Ar}), 7.11 (m, 4H, CH_{Ar}), 3.77 (ddd, 2H, $^3J_{\text{HaHa}} = 10.8$ Hz, N(CH $_q$)), 3.56 (s, 2H, OH), 2.20 (ddd, 2H, $^3J_{\text{HaHa}} = 10.8$ Hz, N(CH $_q$)), 1.78 (s, 18H, *t*Bu), 1.69 (s, 18H, *t*Bu), 1.53–1.32 (m, 8H, $\text{CH}_{2,\beta}$), 1.43 (s, 18H, *t*Bu), 1.39 (s, 18H, *t*Bu), 0.83–0.61 (m, 8H, $\text{CH}_{2,\gamma}$). ^{13}C NMR (100.6 MHz, C_6D_6): 168.4 (CH=N), 164.1 (C-2), 163.4 (C-2'), 160.8 (CH=N), 140.1 (C_{Ar}), 139.4 (C_{Ar}), 137.0 (C_{Ar}), 136.2 (C_{Ar}), 129.6 (CH_{Ar}), 129.1 (CH_{Ar}), 128.9 (CH_{Ar}), 128.5 (CH_{Ar}), 122.5 (C-1), 70.6 [N(CH $_q$)], 66.1 [N(CH $_q$)], 36.0 (*t*Bu), 35.8 (*t*Bu), 34.2 ($\text{CH}_{2,\beta}$), 32.4 (*t*Bu), 31.9 (*t*Bu), 30.2 ($\text{CH}_{2,\beta}$), 27.6 ($\text{CH}_{2,\gamma}$), 25.3 ($\text{CH}_{2,\beta}$). Anal. calcd for $\text{C}_{72}\text{H}_{106}\text{N}_4\text{O}_6\text{Sc}_2$: C, 71.26; H, 8.80; N, 4.62. Found: C, 70.0; H, 7.0; N, 3.9.

General Procedure for the Synthesis of Scandium SALEN Aryloxide Complexes 4. 2,6-Di-*tert*-butylphenol or 2,6-diisopropylphenyl was added to a stirred solution of the respective scandium SALEN bis(dimethylsilyl)amide complex $(\text{SALEN})\text{Sc}[\text{N}(\text{SiHMe}_2)_2]$ in hexane. After the yellow solution had been stirred for 2 h, the solvent was removed in vacuo. The obtained yellow powders were crystallized from toluene and identified as monomeric complexes **4a**, **4b**, and **4c**.

$(\text{Salen})\text{Sc}(\text{OC}_6\text{H}_3\text{tBu}_2\text{-2,6})$ (4a). Following the procedure described above, $(\text{Salen})\text{Sc}[\text{N}(\text{SiHMe}_2)_2]$ (90 mg, 0.13 mmol) and

(31) Anwander, R.; Runte, O.; Eppinger, J.; Gerstberger, G.; Herdtweck, E.; Spiegler, M. *J. Chem. Soc., Dalton Trans.* **1998**, 847–858.

Table 2. Crystallographic Parameters for Compounds **2**, **3a–c**, **4b**, and **5b**

	2	3a	3b
chemical formula	C ₁₀₅ H ₁₅₆ N ₆ O ₆ Sc ₂	C ₁₆₃ H ₂₂₈ N ₈ O ₁₂ Sc ₄	C ₁₀₆ H ₁₄₂ N ₄ O ₆ Sc ₂
<i>M_r</i>	1688.28	2671.37	1658.16
cryst syst	monoclinic	orthorhombic	triclinic
space group	<i>C2/c</i>	<i>Pba2</i>	<i>P1</i>
<i>a</i> /Å	20.5546(15)	19.2322(4)	11.5238(4)
<i>b</i> /Å	22.3221(16)	23.6954(6)	12.6700(4)
<i>c</i> /Å	28.192(2)	17.3634(3)	17.5146(6)
α/deg	90.00	90.00	79.829(1)
β/deg	98.122(1)	90.00	73.811(1)
γ/deg	90.00	90.00	83.451(1)
<i>V</i> /Å ³	12805.4(16)	7912.8(3)	2411.56(14)
<i>Z</i>	4	2	1
<i>F</i> (000)	3672	2884	896
<i>T</i> /K	123(2)	183(2)	123(2)
ρ _{calcd} /g cm ^{−3}	0.876	1.121	1.142
μ/mm ^{−1}	0.148	0.223	0.195
<i>R</i> ₁ (obsd) ^a	0.0805	0.0407	0.0496
<i>wR</i> ₂ (all) ^b	0.2416	0.0926	0.1255
<i>S</i> ^c	1.014	0.915	1.039

	3c	4b	5b
chemical formula	C ₁₀₇ H ₁₄₆ N ₄ O ₆ Sc ₂	C ₅₀ H ₇₃ N ₂ O ₃ Sc	C ₅₂ H ₈₄ ClN ₂ O ₆ Sc
<i>M_r</i>	1674.20	795.06	913.62
cryst syst	orthorhombic	orthorhombic	monoclinic
space group	<i>P2₁2₁2₁</i>	<i>P2₁2₁2₁</i>	<i>P2₁</i>
<i>a</i> /Å	14.7536(9)	10.9304(3)	11.8966(6)
<i>b</i> /Å	17.7288(11)	17.4215(5)	27.1729(13)
<i>c</i> /Å	38.311(2)	25.1227(7)	16.5478(8)
α/deg	90.00	90.00	90.00
β/deg	90.00	90.00	99.805(1)
γ/deg	90.00	90.00	90.00
<i>V</i> /Å ³	10020.8(11)	4784.0(2)	5271.2(4)
<i>Z</i>	4	4	4
<i>F</i> (000)	3624	1728	1984
<i>T</i> /K	103(2)	123(2)	123(2)
ρ _{calcd} /g cm ^{−3}	1.110	1.104	1.151
μ/mm ^{−1}	0.188	0.194	0.237
<i>R</i> ₁ (obsd) ^a	0.0501	0.0340	0.0660
<i>wR</i> ₂ (all) ^b	0.1434	0.0830	0.1956
<i>S</i> ^c	1.078	1.027	1.031

^a $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$, $F_o > 4\sigma(F_o)$. ^b $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. ^c $S = [\sum(w(F_o^2 - F_c^2)^2)/(n_o - n_p)]^{1/2}$.

HOAr^{*t*Bu},^{*t*Bu} (28 mg, 0.13 mmol) gave **4a** (97 mg, 0.13 mmol, >99%). ¹H NMR (600 MHz, C₆D₆): 7.75 (d, 2H, ³*J*_{HH} = 7.8 Hz, OAr), 7.63 (s, 2H, CH=N), 7.50 (d, 2H, ⁴*J*_{HH} = 2.4 Hz, CH_{Ar}), 7.07 (d, 2H, ⁴*J*_{HH} = 2.4 Hz, CH_{Ar}), 6.81 (t, 1H, ³*J*_{HH} = 7.8 Hz, OAr), 3.67 (dd, 2H, ²*J*_{HH} = 12.6 Hz, ³*J*_{HH} = 6.0 Hz, N(CHH)₂N), 2.77 (dd, 2H, ²*J*_{HH} = 12.6 Hz, ³*J*_{HH} = 6.0 Hz, N(CHH)₂N), 1.74 (s, 18H, *t*Bu), 1.41 (s, 18H, *t*Bu), 1.34 (s, 18H, OAr). ¹³C NMR (100.6 MHz, C₆D₆): 169.9 (CH=N), 163.9 (C-2), 162.8 (OAr), 139.6 (C_{Ar}), 138.5 (C_{Ar}), 136.0 (OAr), 130.9 (CH_{Ar}), 128.5 (CH_{Ar}), 125.4 (OAr), 122.2 (C-1), 117.7 (OAr), 57.6 (N(CH₂)₂N), 35.9 (*t*Bu), 34.9 (*t*Bu), 34.3 (OAr), 31.7 (*t*Bu), 30.7 (OAr), 30.4 (*t*Bu). IR (Nujol; cm^{−1}): 1634 (OAr), 1618s (C=N), 1551m, 1536m, 1412s, 1309m, 1242vs, 1201m, 1051w, 984m, 876w, 744m, 542m. Anal. calcd for C₄₆H₆₇N₂O₃Sc: C, 74.56; H, 9.11; N, 3.78. Found: C, 72.2; H, 9.0; N, 3.8.

(Salcyc)Sc(OC₆H₃^{*i*Bu}-2,6) (**4b**). Following the procedure described above, (Salcyc)Sc[N(SiHMe₂)₂] (40 mg, 0.05 mmol) and HOAr^{*t*Bu},^{*t*Bu} (11 mg, 0.05 mmol) gave **4b** (43 mg, 0.05 mmol, >99%). ¹H NMR (600 MHz, C₆D₆): 7.94 (s, 2H, CH=N), 7.81 (d, 1H, ⁴*J*_{HH} = 3.0 Hz, CH_{Ar}), 7.77 (d, 1H, ⁴*J*_{HH} = 3.0 Hz, CH_{Ar}), 7.34 (d, 1H, ⁴*J*_{HH} = 3.0 Hz, CH_{Ar}), 7.27 (d, 2H, ³*J*_{HH} = 7.8 Hz, OAr), 7.18 (d, 1H, ⁴*J*_{HH} = 3.0 Hz, CH_{Ar}), 6.80 (t, 1H, ³*J*_{HH} = 7.8 Hz, OAr), 3.97 (ddd, 2H, ³*J*_{HaHa} = 11.4 Hz, N(CH₂)), 2.34 (ddd, 2H, ³*J*_{HaHa} = 11.4 Hz, N(CH₂)), 1.78 (s, 9H, *t*Bu), 1.76 (s, 9H, *t*Bu),

1.53–1.48 (m, 4H, CH_{2β}), 1.42 (s, 18H, *t*Bu), 1.36 (d, 18H, 3 Hz, *t*Bu), 1.25–1.14 (m, 4H, CH_{2γ}). ¹³C NMR (100.6 MHz, C₆D₆): 169.0 (CH=N), 163.9 (C-2), 163.6 (C-2'), 163.5, 162.8 (OAr), 139.7 (C_{Ar}), 139.6 (C_{Ar}), 138.8 (C_{Ar}), 138.6 (OAr), 138.3 (C_{Ar}), 131.1 (CH_{Ar}), 130.6 (CH_{Ar}), 129.0 (CH_{Ar}), 128.9 (CH_{Ar}), 125.0 (OAr), 123.1, 122.8 (C-1), 117.7 (OAr), 70.8 [N(CH₂)], 65.1 [N(CH₂)], 38.6 (OAr), 36.0 (*t*Bu), 35.9 (*t*Bu), 34.9 (CH_{2β}), 34.2 (OAr), 31.7 (*t*Bu), 31.0 (*t*Bu), 30.5 (CH_{2β}), 30.4 (CH_{2γ}), 30.2 (CH_{2γ}). Anal. calcd for C₅₀H₇₃N₂O₃Sc: C, 75.53; H, 9.25; N, 3.52. Found: C, 75.6; H, 9.1; N, 3.3.

(Salcyc)Sc(OC₆H₃^{*i*Pr}-2,6) (**4c**). Following the procedure described above, (Salcyc)Sc[N(SiHMe₂)₂] (100 mg, 0.14 mmol) and HOAr^{*i*Pr},^{*i*Pr} (25 mg, 0.14 mmol) gave **4c** (40 mg, 0.05 mmol, 38%), upon extraction with toluene from the crude reaction mixture. ¹H NMR (600 MHz, C₆D₆): 8.00 (s, 1H, CH=N), 7.90 (s, 1H, CH=N), 7.79 (d, 1H, ⁴*J*_{HH} = 3.0 Hz, CH_{Ar}), 7.75 (d, 1H, ⁴*J*_{HH} = 3.0 Hz, CH_{Ar}), 7.30 (d, 1H, ⁴*J*_{HH} = 3.0 Hz, CH_{Ar}), 7.18 (d, 1H, ⁴*J*_{HH} = 3.0 Hz, CH_{Ar}), 7.06 (d, 2H, ³*J*_{HH} = 7.8 Hz, OAr), 6.87 (t, 1H, ³*J*_{HH} = 7.8 Hz, OAr), 3.66 (ddd, 2H, ³*J*_{HaHa} = 11.4 Hz, N(CH₂)), 3.44 (s, br, 2H, *i*Pr), 2.36 (ddd, 2H, ³*J*_{HaHa} = 11.4 Hz, N(CH₂)), 1.83 (s, 9H, *t*Bu), 1.76 (s, 9H, *t*Bu), 1.47–1.41 (m, 4H, CH_{2β}), 1.38 (s, 18H, *t*Bu), 1.28–1.20 (m, 4H, CH_{2γ}), 1.17 (d, 6H, ³*J*_{HH} = 7.8 Hz, *i*Pr), 1.06 (d, 6H, ³*J*_{HH} = 7.8 Hz, *i*Pr). ¹³C NMR (100.6 MHz, C₆D₆): 168.2 (CH=N), 163.7 (C-2), 163.5 (C-2'), 163.4 (OAr), 139.7 (C_{Ar}), 139.8 (C_{Ar}), 139.7 (C_{Ar}), 138.5 (OAr), 138.3 (C_{Ar}), 130.8 (CH_{Ar}), 130.6 (CH_{Ar}), 129.0 (CH_{Ar}), 128.8 (CH_{Ar}), 123.0 (OAr), 122.6 (C-1), 69.9 [N(CH₂)], 66.0 [N(CH₂)], 36.0 (*t*Bu), 35.9 (*t*Bu), 34.3 (CH_{2β}), 31.8 (*t*Bu), 30.1 (CH_{2β}), 30.0 (CH_{2γ}), 27.4 (CH_{2γ}), 24.8 (OAr), 23.5 (OAr). IR (Nujol; cm^{−1}): 1634s (OAr), 1613vs (C=N), 1552m, 1534s, 1412w, 1272s, 1254s, 1202m, 1095w, 1028w, 922w, 897m, 876m, 842w, 784w, 744m, 592w, 540m. Anal. calcd for C₄₈H₆₉N₂O₃Sc: C, 75.16; H, 9.07; N, 3.65. Found: C, 76.0; H, 8.7; N, 3.5.

Synthesis of Scandium SALEN Chloride Complexes 5. The chloride complexes **5a** and **5b** were synthesized by different synthesis approaches (Scheme 3). Data reported for **5** were obtained from complexes synthesized by approach **E** or **G**.

General Procedure for Route E (Scheme 3). The amide complexes (SALEN)Sc[N(SiHMe₂)₂] (**1a–c**) were dissolved in 5 mL of thf and 1 equiv of NH₄Cl was added. The reaction mixtures were stirred until all NH₄Cl had dissolved (3–5 days). After evaporation of the volatiles under reduced pressure, **5a** and **5b** were received as yellow powders.

(Salen)Sc(Cl)(thf) (**5a**). When the procedure for route **E** was followed, (Salen)Sc[N(SiHMe₂)₂] (85 mg, 0.13 mmol) and NH₄Cl (7 mg, 0.13 mmol) gave **5a** (80 mg, 0.12 mmol, 98%). ¹H NMR (600 MHz, C₆D₆): 7.72 (s, 2H, CH=N), 7.50 (s, 2H, CH_{Ar}), 7.00 (s, 2H, CH_{Ar}), 3.68 (d, 2H, ³*J*_{HH} = 6.0 Hz, N(CHH)₂N), 3.52 (s, 4H, thf), 2.72 (d, 2H, ³*J*_{HH} = 6.0 Hz, N(CHH)₂N), 1.72 (s, 18H, *t*Bu), 1.37 (s, 18H, *t*Bu), 1.29 (s, 4H, thf). ¹³C NMR (100.6 MHz, C₆D₆): 168.0 (CH=N), 163.0 (C-2), 139.3 (C_{Ar}), 138.1 (C_{Ar}), 130.1 (CH_{Ar}), 128.5 (CH_{Ar}), 122.7 (C-1), 68.5 (thf), 59.0 (N(CH₂)₂N), 35.8 (*t*Bu), 34.2 (*t*Bu), 31.8 (*t*Bu), 30.1 (*t*Bu), 25.6 (thf). IR (Nujol; cm^{−1}): 1621vs (C=N), 1553m, 1538m, 1415m, 1316m, 1279m, 1259m, 1202w, 1171s, 1047w, 969w, 912w, 886w, 866m, 840m, 809w, 783w, 752m, 550s, 478m. Anal. calcd for C₃₆H₅₄ClN₂O₃Sc: C, 67.22; H, 8.46; N, 4.36. Found: C, 65.5; H, 8.4; N, 4.4.

(Salcyc)Sc(Cl)(thf) (**5b**). When the procedure for route **E** was followed, (Salcyc)Sc[N(SiHMe₂)₂] (106 mg, 0.14 mmol) and NH₄Cl (8 mg, 0.15 mmol) gave **5b** (104 mg, 0.15 mmol, >99%). ¹H NMR (600 MHz, C₆D₆): 7.83 (s, 1H, CH=N), 7.76 (m, 3H, CH=N, CH_{Ar}), 7.25 (d, 1H, ⁴*J*_{HH} = 3 Hz, CH_{Ar}), 7.10 (s, 1H, CH_{Ar}), 4.22 (ddd, 1H, ³*J*_{HaHa} = 10.2 Hz, N(CH₂)), 3.56 (s, 4H, thf), 2.34 (ddd,

^1H , $^3J_{\text{H}\alpha\text{H}\alpha} = 10.2$ Hz, $\text{N}(\text{CH}_\alpha)$, 1.75 (s, 9 H, *t*Bu), 1.74 (s, 9 H, *t*Bu), 1.55–1.47 (m, 4H, $\text{CH}_{2,\beta}$), 1.45 (s, 9H, *t*Bu), 1.39 (s, 9H, *t*Bu), 1.35 (m, 4H, thf), 0.94–0.69 (m, 4H, $\text{CH}_{2,\gamma}$). Anal. calcd for $\text{C}_{40}\text{H}_{60}\text{ClN}_2\text{O}_3\text{Sc}$: C, 68.90; H, 8.67; N, 4.02. Found: C, 67.6; H, 8.6; N, 4.0.

General Procedure for Route G (Scheme 3). According to a slightly modified literature procedure, as described for $[(\text{Salen})\text{Y}(\mu\text{-Cl})(\text{thf})]_2$,⁵ the proligands H_2SALEN were dissolved in thf, and 2 equiv of KH were added. After gas evolution had ceased, $\text{ScCl}_3(\text{thf})_3$ was added to the clear yellow solutions. The reaction was stirred overnight and, afterwards, the formed precipitate separated and extracted with thf. Solvent removal from the combined thf fractions gave complexes **5a** and **5b** as a yellow powder.

(Salen)Sc(Cl)(thf) (5a). When the procedure for route **G** was followed, H_2Salen (246 mg, 0.50 mmol), KH (40 mg, 1.00 mmol), and $\text{ScCl}_3(\text{thf})_3$ (184 mg, 0.50 mmol) gave complex **5a** (246 mg, 0.38 mmol, 77%). ^1H NMR (600 MHz, thf- d_8 , route **G**/Scheme 3⁵): 8.33 (s, 2H, $\text{CH}=\text{N}$), 7.43 (s, 2H, CH_{Ar}), 7.14 (s, 2H, CH_{Ar}), 4.07 (m, 2H, $\text{N}(\text{CHH})_2\text{N}$), 3.72 (m, 2H, $\text{N}(\text{CHH})_2\text{N}$), 1.45 (s, 18 H, *t*Bu), 1.27 (s, 18H, *t*Bu).

(Salcyc)Sc(Cl)(thf) (5b). When the procedure for route **G** was followed, H_2Salcyc (300 mg, 0.55 mmol), KH (44 mg, 1.10 mmol), and $\text{ScCl}_3(\text{thf})_3$ (202 mg, 0.55 mmol) gave complex **5b** (317 mg, 0.45 mmol, 83%). ^1H NMR (500 MHz, thf- d_8): 8.38 (s, 1H, $\text{CH}=\text{N}$), 8.36 (s, 1H, $\text{CH}=\text{N}$), 7.46 (s, 2H, CH_{Ar}), 7.25 (s, 2H, CH_{Ar}), 3.98 (m, 2H, $^3J_{\text{H}\alpha\text{H}\alpha} = 10.4$ Hz, $\text{N}(\text{CHH})_2\text{N}$), 3.22 (m, 2H, $^3J_{\text{H}\alpha\text{H}\alpha} = 10.4$ Hz, $\text{N}(\text{CHH})_2\text{N}$), 1.50 (s, 9 H, *t*Bu), 1.47 (s, 9H, *t*Bu), 1.44–1.35 (m, 8H, $\text{CH}_{2,\gamma}$, $\text{CH}_{2,\beta}$), 1.31 (s, 18H, *t*Bu). ^{13}C NMR (100.6 MHz, C_6D_6): 165.8 ($\text{CH}=\text{N}$), 164.9 (C-2), 163.7 (C-2'), 163.5 ($\text{CH}=\text{N}$), 139.2 (C_{Ar}), 139.0 (C_{Ar}), 137.9 (C_{Ar}), 137.8 (C_{Ar}), 130.7 (C_{Ar}), 130.6 (C_{Ar}), 130.3 (C_{Ar}), 123.8 (C-1), 123.7 (C-1'), 70.0 ($\text{N}(\text{CH}_\alpha)$), 36.2 (*t*Bu), 34.8 (*t*Bu), 32.2 ($\text{CH}_{2,\beta}$), 30.5 (*t*Bu), 30.3 (*t*Bu), 30.0 ($\text{CH}_{2,\beta}$), 29.3 ($\text{CH}_{2,\gamma}$), 26.6 ($\text{CH}_{2,\gamma}$). IR (Nujol; cm^{-1}): 1611vs ($\text{C}=\text{N}$), 1554s, 1537s, 1408s, 1362m, 1349m, 1318s, 1272m, 1255s, 1236w, 1199w, 1168s, 1028m, 980w, 964w, 920w, 879m, 862m, 841s, 819m, 783m, 752s, 642m, 558vs, 484s, 468s, 405w. Anal. calcd for $\text{C}_{40}\text{H}_{60}\text{ClN}_2\text{O}_3\text{Sc}$: C, 68.90; H, 8.67; N, 4.02. Found: C, 69.4; H, 8.6; N, 3.8.

Crystallographic Data Collection and Refinement. Crystals of **2**, **3a–c**, **4b**, and **5b** were grown by standard techniques from

saturated solutions using toluene at ambient temperature (**3a**, **3c**), toluene at -35 °C (**4b**), or hexane at -35 °C (**2**, **5b**). Suitable single crystals of **2**, **4b**, and **5b** (selected in a glovebox) and **3b** and **3c** (selected under air) were coated with Paratone-N (Hampton Research), fixed in a nylon loop, and measured on a Bruker SMART 2K CCD diffractometer. A single crystal of **3a** was mounted on a glass fiber and measured on an Oxford Diffraction Xcalibur system with a Ruby detector (Zurich Crystallography School, 2007). All other data were collected using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) performing ω -scans in four ω positions. The program suite CrysAlis^{Pro} was used for data collection, semiempirical absorption correction, and data reduction (**3a**).³² Raw data were collected using the SMART program³³ and reduced and scaled with the SAINT program.³³ Corrections for absorption effects were applied using SHELXTL.³⁴ The structures were solved by a combination of direct methods (SHELXS³⁵ and SIR92³⁶) and difference-Fourier syntheses (SHELXL-97³⁵). Final model refinement was done using SHELXL-97. All plots were generated using the ORTEP-3 program.³⁷ Further details of the refinement and crystallographic data are listed in Table 2 and in CIF files (Supporting Information); CCDC reference numbers 706234–706239.

Acknowledgment. C. M. thanks the Zurich Crystallography School 2007, and Bernhard Spingler for X-ray measuring time (**3a**).

Supporting Information Available: Crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC802082B

(32) *CrysAlisPro Software System*, v.171.32; Oxford Diffraction Ltd.: Oxford, U. K., 2007.

(33) *SMART*, v.5.054; *SAINT*, v.6.45a; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 2005.

(34) *SHELXTL*, v.6.12; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 2002.

(35) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

(36) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343–350.

(37) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565–566.