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Preparation, Characterization, and Reactivity of Scandium Octaethylporphyrin Complexes. X-ray Crystal Structures of (OEP)ScCH$_3$, (OEP)ScCH(SiMe$_3$)$_2$, (OEP)Sc(η^5-C$_9$H$_7$), and [(OEP)Sc]$_2$(μ-OH)$_2$

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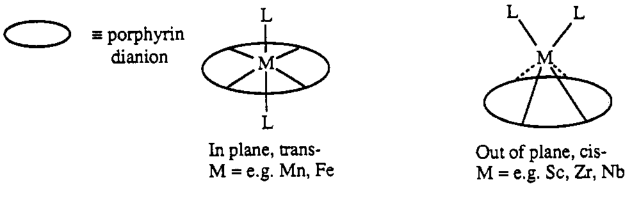
The synthesis of (OEP)ScCl from Li$_2$(OEP)(THF)$_2$ and ScCl$_3$(THF)$_3$ provides a useful entry into the chemistry of a wide range of (OEP)Sc derivatives. Organometallic complexes with σ- and π-bonded ligands have been isolated and fully characterized. These include (OEP)ScR species with R = Me, CH(SiMe$_3$)$_2$, CH$_2$CMe$_3$, (η^5-C$_9$H$_7$), (η^5-C$_5$H$_5$), (η^5-C$_5$H$_4$Me), and (η^5-C$_5$Me$_5$), three of which have been structurally characterized by X-ray crystallography. For [(OEP)ScMe]$_2$·CH$_2$Cl$_2$: space group $P\bar{1}$ with a = 10.088(2) Å, b = 13.882(2) Å, c = 14.813(2) Å, α = 66.469(12)°, β = 81.342(14)°, γ = 76.561(12)°, V = 1845.9(5) Å^3, Z = 1, R = 3.99%, and R_w = 5.34%. For (OEP)ScCH(SiMe$_3$)$_2$: space group $P2_1/n$ with a = 12.372(10) Å, b = 24.194(18) Å, c = 15.393(18) Å, β = 112.55(7)°, V = 4255(12) Å^3, Z = 4, R = 12.6%, and R_w = 12.8%. For (OEP)Sc(η^5-C$_9$H$_7$): space group $Pbca$ with a = 14.899(2) Å, b = 20.999(2) Å, c = 23.722(3) Å, V = 7421.6(26) Å^3, Z = 8, R = 7.44%, and R_w = 5.76%. The σ-alkyls react with ketones and CO$_2$ to produce alkoxides and acetates, respectively. Additional derivatives with R = OCMe$_3$, O(2,4,6-Me$_3$C$_6$H$_2$), N(SiMe$_3$)$_2$, and triflate have also been prepared. Hydrolysis of these complexes yields the dimeric bridging hydroxide [(OEP)Sc(μ-OH)]$_2$ which has also been crystallographically characterized; it crystallizes in the space group $P\bar{1}$ with a = 10.992(2) Å, b = 13.179(2) Å, c = 13.650(2) Å, α = 59.615(16)°, β = 67.226(16)°, γ = 76.234(14)°, V = 1570.6(3) Å^3, Z = 1, R = 3.5%, and R_w = 4.2%.

Introduction

The dimensions of the central core of porphyrin dianions are such that metal ions of radii 0.60–0.65 Å are accommodated in the plane of the N$_4$ ring.[1–3] For smaller ions, the entire ring can ruffle through an S$_4$-type deformation to reduce the hole size. If the metal is only slightly too large, the core can expand somewhat by doming to coordinate the ion. The vast majority of known porphyrin chemistry is based on derivatives involving late transition metals, where an in-plane geometry directs ligands to mutually trans positions, as shown.



For much larger metals, such as those early in the transition series, however, the metal is displaced from the N$_4$ porphyrin plane. As a result, additional ligands on the metal are constrained to be cis to one another. Compared to the latter transition metals, very little is known about the structures, properties, and reactivities of these unusual, electron deficient porphyrin complexes.[2,4–7]

This paper describes the synthesis and characterization of a range of scandium porphyrin complexes. Until quite recently, the list of known scandium porphyrins was quite short. Buchler's pioneering work in this area led to OEP[8] derivatives with acetate, acetylacetonate, and oxo ligands.[2,9] In 1988 Haushalter and co-workers isolated the TTP chloride complex and the μ-oxo species O[(ScTPP)]$_2$ and also described an unsuccessful attempt to prepare organometallic cyclopentadienyl (Cp) derivatives.[10]

A major drawback to studying this general class of compounds has been the lack of clean, high-yield, large-scale preparative routes. Known procedures have several drawbacks, such as the necessity to use very high-boiling solvents, often followed by purification using column chromatography. The latter procedure limits the amount

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(8) Abbreviations: OEP is the dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin; TPP is the dianion of *meso*-tetraphenylporphyrin; TTP is the dianion of *meso*-tetra-*p*-tolylporphyrin.

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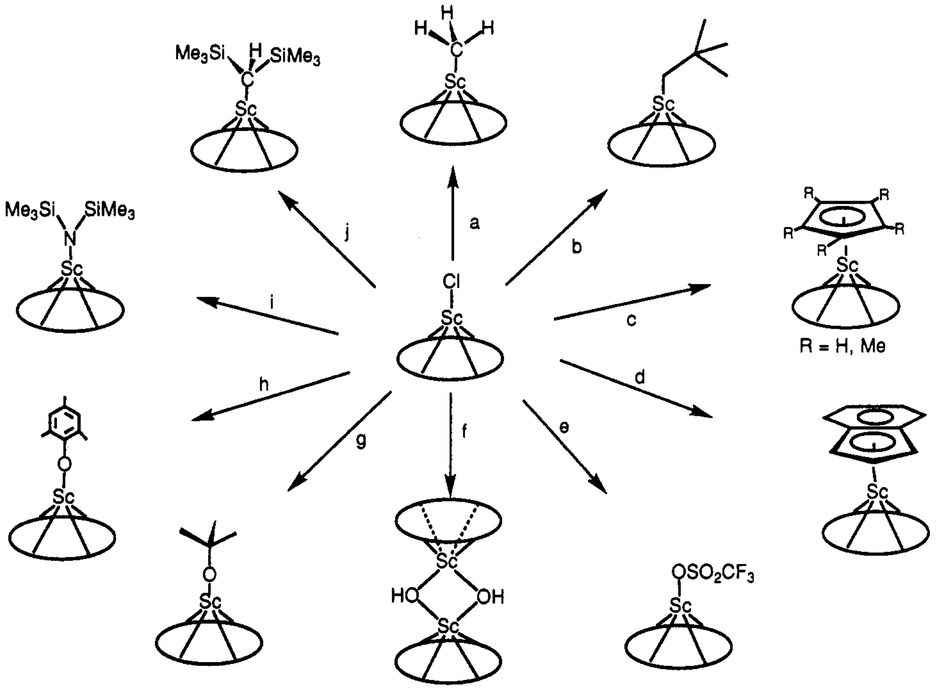
Scheme I [a]



[a] Conditions: (a) Me_2Mg in toluene; (b) Np_2Mg in toluene; (c) NaCp in THF, LiCp* in THF, Li(MeCp) in THF; (d) Na(Ind) in THF; (e) TMSOTf in toluene; (f) H_2O in CH_2Cl_2; (g) $LiOCMe_3$ in toluene; (h) $LiO(Me_3C_6H_2)$ in toluene; (i) $NaN(TMS)_2$ in toluene; (j) $LiCH_2SiMe_3$ in toluene.

of product that may be obtained and has the additional disadvantage that it is generally not suitable for the isolation of air- and moisture-sensitive derivatives which react with commonly used support materials. In spite of the fact that large excesses of metal acetylacetonate or halide starting materials are usually employed, incomplete conversion of the free base porphyrin to the desired metalloporphyrin is not uncommon.

Recent work in our group has led to the development of a new, seemingly general synthetic route to out-of-plane, early metal porphyrin derivatives. Preliminary accounts describing the synthesis of scandium and zirconium OEP derivatives, based on a metathesis reaction between the porphyrin dianion (as the lithium salt[11,12]) and metal halides, have appeared[4-6,13] (eq 1).

$$Li_2(por) + MCl_n \rightarrow (por)MCl_{n-2} + 2LiCl \quad (1)$$

These porphyrin halide complexes are excellent starting materials for the preparation of a number of organometallic and coordination complexes, demonstrating that out-of-plane metalloporphyrin geometries are quite stable platforms for a variety of ligand systems. As such, $(por)MX_n$ systems compare favorably with the more well-studied metallocene species Cp_2MX_n.[14-17] In this paper, our focus is on organometallic scandium porphyrin complexes. Organometallic porphyrins are relatively rare; however, they have a rich and varied chemistry as described in several excellent reviews.[18-20]

Results and Discussion

Reaction of the dilithium salt of OEP with a slight excess of $ScCl_3(THF)_3$ in refluxing toluene affords high yields (>90%) of (OEP)ScCl (eq 2). The reaction is easy to carry out on large scales, and there are no detectable side reactions. The workup procedure involves a simple hot

$$Li_2(OEP)(THF)_2 + ScCl_3(THF)_3 \rightarrow (OEP)ScCl + 2LiCl + 5THF \quad (2)$$

filtration, after which the product crystallizes from the solution as analytically pure red needles that may be handled in air without deterioration. The complex is practically insoluble in hexane or diethyl ether; however it dissolves in moderately polar solvents such as THF, CH_2Cl_2, and acetone to form bright red, moisture-sensitive solutions. The UV–vis spectrum shows similar features to those reported for other (OEP)Sc derivatives and is unremarkable.[2,3] As expected, the methylene protons are diastereotopic, giving rise to a complex multiplet centered at δ 4.19 in the ^1H NMR spectrum recorded in $CDCl_3$. It is interesting to note that despite the low formal electron count on the metal (10 electrons) the compound shows no tendency to form adducts with Lewis bases such as THF, pyridine, or PMe_3.

(OEP)ScCl functions as an excellent starting material for the preparation of a wide range of organometallic and coordination compounds, as shown in Scheme I. These

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Table I. Crystal Data and Collection Parameters

	(OEP)ScMe·1.5(CH_2Cl_2)	(OEP)ScCH($SiMe_3$)$_2$	(OEP)Sc(η^5-C_9H_7)	[(OEP)Sc(μ-OH)]$_2$
formula	$C_{77}H_{100}N_8Sc_2Cl_6$	$C_{43}H_{63}N_4ScSi_2$	$C_{45}H_{51}N_4Sc$	$C_{36}H_{45}N_4OSc$
mol wt	1440.3	737.1	692.88	594.7
space group	$P\bar{1}$	$P2_1/n$	*Pbca*	$P\bar{1}$
temp (°C)	–134	–85	–95	–118
a (Å)	10.088(2)	12.372(10)	14.899(2)	10.992(2)
b (Å)	13.882(2)	24.194(18)	20.999(2)	13.179(2)
c (Å)	14.813(2)	15.393(18)	23.722(3)	13.650(2)
V (Å^3)	1845.9(5)	4255(12)	7421.6(26)	1570.6(3)
α (deg)	66.469(12)	90	90	59.615(16)
β (deg)	81.342(14)	112.55(7)	90	67.226(16)
γ (deg)	76.561(12)	90	90	76.234(14)
Z	1	4	8	1
μ (cm^{-1})	4.5	2.6	2.3	3.0
cryst dimens (mm)	0.40 × 0.45 × 0.55	0.21 × 0.30 × 0.47	0.12 × 0.28 × 0.35	0.13 × 0.27 × 0.40
reflcns measd	$+h,\pm k,\pm l$	$+h,+k,\pm l$	$+h,+k,+l$	$+h,\pm k,\pm l$
scan rate (deg min^{-1})	5.49	6.70	5.50	5.50
2θ range (deg)	3 → 45	3 → 45	3 → 45	3 → 45
scan type	θ–2θ	ω	θ–2θ	θ–2θ
no. of reflcns measd	4804	5150	5368	4384
no. of unique reflcns	4804	5006	4828	4114
no. of reflcns	3993 ($I > 3\sigma_I$)	2979 ($I > 2\sigma_I$)	2316 ($I > 2\sigma_I$)	3359 ($I > 3\sigma_I$)
no. of params	439	216	351	380
R (%)	3.99	12.6	7.44	3.5
R_w (%)	5.34	12.8	5.76	4.2
GOF	2.09	3.47	1.30	1.654

reactions occur straightforwardly on treatment of the chloride with 1 equiv of the indicated reagent, and workup procedures are very simple, affording the products as red crystals in good to high yields. All derivatives shown in Scheme I have been characterized by elemental analysis, NMR and IR spectroscopy, and in several cases, mass spectrometry and X-ray diffraction (see below).

The σ-alkyl complexes (OEP)ScR, where R = Me, CH($SiMe_3$)$_2$, and CH_2CMe_3, are extremely air- and moisture-sensitive, as might be expected for (formally) 10-electron species. As is commonly observed in alkylporphyrins, large upfield shifts were observed in the ^{1}H NMR resonances of metal-bound alkyl groups. For example, the methyl group appears as a slightly broadened singlet at –5.0 ppm. Substitution of a *tert*-butyl group in place of one of the methyl hydrogens shifts the remaining two protons (still slightly broadened) to slightly lower field (δ –4.7 ppm); the *tert*-butyl group also gives rise to an unusually high-field resonance (δ –1.63 ppm). This trend continues similarly for the bis(trimethylsilyl)methyl complex.

The alkyls react extremely rapidly with unsaturated small molecules such as CO and xylyl isocyanide; however, these reactions are not simple as judged by ^{1}H NMR and we have been unable to isolate any pure products as a result. Reactions with CO_2 and acetone are also fast at room temperature, but in these two cases the conversions are much cleaner, leading to the known acetate and *tert*-butoxide derivatives, respectively (see below).

Two of these σ-alkyl complexes have been structurally characterized by X-ray crystallography (Table I). The geometries of (OEP)ScMe and (OEP)ScCH($SiMe_3$)$_2$ are quite similar, as shown in Figures 1–3 and Table II. The (OEP)ScMe molecule features a scandium coordinated in a regular square pyramidal fashion with Sc–N distances of 2.151(2)–2.158(2) Å and N–Sc–C angles ranging from 107.3 to 108.8°. The scandium sits atop a planar N_4 ring at a distance of 0.66 Å. The OEP ligand as a whole is slightly domed and ruffled, although distances and angles within the porphyrin are normal. The Sc–C bond is 2.246(3) Å, and the refined C–H distances are 0.64, 0.77, and 0.81 Å. The latter distances are very short compared to "normal" refined C–H bonds of 0.95 Å. The isotropic thermal parameter for the carbon is lower than that for the Sc, and the rms amplitudes of vibration are similarly small and highly anisotropic. Suspecting the presence of some (OEP)ScCl in the crystal, we analyzed a sample from the batch used for X-ray crystallography by EI-MS, which indeed confirmed this notion. Subsequently, we deter-

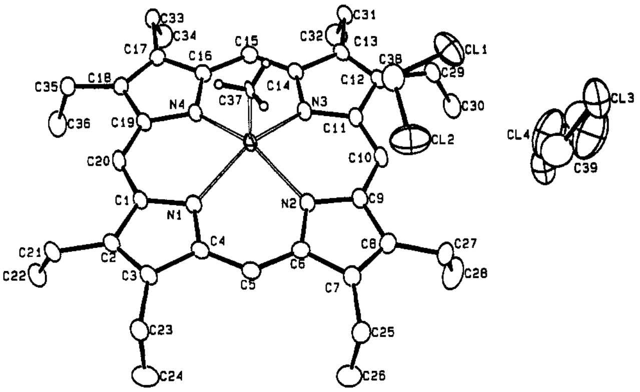

Figure 1. ORTEP view of (OEP)ScMe including disordered CH_2Cl_2 solvent.

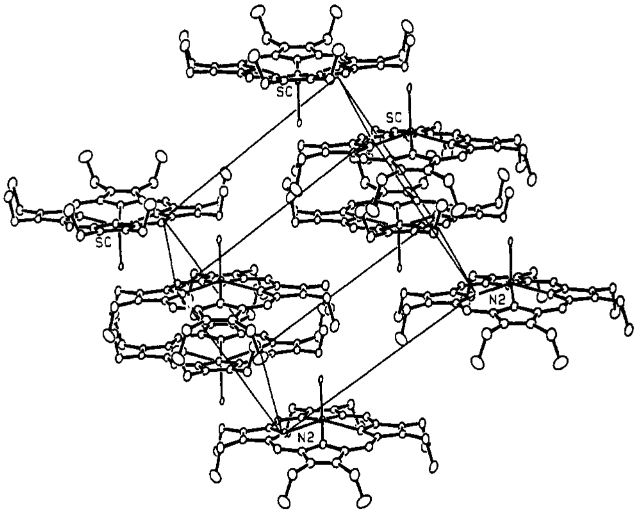

Figure 2. Packing diagram for (OEP)ScMe.

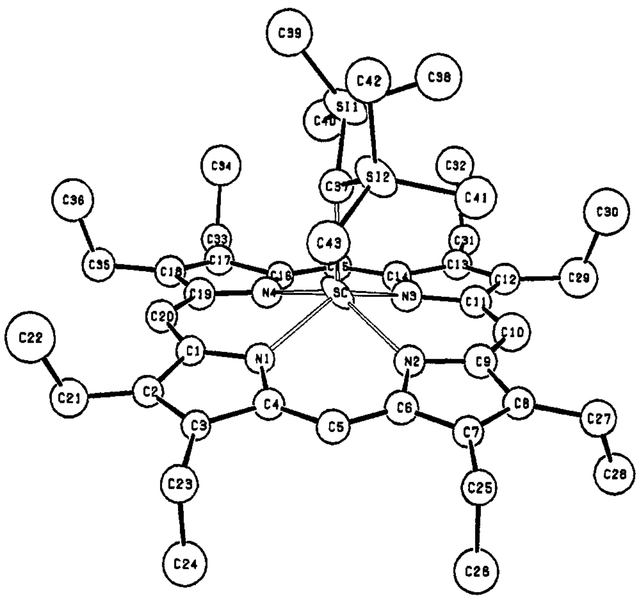

Figure 3. ORTEP view of (OEP)ScCH$(SiMe_3)_2$.

Table II. Comparison of Bond Lengths and Angles in (OEP)ScMe and (OEP)ScCH$(SiMe_3)_2$

	(OEP)ScMe	(OEP)ScCH$(SiMe_3)_2$
	Bond Lengths (Å)	
Sc–N(1)	2.151(2)	2.196(6)
Sc–N(2)	2.152(2)	2.151(6)
Sc–N(3)	2.157(2)	2.142(6)
Sc–N(4)	2.158(2)	2.162(6)
Sc–C(37)	2.246(3)	2.243(8)
C(37)–H(1)	0.77(3)	
C(37)–H(2)	0.81(3)	
C(37)–H(3)	0.64(3)	
N_4 plane–Sc	0.66	0.71
	Angles (deg)	
N(1)–Sc–N(2)	84.83(8)	82.9(2)
N(2)–Sc–N(3)	84.33(8)	85.4(2)
N(3)–Sc–N(4)	84.50(8)	82.9(2)
N(4)–Sc–N(1)	84.69(8)	83.7(2)
N(1)–Sc–N(3)	144.55(8)	141.2(2)
N(1)–Sc–C(37)	107.6(1)	107.0(2)
N(2)–Sc–C(37)	107.3(1)	110.3(3)
N(3)–Sc–C(37)	107.9(1)	111.8(2)
N(4)–Sc–C(37)	108.82(9)	108.4(3)

mined using ^{1}H NMR spectroscopy that (OEP)ScMe reacts slowly with halogenated solvents such as the CH_2Cl_2 used in the recrystallization. The compound reacts much faster with $CHCl_3$, again forming (OEP)ScCl. A combination of the data above and several refinement experiments detailed in the Experimental Section lead us to believe that the apparent Sc–C bond length has been "lengthened" by no more than 0.02 Å as a result of the chloride impurity. For comparison, the Sc–C distance in Cp^*_2ScMe is 2.243(11) Å.[16]

Determination of the structure of (OEP)ScCH$(SiMe_3)_2$ was hampered by relatively poor crystal quality that led to rather high *R* factors ($R = 12.6\%$; $R_w = 12.8\%$); however, the overall molecular structure is clearly defined, as shown in Figure 3. Sc–N bond lengths are similar to those of the methyl derivative, ranging from 2.142(6) to 2.196(6) Å, and the Sc is displaced from the N_4 plane slightly more than in the methyl (0.71 Å) perhaps due to the presence of two bulky $-SiMe_3$ groups in the former. The Sc–C bond length is 2.243(8) Å, again quite close to the OEP methyl and related species. Related lanthanide OEP alkyl derivatives were recently reported by Schaverien and Orpen. Although the parent methyl species were not isolated, a number of substituted alkyls were described, the corresponding Lu complex was structurally characterized, and the reactivities of these compounds toward O_2 and water were investigated.[21]

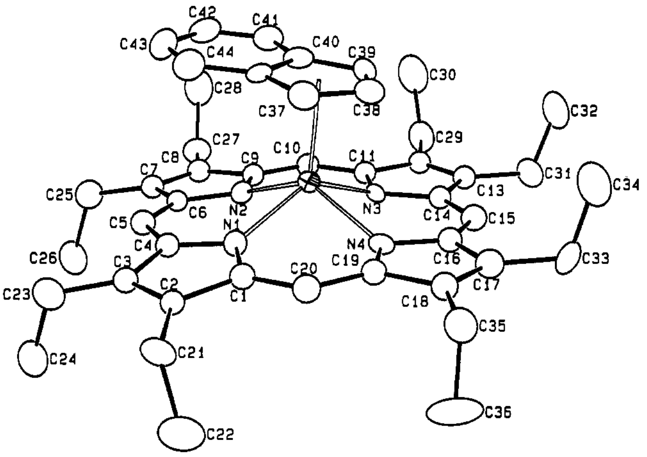

Figure 4. ORTEP view of (OEP)Sc(η^5-C_9H_7).

The out-of-plane, electron deficient nature of the (OEP)Sc fragment led us to investigate the formation of π-complexes. Metalloporphyrin π-complexes are rare, and most of these are limited to η^2-derivatives. For the majority of metalloporphyrins, it is unsurprising that these electron rich, in-plane metals are not inclined to form stable complexes with many electron, multihapto ligands. Although related TTP derivatives do not appear to be stable,[10] we found that a range of cyclopentadienyl derivatives form extremely inert η^5-complexes on treatment of (OEP)ScCl with 1 equiv of the respective Cp anion in THF. These compounds were isolated as air-stable crystals in high yields and have been fully characterized. The η^5-indenylide is the only derivative sensitive to hydrolysis in solution, a result that can be ascribed to the well-known lability of indenyl ligands relative to Cp or Cp*.[22] Once again, large upfield shifts are observed in the ^{1}H NMR spectra of coordinated ligands: for example, the Cp resonance in (OEP)Sc(η^5-Cp) was found at δ 1.68 ppm, a value that is some 3–4 ppm upfield of Cp ligands in nonporphyrin complexes. For the related η^5-indenylide complex, similar upfield shifts were observed for the three cyclopentadienyl protons. The shielding effect is lower for protons on the phenyl ring, although even these are shifted upfield some 2 ppm relative to the free ligand.

The X-ray crystal structure of (OEP)Sc(η^5-C_9H_7) consists of well-separated molecules, as shown in Figure 4 with metrical data in Table III. Although the indene ring is bound in an η^5 fashion, the side view clearly shows that the effectively planar indene ligand is tilted with respect to the porphyrin ring. It is also evident that the η^5-C_5 ring is slid slightly with respect to the scandium: the average bond length between the scandium and C(37) and C(38) is 2.504(8) Å, compared to the average Sc–C bond length for C(39) and C(45) of 2.540(8) Å and the Sc–C(40) bond length of 2.580(8) Å. The average bond length between the scandium and the nitrogens of the core is 2.182(6) Å. The porphyrin itself is remarkably planar showing no marked ruffling or doming. The N_4 plane is quite exact with angles of the pyrrole rings to this plane ranging from 8.8° to zero. The pyrrole containing N(4) is bent slightly out of the plane away from the scandium rather than

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Table III. Comparison of Bond Lengths and Angles in (OEP)Sc(η^5-C_9H_7) and (OEP)Sc(η^5-C_5H_5)[a]

	(OEP)Sc(η^5-C_9H_7)	(OEP)Sc(η^5-C_5H_5)
	Bond Lengths (Å)	
Sc-N(1)	2.189(6)	2.184(3)
Sc-N(2)	2.190(6)	2.195(3)
Sc-N(3)	2.180(6)	2.184(3)
Sc-N(4)	2.170(6)	2.197(3)
Sc-Cp centroid	2.232(6)	2.196
Sc-C(37)	2.499(8)	2.493(4) Sc-Cp(av)
Sc-C(38)	2.508(9)	
Sc-C(39)	2.539(8)	
Sc-C(40)	2.580(8)	
Sc-C(45)	2.540(8)	
N_4 plane-Sc	0.78	0.80
	Angles (deg)	
N(1)-Sc-N(2)	81.9(3)	82.1(1)
N(2)-Sc-N(3)	82.69(24)	82.4(1)
N(3)-Sc-N(4)	82.86(24)	82.4(1)
N(4)-Sc-N(1)	83.2(3)	82.8(1)
N(1)-Sc-N(3)	138.15(22)	136.9(1)

[a] Data from: Arnold, J.; Hoffman, C. G. *J. Am. Chem. Soc.* **1990**, *112*, 8620.

toward it. The scandium sits 0.78 Å above the mean plane containing the four core nitrogens and is 2.233 Å from the indene Cp centroid.

These data may be compared to the closely related (OEP)Sc(η^5-C_5H_5) structure where both the porphyrin and the Cp ring are regularly coordinated to the scandium.[4] The bond distances to the individual atoms in each ligand are the same within experimental error, with the average Sc–N bond length equal to 2.190(3) Å and the average Sc–C bond length equal to 2.493(4) Å. The scandium is 0.80 Å removed from the mean plane of the nitrogen core and 2.196 Å from the mean plane of the Cp ligand. For comparison the Sc–Cp* distance in $Cp^*{}_2ScMe$ is 2.1701(12) Å.[16] The porphyrin core is slightly ruffled, with two pyrrole rings tilted down with respect to the scandium and the other two rings pointed up. The angles between the pyrrole planes and the mean plane of the porphyrin are −1.7, 5.6, −1.7, and 5.6°.

Representative derivatives with amide, aryloxide, and alkoxide ligands were also prepared and fully characterized (Scheme I). In all cases, the OEP methylene groups are diastereotopic and signals due to groups in close proximity to the ring are shifted to higher field than in the free ligand, by up to 2–3 ppm. For example, in the silylamide derivative, a singlet for the $-SiMe_3$ protons was observed at δ −2.28 ppm compared to δ 0.072 ppm for the free amine. In the mesitoxide complex, the ortho-methyl group protons resonate some 2.5 ppm upfield from the peak due to the para-methyl group. The triflate derivative was prepared by reaction of the chloride with trimethylsilyl triflate in toluene. No doubt due to the well-known lability of the triflate group, the complex appears to be a useful precursor to other (OEP)Sc derivatives, as judged by small-scale reactions monitored by ^1H NMR spectroscopy.

Hydrolysis of all (OEP)ScX derivatives produces the bright red bis(μ-hydroxide) dimer $[(OEP)Sc(\mu\text{-}OH)]_2$. Since the solubility properties of (OEP)ScX species and the latter are quite similar, care must be taken to exclude water, as once it is formed, the hydroxide is very difficult to remove. A diagnostic ^1H NMR signal integrating to one proton per OEP was observed at δ −7.5 ppm in C_6D_6 (δ −7.9 ppm in $CDCl_3$). This signal was absent in the spectrum of the deuterium labeled compound prepared by hydrolysis of (OEP)ScCl with D_2O. In addition, the

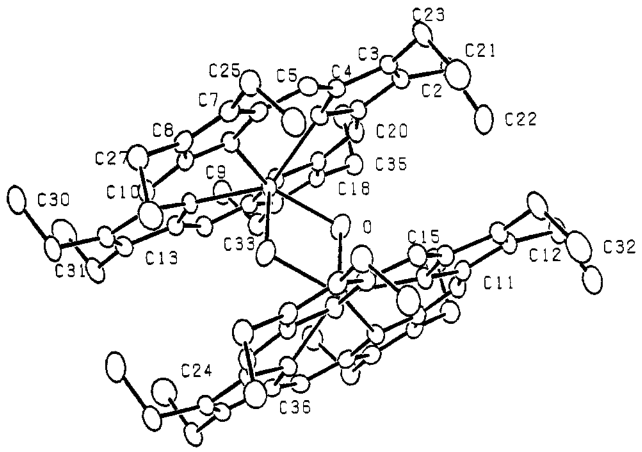

Figure 5. ORTEP view of $[(OEP)Sc(\mu\text{-}OH)]_2$.

frequency of the meso proton resonance (δ 9.43 ppm) is shifted upfield from those seen in monomeric (OEP)MX species, usually observed in the range δ 10.0–10.5 ppm; this is no doubt a result of the electronic influence of two OEP rings on each other (cf. related upfield shifts in sandwich complexes of the type $(OEP)_2M$[13,23,24]).

Buchler and co-workers reported the following equilibrium between the μ-oxo and hydroxide species some time ago:[25]

$$[(OEP)Sc]_2(\mu\text{-}O) + H_2O \rightarrow 2(OEP)ScOH$$

We found evidence for the μ-oxo complex in the EI mass spectrum where a molecular ion corresponding to $[(OEP)Sc]_2(\mu\text{-}O)$ (*m/e* 1170) was the highest mass peak detected; evidently, dehydration of $[(OEP)Sc(\mu\text{-}OH)]_2$ is facile under these conditions. Analogous Y and Lu hydroxide species with spectroscopic properties similar to those described above for $[(OEP)Sc(\mu\text{-}OH)]_2$ were reported recently.[21]

Confirmation of the structure of the hydroxide complex was obtained by X-ray crystallography. ORTEP views are provided in Figures 5 and 6 with metrical information in Table IV. The structure was refined to an *R* value of 3.5% using a model which included two full-occupancy bridging oxygens; the hydroxyl hydrogens were not located. There is slight disorder in the oxygen positions with approximately 15% of each oxygen's electron density residing across the mirror plane (see supplementary material for a picture of the disorder model). As seen in Figure 6, the two OEP rings are eclipsed with a separation of 5.06 Å between the N_4 planes. The Sc–O–Sc bond angle was found to be 109.89(7)° with an average Sc–O bond length of 2.078(2) Å. This structure may be compared to that determined for the bent *μ-oxo* derivative $[(TTP)Sc]_2(\mu\text{-}O)$ which shows the average Sc–O–Sc bond angle to be 110(3)° and the average Sc–O bond length to be 2.08(3) Å. Related Mo derivatives with single μ-oxo bridges, such as $(\mu\text{-}O)[Mo(O)TPP]_2$,[26] feature, by contrast, almost linear M–O–M interactions (Mo–O–Mo = 178.63(6)°). Niobium(V) TPP complexes with bridging Nb_2O_3 units were reported by two separate groups some time ago.[26,27]

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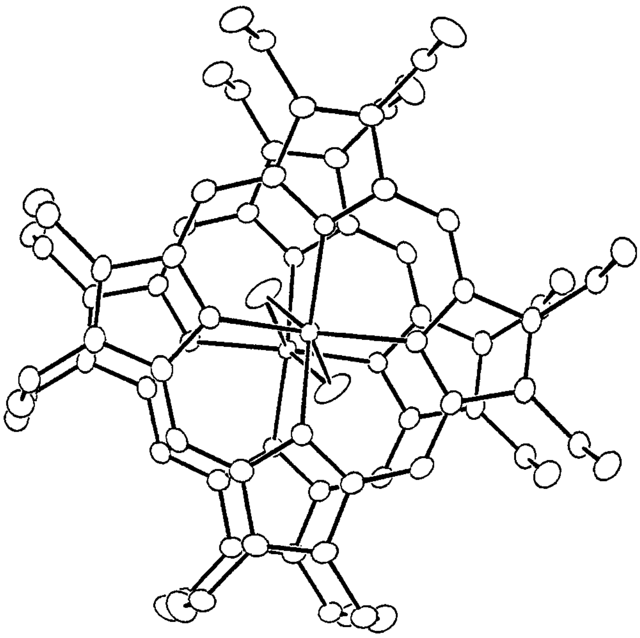

Figure 6. ORTEP view of $[(OEP)Sc(\mu\text{-}OH)]_2$ looking down the Sc–Sc vector.

Table IV. Bond Lengths and Angles in $[(OEP)Sc(\mu\text{-}OH)]_2$

	Bond Lengths (Å)		
Sc–N(1)	2.197(2)	Sc–Sc	3.404(1)
Sc–N(2)	2.195(2)	Sc–O	2.084(2)
Sc–N(3)	2.216(2)	Sc–O	2.072(2)
Sc–N(4)	2.203(2)	Sc–O′	2.066(1)
N_4 plane–Sc	0.84	Sc–O′	1.992(1)
	Angles (deg)		
N(1)–Sc–N(2)	81.75(6)	Sc–O–Sc	109.89(7)
N(2)–Sc–N(3)	82.26(6)	Sc–O′–Sc	113.93(1)
N(3)–Sc–N(4)	81.01(6)	O–Sc–O	70.11(7)
N(4)–Sc–N(1)	82.57(6)	O′–Sc–O′	66.07(1)
N(1)–Sc–N(3)	135.15(6)		

Experimental Section

All manipulations were carried out under dry nitrogen or argon unless stated otherwise. Glassware was oven-dried at 140 °C for at least 24 h prior to use. Literature procedures were used to prepare $LiCH(SiMe_3)_2$[28] and $Li_2(OEP)(THF)_2$.[11,12] Lithium alkoxides and cyclopentadienylides were isolated as base-free solids by the addition of *n*-BuLi to hexane solutions of the appropriate alcohol or cyclopentadiene, respectively. Dineopentylmagnesium was prepared by the literature method;[29] $MgMe_2$(dioxane) was prepared similarly but was not sublimed. Other reagents were commercially supplied and used as received. Tetrahydrofuran (THF), diethyl ether, toluene, and hexane were predried over 4-Å molecular sieves and distilled from sodium/benzophenone under N_2. Dichloromethane was distilled from calcium hydride under N_2. All NMR solvents were treated similarly but were distilled under vacuum. Melting points were determined in sealed capillary tubes under nitrogen and are uncorrected. IR spectra were measured as Nujol mulls between KBr or CsI plates. Chemical shifts (δ) for ^1H NMR spectra are reported in δ values relative to the residual proton signal of the deuterated solvent (i.e. C_6D_6 at δ 7.15 ppm, $CDCl_3$ at δ 7.24 ppm). UV–vis spectra were recorded in 0.5-cm quartz cells and are reported in the form λ_{max} in nm (log ϵ). Elemental analyses and mass spectra (EI, 70 eV) were performed at the departmental facility of the College of Chemistry, U. C. Berkeley.

(OEP)ScCl. A 250-mL single neck round-bottom Schlenk flask was charged with 1.00 g (1.45 mmol) of $Li_2(OEP)(THF)_2$ and 0.54 g (1.47 mmol) of $ScCl_3(THF)_3$. Via cannula, 150 mL of toluene was transferred into the flask and the flask was fitted with a reflux condenser. The stirred mixture was refluxed for 2 h to give a homogeneous red solution. The hot solution was filtered, hexane (100 mL) was added, and the solution was cooled to −40 °C overnight. Red crystals of the mono(toluene) solvate of (OEP)ScCl were isolated by filtration. Although this material is sufficiently pure for synthetic purposes, recrystallization from CH_2Cl_2 gave analytically pure, toluene-free compound in 92% yield (0.818 g). This procedure has been scaled up by a factor of 5 without diminution in yield. Mp: 366–370 °C. IR: 1312 (m), 1266 (m), 1211 (w), 1148 (vs), 1127 (vw), 1109 (m), 1056 (s), 1014 (vs), 978 (m), 959 (s), 913 (m), 872 (w), 849 (m), 745 (m), 729 (s), 713 (m), 695 (w), 668 (w), 545 (vw), 465 (w) cm^{-1}. ^1H NMR: (400 MHz, C_6D_6, 20 °C) δ 1.81 (t, *J* = 7 Hz, 24 H, CH_2CH_3), 3.97 (m, 16 H, CH_2CH_3), 10.54 (s, 4 H, *CH*); (300 MHz, $CDCl_3$, 20 °C) δ 1.96 (t, *J* = 7.6 Hz, 24 H, CH_2CH_3), 4.20 (m, 16 H, CH_2CH_3), 10.46 (s, 4 H, CH). UV–vis (CH_2Cl_2): 337 (4.2), 406

Table V. Positional Parameters for (OEP)ScMe

atom	*x*	*y*	*z*	B^a (Å^2)
Sc	0.23633(1)	0.86530(1)	0.32605(1)	1.20(1)
Cl1	0.30072(9)	0.49348(6)	0.24115(7)	4.40(2)
Cl2	0.1103(1)	0.68405(8)	0.13297(7)	4.84(3)
Cl3	0.3655(3)	0.4232(2)	0.0152(2)	5.57(5)
Cl4	0.5866(3)	0.5171(2)	0.0260(2)	7.55(7)
N1	0.1452(2)	1.0319(2)	0.2853(1)	1.41(5)
N2	0.2725(2)	0.9044(2)	0.1696(1)	1.41(5)
N3	0.4267(2)	0.7531(2)	0.3352(1)	1.43(5)
N4	0.3018(2)	0.8810(2)	0.4509(1)	1.31(5)
C1	0.0999(3)	1.0839(2)	0.3501(2)	1.27(6)
C2	0.0041(3)	1.1819(2)	0.3035(2)	1.44(6)
C3	−0.0068(3)	1.1883(2)	0.2102(2)	1.52(6)
C4	0.0823(3)	1.0950(2)	0.1995(2)	1.43(6)
C5	0.1056(3)	1.0724(2)	0.1138(2)	1.54(6)
C6	0.1957(3)	0.9873(2)	0.0976(2)	1.46(6)
C7	0.2270(3)	0.9742(2)	0.0043(2)	1.63(6)
C8	0.3239(3)	0.8835(2)	0.0202(2)	1.66(6)
C9	0.3515(3)	0.8394(2)	0.1238(2)	1.53(6)
C10	0.4420(3)	0.7458(2)	0.1714(2)	1.54(6)
C11	0.4784(3)	0.7049(2)	0.2686(2)	1.41(6)
C12	0.5791(3)	0.6094(2)	0.3142(2)	1.46(6)
C13	0.5906(3)	0.6027(2)	0.4072(2)	1.45(6)
C14	0.4944(3)	0.6926(2)	0.4201(2)	1.38(6)
C15	0.4734(3)	0.7159(2)	0.5052(2)	1.49(6)
C16	0.3869(3)	0.8036(2)	0.5198(2)	1.40(6)
C17	0.3767(3)	0.8289(2)	0.6065(2)	1.39(6)
C18	0.2853(3)	0.9233(2)	0.5890(2)	1.38(6)
C19	0.2384(3)	0.9556(2)	0.4916(2)	1.32(6)
C20	0.1438(3)	1.0468(2)	0.4450(2)	1.48(6)
C21	−0.0646(3)	1.2600(2)	0.3502(2)	1.62(6)
C22	0.0236(3)	1.3362(2)	0.3471(2)	2.24(7)
C23	−0.0887(3)	1.2769(2)	0.1303(2)	2.00(6)
C24	−0.0071(4)	1.3598(2)	0.0631(2)	3.24(8)
C25	0.1678(3)	1.0510(2)	−0.0912(2)	2.03(6)
C26	0.2404(4)	1.1448(2)	−0.1418(2)	2.97(8)
C27	0.3993(3)	0.8390(2)	−0.0544(2)	2.20(7)
C28	0.5381(4)	0.8695(3)	−0.0883(2)	3.82(8)
C29	0.6542(3)	0.5332(2)	0.2663(2)	1.88(6)
C30	0.7783(3)	0.5680(2)	0.1998(2)	2.79(7)
C31	0.6894(3)	0.5251(2)	0.4811(2)	1.75(6)
C32	0.8139(3)	0.5708(2)	0.4777(2)	2.58(7)
C33	0.4570(3)	0.7647(2)	0.6961(2)	1.80(6)
C34	0.5990(3)	0.7894(2)	0.6840(2)	2.67(7)
C35	0.2442(3)	0.9873(2)	0.6533(2)	1.68(6)
C36	0.3228(3)	1.0774(2)	0.6241(2)	2.81(7)
C37	0.0665(2)	0.7720(2)	0.3781(2)	0.90(5)
C38	0.1744(3)	0.6012(2)	0.2467(2)	2.95(8)
C39	0.4221(9)	0.5439(6)	−0.0159(6)	5.0(2)*

[a] The starred value refers to the atom that was included with isotropic thermal parameters. The thermal parameter given for anisotropically refined atoms is the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$, where *a*, *b*, and *c* are real cell parameters and $\beta(i,j)$ are anisotropic β's.

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Table VI. Positional Parameters for (OEP)ScCH(SiMe$_3$)$_2$

atom	*x*	*y*	*z*	B^a (Å^2)
Sc	0.4258(2)	0.0669(1)	0.1515(2)	2.26(6)
Si1	0.2110(4)	0.1757(2)	0.0717(3)	3.2(1)
Si2	0.3124(4)	0.1471(2)	0.2846(3)	3.1(1)
N1	0.4021(9)	–0.0138(4)	0.2069(6)	1.9(2)*
N2	0.5808(9)	0.0694(4)	0.2784(6)	2.1(2)*
N3	0.5305(9)	0.1074(4)	0.0874(7)	2.4(2)*
N4	0.3527(9)	0.0255(4)	0.0169(6)	2.2(2)*
C1	0.313(1)	–0.0494(5)	0.1569(8)	1.8(3)*
C2	0.303(1)	–0.0932(5)	0.2212(8)	2.0(3)*
C3	0.391(1)	–0.0826(5)	0.3048(8)	1.8(3)*
C4	0.455(1)	–0.0323(5)	0.2965(8)	2.0(3)*
C5	0.547(1)	–0.0083(5)	0.3691(8)	2.3(3)*
C6	0.611(1)	0.0392(5)	0.3615(8)	2.4(3)*
C7	0.705(1)	0.0626(5)	0.4350(8)	1.9(3)*
C8	0.745(1)	0.1068(5)	0.3964(8)	2.1(3)*
C9	0.667(1)	0.1096(5)	0.3006(8)	2.5(3)*
C10	0.687(1)	0.1462(6)	0.2338(9)	3.3(3)*
C11	0.620(1)	0.1448(5)	0.1374(8)	2.4(3)*
C12	0.645(1)	0.1787(5)	0.0671(8)	2.3(3)*
C13	0.577(1)	0.1605(5)	–0.0191(8)	2.3(3)*
C14	0.508(1)	0.1150(5)	–0.0048(8)	2.1(3)*
C15	0.425(1)	0.0848(5)	–0.0794(8)	2.0(3)*
C16	0.358(1)	0.0435(5)	–0.0673(8)	1.9(3)*
C17	0.264(1)	0.0150(5)	–0.1462(8)	2.3(3)*
C18	0.211(1)	–0.0214(5)	–0.1063(8)	2.4(3)*
C19	0.270(1)	–0.0153(5)	–0.0046(8)	2.4(3)*
C20	0.244(1)	–0.0490(5)	0.0599(8)	2.3(3)*
C21	0.219(1)	–0.1403(6)	0.1939(9)	3.1(3)*
C22	0.102(1)	–0.1258(7)	0.211(1)	5.1(4)*
C23	0.426(1)	–0.1183(5)	0.3943(9)	2.7(3)*
C24	0.528(1)	–0.1590(6)	0.394(1)	3.9(4)*
C25	0.759(1)	0.0393(5)	0.5337(8)	2.4(3)*
C26	0.856(1)	–0.0055(6)	0.5421(9)	3.9(4)*
C27	0.851(1)	0.1425(5)	0.4469(9)	2.8(3)*
C28	0.955(1)	0.1237(6)	0.4218(9)	3.6(4)*
C29	0.739(1)	0.2252(6)	0.098(1)	3.8(4)*
C30	0.680(2)	0.2779(7)	0.126(1)	5.2(4)*
C31	0.570(1)	0.1834(5)	–0.1112(9)	2.6(3)*
C32	0.457(1)	0.2236(6)	–0.150(1)	3.8(4)*
C33	0.241(1)	0.0257(5)	–0.2487(9)	2.5(3)*
C34	0.148(1)	0.0739(6)	–0.286(1)	4.5(4)*
C35	0.112(1)	–0.0618(6)	–0.1566(9)	2.8(3)*
C36	–0.004(1)	–0.0386(6)	–0.162(1)	4.3(4)*
C37	0.289(1)	0.1236(5)	0.1646(8)	2.5(3)*
C38	0.287(2)	0.2460(7)	0.103(1)	4.9(4)*
C39	0.053(1)	0.1826(6)	0.052(1)	4.7(4)*
C40	0.210(1)	0.1600(6)	–0.049(1)	4.1(4)*
C41	0.449(1)	0.1904(6)	0.3371(9)	3.6(4)*
C42	0.190(1)	0.1902(6)	0.300(1)	4.0(4)*
C43	0.324(1)	0.0849(6)	0.3643(9)	3.6(4)*

[a] Starred values refer to atoms that were included with isotropic thermal parameters. The thermal parameter given for anisotropically refined atoms is the isotropic equivalent thermal parameter defined as (4/3)[$a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)$] where *a*, *b*, and *c* are real cell parameters and $\beta(i,j)$ are anisotropic β's.

Table VII. Positional Parameters for (OEP)Sc(η^5-C$_9$H$_7$)

atom	*x*	*y*	*z*	B^a (Å^2)
Sc1	0.0371(1)	–0.01379(6)	0.37022(1)	1.74(3)
N1	0.0432(4)	0.0833(3)	0.3369(2)	1.8(1)
N2	–0.1052(4)	0.0104(3)	0.3791(2)	1.9(1)
N3	0.0148(4)	–0.0607(3)	0.4510(2)	1.7(1)
N4	0.1639(4)	0.0123(3)	0.4088(2)	1.9(1)
C1	0.1213(5)	0.1166(3)	0.3255(3)	1.9(2)*
C2	0.1008(5)	0.1720(3)	0.2916(3)	1.6(2)*
C3	0.0118(5)	0.1709(3)	0.2804(3)	1.8(2)*
C4	–0.0233(5)	0.1156(3)	0.3097(3)	1.7(2)*
C5	–0.1142(5)	0.0993(4)	0.3133(3)	2.0(2)*
C6	–0.1527(5)	0.0529(3)	0.3456(3)	1.5(2)*
C7	–0.2485(5)	0.0412(3)	0.3529(3)	1.9(2)*
C8	–0.2574(5)	–0.0079(4)	0.3895(3)	2.1(2)*
C9	–0.1681(5)	–0.0264(3)	0.4066(3)	1.8(2)*
C10	–0.1473(5)	–0.0728(4)	0.4448(3)	2.0(2)*
C11	–0.0629(5)	–0.0899(3)	0.4666(3)	1.8(2)*
C12	–0.0452(5)	–0.1391(3)	0.5081(3)	2.0(2)*
C13	0.0441(5)	–0.1373(3)	0.5173(3)	2.0(2)*
C14	0.0835(5)	–0.0888(3)	0.4822(3)	1.7(2)*
C15	0.1738(5)	–0.0728(4)	0.4779(3)	2.2(2)*
C16	0.2120(5)	–0.0270(3)	0.4450(3)	1.8(2)*
C17	0.3057(5)	–0.0119(4)	0.4416(3)	2.4(2)*
C18	0.3159(5)	0.0373(3)	0.4051(3)	2.0(2)*
C19	0.2257(5)	0.0520(4)	0.3844(3)	1.8(2)*
C20	0.2039(5)	0.1009(4)	0.3464(3)	2.1(2)*
C21	0.1681(5)	0.2212(4)	0.2762(3)	2.8(2)
C22	0.1929(6)	0.2659(4)	0.3240(4)	4.3(3)
C23	–0.0426(5)	0.2180(3)	0.2484(3)	2.7(2)
C24	–0.0835(6)	0.2697(4)	0.2858(3)	3.7(2)
C25	–0.3204(5)	0.0807(4)	0.3275(3)	2.6(2)
C26	–0.3406(6)	0.1419(4)	0.3599(4)	3.6(2)
C27	–0.3408(5)	–0.0412(4)	0.4083(3)	2.8(2)
C28	–0.3582(5)	–0.1012(4)	0.3748(4)	3.8(2)
C29	–0.1148(6)	–0.1844(4)	0.5293(3)	3.1(2)
C30	–0.1356(6)	–0.2357(4)	0.4878(4)	5.1(3)
C31	0.0966(6)	–0.1806(4)	0.5564(3)	3.1(2)
C32	0.1196(6)	–0.2436(4)	0.5297(4)	4.7(3)
C33	0.3781(5)	–0.0501(4)	0.4692(3)	2.9(2)
C34	0.4035(6)	–0.1080(4)	0.4356(4)	4.1(2)
C35	0.3988(6)	0.0731(4)	0.3904(3)	2.8(2)
C36	0.4094(6)	0.1332(4)	0.4243(4)	4.7(3)
C37	0.1133(5)	–0.0507(4)	0.2822(3)	2.3(2)
C38	0.1384(5)	–0.0937(4)	0.3240(3)	2.6(2)
C39	0.0647(5)	–0.1288(3)	0.3420(3)	2.5(2)
C40	–0.0095(5)	–0.1101(3)	0.3093(3)	2.4(2)
C41	–0.1003(6)	–0.1281(4)	0.3078(3)	2.8(2)
C42	–0.1576(5)	–0.1005(4)	0.2701(3)	3.0(2)
C43	–0.1284(5)	–0.0520(4)	0.2335(3)	3.4(2)
C44	–0.0401(6)	–0.0327(4)	0.2338(3)	3.1(2)
C45	0.0204(5)	–0.0609(3)	0.2721(3)	1.9(2)

[a] Starred values refer to atoms that were included with isotropic thermal parameters. The thermal parameter given for anisotropically refined atoms is defined as (4/3)[$a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)$] where *a*, *b*, and *c* are real cell parameters and $B(i,j)$ are anisotropic β's.

(5.4), 538 (4.1), 576 (4.2). EI-MS: 612 (M$^+$), 597, 577. Anal. Calcd for $C_{38}H_{44}ClN_4Sc$: C, 70.5; H, 7.23; N, 9.14. Found: C, 70.6; H, 7.10; N, 9.04.

(OEP)ScMe. A 30-mL aliquot of toluene was added via cannula to 0.50 g (0.71 mmol) of Sc(OEP)Cl(toluene) and 0.30 g (2.6 mmol) of $(CH_3)_2Mg$(dioxane) in a 75-mL Schlenk tube. The reaction mixture was allowed to stir for 12 h and filtered through a Schlenk frit, and the filtrate was concentrated to 15 mL. The solution was cooled to –40 °C overnight, affording the crystalline brick-red product as a hemitoluene solvate (0.25 g, in two crops, 59%). Mp: 297 °C dec. IR: 1149 (s), 1055 (m), 1014 (s), 995 (s), 844 (m), 720 (m), 697 (w). ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C), δ: –6.06 (br s, 3 H, C*H*$_3$), 2.00 (t, *J* = 8 Hz, 24 H, CH$_2$C*H*$_3$), 4.21 (m, 16 H, C*H*$_2$CH$_3$), 10.53 (s, 4 H, C*H*). ^{13}C NMR (400 MHz, CD_2Cl_2, 20 °C), δ: 18.7, 20.4, 27.3, 129.3, 143.1, 146.4. UV–vis (hexanes): 332 (4.7), 392 (5.4), 534 (4.5), 576 (4.6). Anal. Calcd for $C_{40.5}H_{51}N_4Sc$: C, 76.15; H, 8.05; N, 8.77 Found: C, 76.01; H, 7.99; N, 8.67.

(OEP)ScCH$_2$CMe$_3$. A Schlenk tube was charged with 0.125 g (0.177 mmol) of Sc(OEP)Cl(toluene) and 0.100 g (0.44 mmol) of Mg[CH$_2$C(CH$_3$)$_3$]$_2$. Via cannula, 20 mL of toluene was added and the reaction mixture allowed to stir 4 h. The solution was filtered through a Schlenk frit and the filtrate concentrated under reduced pressure to 10 mL. An equal volume of hexanes was added and the solution allowed to cool to –40 °C, affording 0.085 g (74%) of burgundy crystals. Mp: 265 °C dec. IR: 1145 (s), 1053 (m), 1013 (s), 954 (m), 843 (m), 724 (s). ^{1}H NMR (400 MHz, C_6D_6, 20 °C), δ: –4.7 (br s, 2 H, C*H*$_2$CMe$_3$), –1.63 (s, 9 H, –CH$_2$C*Me*$_3$), 1.88 (t, *J* = 8 Hz, 24 H, CH$_2$C*H*$_3$), 4.06 (m, 16 H, C*H*$_2$CH$_3$), 10.63 (s, 4 H, C*H*). ^{13}C NMR (400 MHz, CD_2Cl_2, 20 °C), δ: 18.8, 20.3, 32.0, 100.4, 142.7, 146.6. UV–vis (hexanes): 332 (4.6), 392 (5.4), 538 (4.3), 574 (4.5). Anal. Calcd for $C_{41}H_{55}N_4Sc$: C, 75.89; H, 8.54; N, 8.63. Found: C, 75.95; H, 8.53; N, 8.26.

Table VIII. Positional Parameters for $[(OEP)Sc(\mu\text{-}OH)]_2$

atom	*x*	*y*	*z*	B^a (Å^2)
Sc	0.06250(4)	0.05948(4)	0.05480(4)	1.25(1)
O	–0.0120(2)	0.0954(2)	–0.0793(2)	2.93(6)
O′	0.097	–0.002	–0.067	4.0*
N1	0.2050(2)	0.1899(2)	–0.0945(2)	1.47(5)
N2	0.2442(2)	–0.0414(2)	0.0898(2)	1.51(5)
N3	–0.0097(2)	–0.0119(2)	0.2522(1)	1.48(5)
N4	–0.0515(2)	0.2171(2)	0.0667(1)	1.50(5)
C1	0.1668(2)	0.2991(2)	–0.1718(2)	1.50(6)
C2	0.2644(2)	0.3386(2)	–0.2895(2)	1.65(6)
C3	0.3626(2)	0.2525(2)	–0.2824(2)	1.65(6)
C4	0.3244(2)	0.1595(2)	–0.1600(2)	1.47(6)
C5	0.3939(2)	0.0518(2)	–0.1151(2)	1.56(6)
C6	0.3575(2)	–0.0423(2)	–0.0002(2)	1.53(6)
C7	0.4305(2)	–0.1546(2)	0.0407(2)	1.66(6)
C8	0.3601(2)	–0.2214(2)	0.1575(2)	1.57(6)
C9	0.2438(2)	–0.1495(2)	0.1873(2)	1.56(6)
C10	0.1450(2)	–0.1839(2)	0.2978(2)	1.70(6)
C11	0.0302(2)	–0.1201(2)	0.3298(2)	1.56(6)
C12	–0.0650(2)	–0.1580(2)	0.4490(2)	1.74(6)
C13	–0.1621(2)	–0.0718(2)	0.4429(2)	1.71(6)
C14	–0.1267(2)	0.0199(2)	0.3192(2)	1.60(6)
C15	–0.1982(2)	0.1258(2)	0.2735(2)	1.67(6)
C16	–0.1635(2)	0.2188(2)	0.1577(2)	1.52(6)
C17	–0.2367(2)	0.3307(2)	0.1159(2)	1.61(6)
C18	–0.1673(2)	0.3976(2)	–0.0008(2)	1.57(6)
C19	–0.0512(2)	0.3253(2)	–0.0306(2)	1.52(6)
C20	0.0486(2)	0.3605(2)	–0.1405(2)	1.65(6)
C21	0.2492(3)	0.4483(2)	–0.3991(2)	2.08(7)
C22	0.1539(3)	0.4346(2)	–0.4468(2)	2.85(8)
C23	0.4823(3)	0.2457(2)	–0.3813(2)	2.07(7)
C24	0.4555(3)	0.1849(2)	–0.4397(2)	3.14(8)
C25	0.5549(2)	–0.1894(2)	–0.0353(2)	1.96(7)
C26	0.5279(3)	–0.2276(2)	–0.1126(2)	2.48(7)
C27	0.3888(2)	–0.3470(2)	0.2385(2)	2.01(7)
C28	0.3254(3)	–0.4320(2)	0.2302(2)	2.71(8)
C29	–0.0513(3)	–0.2692(2)	0.5583(2)	2.08(7)
C30	0.0480(3)	–0.2629(2)	0.6070(2)	2.81(8)
C31	–0.2798(3)	–0.0671(2)	0.5440(2)	2.24(7)
C32	–0.2525(3)	–0.0168(2)	0.6101(2)	3.41(8)
C33	–0.3614(2)	0.3665(2)	0.1916(2)	2.02(7)
C34	–0.3375(3)	0.4067(2)	0.2684(2)	2.39(7)
C35	–0.1972(2)	0.5230(2)	–0.0832(2)	1.84(6)
C36	–0.1369(3)	0.6111(2)	–0.0776(2)	2.33(7)

[a] Starred values refer to atoms that were included with isotropic thermal parameters. The thermal parameter given for anisotropically refined atoms is the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$ where *a*, *b*, and *c* are real cell parameters, and $B(i,\bullet)$ are anisotropic β's.

$(OEP)ScCH(SiMe_3)_2$. $(OEP)ScCl$ (0.25 g, 0.41 mmol) and $LiCH(SiMe_3)_2$ (0.068 g, 0.41 mmol) were combined in a 100-mL flask. Addition of toluene (20 mL) gave a dark red solution that was stirred for 20 min before being evaporated under vacuum. The residue was extracted with Et_2O (50 mL), and the solution was filtered, concentrated, and cooled to –40 °C overnight. The product was filtered off as dark red crystals (0.15 g, 50%, mp 237–245 °C). IR: 1239 (m), 1149 (s), 1108 (m), 1057 (s), 1013 (s), 957 (s), 913 (m), 867 (s), 840 (s), 731 (m), 664 (m) cm^{-1}. EI-MS: 735 (M^+ – H), 721, 577. ^1H NMR (250 MHz, C_6D_6, 20 °C), δ: –5.78 (s, 1 H, $C\mathit{H}(SiMe_3)_2$), –1.84 (s, 18 H, $CH(Si\mathit{Me}_3)_2$), 1.87 (t, J = 7 Hz, 24 H, $CH_2C\mathit{H}_3$), 4.03 (m, 16 H, $C\mathit{H}_2CH_3$), 10.58 (s, 4 H, CH). UV–vis (CH_2Cl_2): 570 (4.3), 530 (4.0), 390 (5.3). Anal. Calcd for $C_{41}H_{49}N_4Sc$: C, 70.1; H, 8.61; N. 7.60. Found: C, 70.3; H, 8.57; N, 7.40.

$(OEP)Sc(\eta^5\text{-}C_5H_5)$. Addition of THF (10 mL) to a mixture of $(OEP)ScCl$ (0.10 g, 0.16 mmol) and LiCp (0.012 g, 0.16 mmol) gave a bright red solution that was stirred for 3 h before being evaporated under vacuum. The residue was extracted with toluene (10 mL), filtered, concentrated to ca. 2 mL, and layered with pentane (5 mL). The layers were allowed to diffuse at 0 °C for 2 days. Red needles of the product (mp 312–317 °C) were isolated by filtration (0.10 g, 95%). IR: 1312 (w), 1269 (m), 1147 (s), 1107 (m), 1057 (s), 1009 (s), 979 (m), 957 (s), 842 (s), 741 (m), 700 (m) cm^{-1}. EI-MS: 642 (M^+), 577. ^1H NMR (300 MHz, C_6D_6, 20 °C), δ: 1.68 (s, 5 H, Cp), 1.87 (t, J = 7 Hz, 24 H, $CH_2C\mathit{H}_3$), 4.00 (m, 16 H, $C\mathit{H}_2CH_3$), 10.44 (s, 4 H, CH). UV–vis (CH_2Cl_2): 568 (4.4), 532 (4.1), 390 (5.4). Anal. Calcd for $C_{41}H_{49}N_4Sc$: C, 76.6; H, 7.68; N, 8.72. Found: C, 76.6; H, 7.71; N, 8.53.

$(OEP)Sc(\eta^5\text{-}C_5Me_5)$. Replacing LiCp in the above reaction with $Li(C_5Me_5)$ produced 0.11 g (96%) of bright red needles (mp 290–292 °C). IR: 1690 (w), 1313 (w), 1266 (m), 1147 (s), 1109 (m), 1056 (s), 1012 (s), 978 (m), 954 (s), 843 (s), 741 (m), 699 (m) cm^{-1}. EI-MS: 712 (M^+), 577. ^1H NMR (300 MHz, C_6D_6, 20 °C), δ: –0.61 (s, 15 H, C_5Me_5), 1.94 (t, J = 7 Hz, 24 H, $CH_2C\mathit{H}_3$), 4.00 (m, 16 H, $C\mathit{H}_2CH_3$), 10.44 (s, 4 H, CH). UV–vis (CH_2Cl_2): 568 (4.4), 532 (4.1), 390 (5.4). Anal. Calcd for $C_{41}H_{49}N_4Sc$: C, 77.5; H, 8.34; N, 7.86. Found: C, 77.5; H, 8.37; N, 7.73.

$(OEP)Sc(\eta^5\text{-}C_5H_4Me)$. Replacing LiCp in the above reaction with $Li(C_5H_4Me)$ produced 0.085 g (81%) of bright red needles (mp 245–247 °C). IR: 1314 (w), 1267 (m), 1146 (s), 1055 (s), 1016 (s), 956 (s), 912 (w), 843 (s), 780 (s), 746 (m), 697 (m) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 20 °C), δ: –0.62 (s, 3 H, $C_5H_4\mathit{Me}$), 1.49 (t, J = 2 Hz, 2 H, $C_5\mathit{H}_4Me$), 1.57 (t, J = 2 Hz, 2 H, $C_5\mathit{H}_4Me$), 1.88 (t, J = 7 Hz, 24 H, $CH_2C\mathit{H}_3$), 4.03 (m, 16 H, $C\mathit{H}_2CH_3$), 10.44 (s, 4 H, CH). UV–vis (CH_2Cl_2): 568 (4.6), 532 (4.3), 402 (5.5). Anal. Calcd for $C_{42}H_{51}N_4Sc$: C, 76.8; H, 7.83; N, 8.54. Found: C, 76.1; H, 7.66; N, 8.34.

$(OEP)Sc(\eta^5\text{-}C_9H_7)$. A 100-mL round-bottom Schlenk flask was charged with 0.400 g (0.652 mmol) of $(OEP)ScCl$ and 0.084 g (0.688 mmol) of LiC_9H_7 (prepared by the deprotonation of freshly distilled indene in hexanes with *n*-butyllithium). Via cannula, 50 mL of toluene was transferred into the flask. The solution was allowed to stir for 15 min at room temperature, turning bright red. The reaction mixture was transferred to a Schlenk frit, and the LiCl was removed by filtration of the solution through the frit. The filtrate was concentrated under reduced pressure to approximately 15 mL and placed in the –40 °C freezer for 48 h; 0.293 g (65%) of crystalline $(OEP)Sc(\eta^5\text{-}C_9H_7)$ was obtained. Mp: 265–269 °C. IR: 1455 (vs), 1334 (m), 1312 (m), 1265 (m), 1214 (m), 1186 (w), 1146 (s), 1129 (w), 1109 (m), 1056 (vs), 1046 (m), 1013 (vs), 978 (m), 953 (vs), 912 (m), 849 (m), 842 (s), 826 (w), 803 (w), 774 (vs), 747 (m), 739 (s), 731 (s), 706 (m), 603 (w), 543 (w), 493 (w), 485 (w), 436 (s) cm^{-1}. ^1H NMR: (300 MHz, $CDCl_3$, 20 °C) δ 1.46 (br s, 3 H, H(1), H(2), H(3)), 2.00 (t, J = 7 Hz, 24 H, $CH_2C\mathit{H}_3$), 4.15 (m, 16 H, $C\mathit{H}_2CH_3$), 4.73 (m, 2 H, H(5), H(8)), 5.64 (m, 2 H, H(6), H(7)), 10.20 (s, 4 H, CH); (500 MHz, C_6D_6, 20 °C) δ 1.86 (br s, 3 H, H(1), H(2), H(3)), 1.92 (t, J = 7 Hz, 24 H, $CH_2C\mathit{H}_3$), 4.02 (m, 16 H, $C\mathit{H}_2CH_3$), 5.01 (m, 2 H, H(5), H(8)), 5.82 (m, 2 H, H(6), H(7)), 10.34 (s, 4 H, CH). ^{13}C NMR (400 MHz, $CDCl_3$, 20 °C), δ: 18.7 (CH_3), 20.0 (CH_2–), 94.5 (CH), 99.6 (CH), 112.7 (CH), 117.8 (CH), 119.1 (CH), 120.4 (CH), 142.2 (CH), 146.1 (CH). UV–vis (CH_2Cl_2): 333 (4.3), 402 (5.4), 534 (4.2), 570 (4.4). EI-MS: 692 (M^+), 577. Anal. Calcd for $C_{45}H_{51}N_4Sc$: C, 78.0; H, 7.42; N, 8.09. Found: C, 77.6; H, 7.43; N, 8.09.

$(OEP)ScOTf$. $Me_3SiO_3SCF_3$ (160 μL, 0.83 mmol) was added by syringe to 0.30 g (0.43 mmol) of $Sc(OEP)Cl$(toluene) in 40 mL of toluene, and the solution was allowed to stir for 6 h. The toluene was removed and the solid dried under vacuum and then extracted with a 40-mL portion of toluene. The extract was concentrated and allowed to stand at –40 °C overnight. Bright red crystals of the hemi-toluene solvate (0.21 g, 63%) were collected and dried *in vacuo* to remove residual solvent. Mp: 302–304 °C. IR: 1318 (m), 1261 (m), 1235 (s), 1188 (w), 1146 (w), 1054 (m), 1030 (m), 1012 (m), 976 (w), 950 (m), 843 (m), 730 (m), 694 (m), 623 (s). ^1H NMR (300 MHz, C_6D_6, 20 °C), δ: 1.72 (t, J = 8 Hz, 24 H, $CH_2C\mathit{H}_3$), 3.84 (m, 16 H, $C\mathit{H}_2CH_3$), 10.22 (s, 4 H, $C\mathit{H}$). $^{19}F\{^1H\}$ NMR (376.4 MHz, C_6D_6, 20 °C), δ: –17.0. UV–vis (hexanes): 332 (4.3), 402 (5.3), 536 (4.2), 572 (4.4). EI-MS: 726 (M^+, 100%). Anal. Calcd for $C_{40.5}H_{48}F_3N_4O_3SSc$: C, 62.94; H, 6.26; N, 7.37. Found: C, 63.36; H, 6.34; N, 7.20.

$(OEP)ScO^tBu$. A 100-mL round-bottom Schlenk flask was charged with 0.400 g (0.652 mmol) of $(OEP)ScCl$ and 0.052 g (0.652 mmol) of $LiOC(CH_3)_3$. Via cannula, 50 mL of toluene was transferred into the flask. The solution was allowed to stir for 15 min at room temperature, during which time the solution became deep ruby red in color. The reaction mixture was transferred to a Schlenk frit, and the LiCl was removed by filtration of the solution through the frit. The filtrate was concentrated under reduced pressure to approximately 15 mL and placed in a −40 °C freezer overnight to yield 0.263 g (62%) of deep red crystalline (OEP)ScOC$(CH_3)_3$. Mp: 250–254 °C. IR: 1686 (w), 1576 (w), 1350 (m), 1315 (m), 1267 (m), 1203 (s), 1148 (s), 1107 (m), 1055 (s), 1013 (vs), 976 (m), 955 (s), 911 (m), 841 (s), 804 (w), 780 (m), 745 (m), 733 (s), 721 (m), 700 (m), 561 (s), 474 (w) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 20 °C), δ: −1.76 (br s, 9 H, $-OMe_3$), 1.95 (t, *J* = 7 Hz, 24 H, CH_2CH_3), 4.19 (m, 16 H, CH_2CH_3), 10.36 (s, 4 H, CH). UV–vis (CH_2Cl_2): 335 (4.3), 391 (5.2), 404 (5.2), 538 (4.1), 576 (4.2). EI-MS: 650 (M^+), 577. Anal. Calcd for $C_{40}H_{53}N_4OSc$: C, 73.8; H, 8.21; N, 8.61. Found: C, 73.6; H, 8.08; N, 8.35.

(OEP)ScO(2,4,6-$Me_3C_6H_2$). Toluene (40 mL) was added to a mixture of (OEP)ScCl (0.300 g, 0.489 mmol) and LiO(2,4,6-$Me_3C_6H_2$) (0.070 g, 0.493 mmol). The solution was stirred for 15 min at room temperature, during which time the solution became deep ruby red. Filtration, concentration under reduced pressure to approximately 10 mL, and cooling to −40 °C overnight afforded 0.227 g of red crystalline (OEP)ScO(2,4,6-$Me_3C_6H_2$) (65%). Mp: 295–296 °C. IR: 1683 (w), 1607 (w), 1525 (vw), 1319 (vs), 1273 (vs), 1212 (m), 1157 (m), 1148 (s), 1108 (m), 1062 (m), 1052 (s), 1013 (s), 975 (m), 956 (s), 910 (m), 865 (s), 851 (s), 840 (s), 804 (m), 735 (s), 702 (m), 562 (s), 496 (w), 465 (w) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 20 °C), δ: −1.02 (br s, 6 H, −O(2,4,*6*-$Me_3C_6H_2$)), 1.46 (s, 3 H, −O(2,*4*,6-$Me_3C_6H_2$)), 1.98 (t, *J* = 7 Hz, 24 H, CH_2CH_3), 4.20 (m, 16 H, CH_2CH_3), 5.49 (s, 2 H, −O(2,4,6-$Me_3C_6H_2$)), 10.43 (s, 4 H, CH). UV–vis (CH_2Cl_2): 336 (4.1), 399 (5.5), 534 (4.0), 570 (4.2). EI-MS: 712 (M^+), 577. Anal. Calcd for $C_{45}H_{55}N_4OSc$: C, 75.8; H, 7.78; N, 7.86. Found: C, 75.7; H, 7.85; N, 7.53.

(OEP)ScN$(SiMe_3)_2$. The method used to prepare the mesitoxide above was followed using 0.400 g (0.652 mmol) of (OEP)-ScCl and 0.114 g (0.681 mmol) of LiN$(SiMe_3)_2$. Deep red crystalline (OEP)ScN$(SiMe_3)_2$ was obtained in 58.6% yield (0.282 g). Mp: 280–285 °C. ^1H NMR: (300 MHz, C_6D_6, 20 °C) δ −1.82 (s, 18 H, $-SiMe_3$), 1.88 (t, *J* = 7 Hz, 24 H, CH_2CH_3), 3.98 (m, 16 H, CH_2CH_3), 10.46 (s, 4 H, CH); (300 MHz, $CDCl_3$, 20 °C) δ −2.28 (s, 18 H, $-SiMe_3$), 1.94 (t, *J* = 7 Hz, 24 H, CH_2CH_3), 4.13 (m, 16 H, CH_2CH_3), 10.30 (s, 4 H, CH). UV–vis (CH_2Cl_2): 335 (4.2), 400 (5.4), 534 (4.1), 572 (4.3). EI-MS: 737 (M^+), 722, 577. Anal. Calcd for $C_{42}H_{62}N_5ScSi_2$: C, 68.3; H, 8.47; N, 9.49. Found: C, 67.9; H, 8.47; N, 9.41.

[(OEP)Sc(μ-OH)]$_2$. A 100-mL round-bottom Schlenk flask was charged with 0.100 g (0.162 mmol) of (OEP)ScCl and 0.027 g (0.162 mmol) of LiN$(SiMe_3)_2$. Via cannula, 20 mL of toluene was transfered into the flask. The solution was allowed to stir for 20 min at room temperature, turning deep wine red. A 100-μL aliquot of degassed H_2O was added by syringe. The toluene was evaporated, and the residue was extracted with CH_2Cl_2 (50 mL) and filtered. Concentration, followed by cooling to −40 °C overnight, gave dark red crystals of the product as a methylene chloride solvate in 85% yield. Mp: 410–420 °C. IR: 1318 (w), 1266 (m), 1212 (w), 1146 (s), 1109 (m), 1057 (s), 1013 (vs), 978 (m), 954 (vs), 911 (w), 839 (vs), 802 (w), 748 (s), 718 (s), 701 (m), 668 (vw), 578 (vw), 512 (m), 465 (w), 419 (w) cm^{-1}. ^1H NMR: (500 MHz, C_6D_6, 20 °C) δ −7.52 (s, 1 H, −O*H*), 1.67 (t, *J* = 7 Hz, 24 H, CH_2CH_3), 3.85 (m, 16 H, CH_2CH_3), 9.55 (s, 4 H, CH); (500 MHz, $CDCl_3$, 20 °C) δ −7.93 (s, 1 H, −O*H*), 1.64 (t, *J* = 7 Hz, 24 H, CH_2CH_3), 3.94 (m, 16 H, CH_2CH_3), 9.43 (s, 4 H, CH). UV–vis (CH_2Cl_2): 335 (4.6), 404 (5.7), 536 (4.4), 574 (4.6). EI-MS: 1170 (M^+), 596, 577. Anal. Calcd for $C_{73}H_{92}Cl_2N_8O_2Sc_2$: C, 78.8; H, 7.28; N, 8.79. Found: C, 69.0; H, 7.50; N, 8.66.

X-ray Crystallography. Table I lists a summary of crystallographic data for all four structurally characterized compounds. General operating procedures (instrumentation, computation, etc.) were as previously described.[30] Crystals were covered with a layer of Paratone-N hydrocarbon oil, removed from the drybox, inspected, and mounted on glass fibers as described by Hope.[31] Mo Kα radiation (λ = 0.710 73 Å) was used throughout. The structures were determined at the CHEXRAY facility, University of California, Berkeley. The structure of the hydroxide was determined by P. J. Bonasia and Tim Patten under the supervision of Dr. Hollander. All ORTEP views show ellipsoids scaled to the 50% probability level.

(OEP)ScMe. Automatic peak search and indexing procedures yielded a triclinic reduced primitive cell. The 4804 unique raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. The data were corrected for a 6% intensity decay. The choice of the centric space group was confirmed by the successful solution and refinement of the structure. The structure was solved by direct methods (SHELXS) and refined by standard least-squares and Fourier techniques. In a difference Fourier map calculated following refinement of all non-hydrogen atoms with anisotropic thermal parameters, peaks were found corresponding to the positions of all the hydrogens except those on the disordered dichloromethane molecule. Most of the hydrogens were assigned idealized locations and were not refined; however, hydrogens on the metal-bonded methyl were refined with a common thermal parameter for all three. Inspection of the residuals ordered in ranges of $(\sin\theta)/\lambda$, $|F_o|$, and parity and value of the individual indexes showed no unusual features or trends. The largest peak in the final difference Fourier map had an electron density of 0.74 e/Å^3 and the lowest excursion −0.09 e/Å^3. The largest peak was located near the chlorines of the dichloromethane.

Two experiments were carried out following final refinement in attempts to gauge the effect of the presence of (OEP)ScCl in the crystal. In the first, the position of the methyl carbon was artificially moved inward to see what the effect on the C–H distances and Sc–C–H and H–C–H angles would be. This was based on the assumption that the overlapping Sc–*C* and Sc–*Cl* positions would result in a lengthening of the apparent Sc–C distance. However, any movement of the carbon position sufficient to result in reasonable C–H distances also resulted in highly unreasonable Sc–C–H angles. In the second experiment, a fractional-occupancy Cl atom was constrained to the same position as the C atom with a fixed B_{iso} of 1.5 Å^2. With a Cl occupancy of 0.1, the thermal parameters for C37 were large and the hydrogens refined to large C–H distances. At 0.05 chlorine occupancy, the B_{eq} for the carbon was 1.9 Å^2 with reasonable C–H distances. The Sc–C distance did not change significantly (2.250 Å). Changes in *R* values in both experiments were small.

(OEP)ScCH$(SiMe_3)_2$. Automatic peak search and indexing procedures yielded a monoclinic reduced primitive cell. Inspection of the Niggli values revealed no conventional cell of higher symmetry. The 5006 unique raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. No absorption correction was applied. The structure was solved by direct methods (SHELXS) and refined by standard least-squares and Fourier techniques. In a difference Fourier map calculated following refinement of all non-hydrogen atoms with anisotropic thermal parameters, peaks were found corresponding to most of the positions of the hydrogens. Hydrogen atoms were assigned idealized locations and values of B_{iso} approximately 1.25 times the B_{eq} of the atoms to which they were bonded. They were included in the structure factor calculations, but not refined. Inspection of the residuals ordered in ranges of $(\sin\theta)/\lambda$, $|F_o|$, and parity and value of the individual indexes showed no unusual features or trends.

(OEP)Sc(η^5-C_9H_7). Automatic peak search and indexing procedures yielded an orthorhombic reduced primitive cell. Inspection of the Niggli values revealed no conventional cell of

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[30] Bonasia, P. J.; Arnold, J. *Inorg. Chem.* **1992**, *31*, 2508.

[31] Hope, H. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; p 257.

higher symmetry. The 5368 raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. The structure was solved by direct methods (SHELXS) and refined by standard least-squares and Fourier techniques. Hydrogens were located and treated as above; they were included in the structure factor calculations, but not refined. Inspection of the residuals ordered in ranges of $(\sin\theta)/\lambda$, $|F_o|$, and parity and value of the individual indexes showed no unusual features or trends. There was no indication of secondary extinction in the high-intensity low-angle data.

[(OEP)Sc(μ-OH)]$_2$. The unit cell was determined to be primitive triclinic with space group $P\bar{1}$. The 4384 raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. The structure was solved by Patterson methods and refined by standard least-squares and Fourier techniques. The final residuals for 380 variables refined against the 3359 accepted data for which $F^2 > 3\sigma(F^2)$ were $R = 0.035$, $R_w = 0.042$, and GOF = 1.654. Hydrogens were located and treated as above; they were included in the structure factor calculations, but not refined. Inspection of the residuals ordered in ranges of $(\sin\theta)/\lambda$, $|F_o|$, and parity and value of the individual indexes showed no unusual features or trends.

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Supplementary Material Available: Tables of temperature factor expressions, positional parameters, intramolecular distances and angles, torsion angles, least-squares planes, and anisotropic thermal parameters and a figure showing a view of the disorder in [(OEP)Sc]$_2$(μ-OH)$_2$ (30 pages). Ordering information is given on any current masthead page.

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