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Synthesis and structure of inorganic and organometallic *N*,*N*′-bis(3, 5-di-*tert*-butylsalicylidene)ethylenediamine yttrium complexes

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Abstract

The utility of the chloride precursor [(salen′)Y(μ-Cl)(THF)]$_2$, **1** (salen′ = *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)ethylenediamine), in preparing amide, aryloxide, and organometallic derivatives of this ancillary ligand system is described. **1** reacts with KN(SiMe$_3$)$_2$ to form (salen′)Y[N(SiMe$_3$)$_2$](THF), **2**, but does not readily form an aryloxide derivative by reaction with LiOAr′ (OAr′ = 2,6-di-*tert*-butylphenoxide). However, (salen′)Y(OAr′), **3**, can be obtained by reaction of Y(OAr′)$_3$ with H$_2$salen′ and crystallizes from toluene–THF as (salen′)Y(OAr′)(THF), **4**. **4** can also be prepared by reaction of **2** with HOAr′ in THF. The hexafluoroacetylacetonate (hfac) complex, (salen′)Y(hfac)(THF)$_2$, **5**, and the organometallic derivative, (salen′)Y(C$_5$Me$_5$), **6**, can be prepared by reaction of **1** with Na(hfac) and KC$_5$Me$_5$, respectively.

Keywords: Yttrium; Salen; Amide; Aryloxide; Organometallic

1. Introduction

Efforts to diversify the ancillary ligands useful in lanthanide and yttrium chemistry beyond the commonly used cyclopentadienyl complexes have led to the exploration of a variety of polyhapto oxygen and/or nitrogen donor atom alternatives. Examples include benzamidinates [1], 4,13-diaza-18-crown-6 (DAC) [2], porphyrins [3], and calix-pyrroles [4]. Schiff base ligands are attractive in this regard due their stability and the ease by which modified variations can be obtained: this class of ligands is flexible in terms of both size and charge. To date, however, the number of structural [5–12] and catalytic [12,13] investigations of lanthanide Schiff base complexes in the literature is small compared with that for other ligand systems.

Recently, we reported synthetic and structural information on two non-aqueous yttrium Schiff base complexes utilizing *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-ethylenediamine) (salen′), namely [(salen′)Y(μ-Cl)-(THF)]$_2$, **1**, and Y(salen′)$_2$K(THF)$_2$ [14]. In this study, we explore the synthetic utility of **1** as a precursor to the several types of derivatives commonly explored when characterizing any new ancillary ligand system, e.g. an amide N(SiMe$_3$)$_2$, an aryloxide OC$_6$H$_3^t$Bu$_2$-2,6, and a cyclopentadienyl derivative. Structural details and chemical reactivity of these new complexes are discussed and compared with the data in the literature on (salen′)-Y[N(SiMe$_2$H)$_2$](THF) and (salen′)Y(OC$_6$H$_3^t$Bu$_2$-2,6)-(THF), whose preparation depended critically upon Y[N(SiMe$_2$H)$_2$]$_3$ [7].

2. Results and discussion

2.1. Synthesis of (salen′)Y[N(SiMe$_3$)$_2$](THF), 2

Complex **1** was initially examined as a precursor to the amido complex, (salen′)Y[N(SiMe$_3$)$_2$](THF) since the analogous (salen′)Y[N(SiMe$_2$H)$_2$](THF) had been reported in the literature and crystallographically characterized [7]. Reaction of **1** and KN(SiMe$_3$)$_2$ in toluene produces a dark orange alkane soluble solid in good yield as shown in Scheme 1. Both the ^{1}H NMR and IR spectra of **2** were similar to those of (salen′)-Y[N(SiMe$_2$H)$_2$](THF), including a strong IR peak at 1617 cm^{-1} appropriate for the imine functionality in

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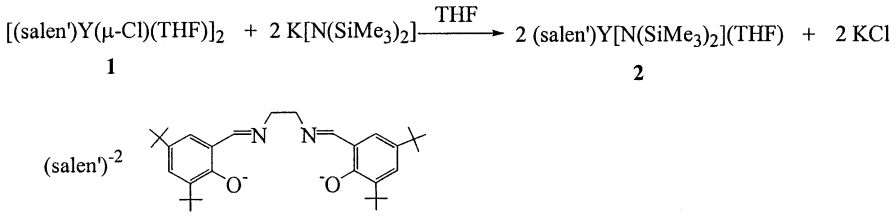


Scheme 1.

salen′. Complexometric analysis was consistent with the formula (salen′)Y[N(SiMe$_3$)$_2$](THF), **2**.

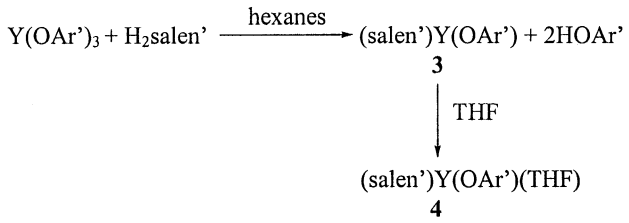
2.2. Synthesis of [(salen′)Y(OC$_6$H$_3^t$Bu$_2$-2,6)], 3, and [(salen′)Y(OC$_6$H$_3^t$Bu$_2$-2,6)] (THF), 4

The synthesis of an aryloxide complex from **1** was subsequently attempted since it had been reported previously that (salen′)Y(OC$_6$H$_3^t$Bu$_2$-2,6)](THF) could be made [7]. Ionic metathesis of **1** with LiOAr′ (OAr′ = OC$_6$H$_3^t$Bu$_2$-2,6) did not produce a pure aryloxide by ^{1}H NMR spectroscopy. Instead, the ^{1}H NMR spectrum of the product was complicated and suggested that multiple products had formed.

However, reaction of Y(OAr′)$_3$ [15] and H$_2$salen′ in hexanes precipitated a yellow solid that had a simple NMR spectrum consistent with (salen′)Y(OAr′), **3**. Complex **3** displayed high solubility in coordinating solvents, such as THF, and was moderately soluble in benzene and toluene, but had only limited solubility in alkanes. Attempts to crystallize **3** in a non-coordinating medium were unsuccessful. However, when **3** is concentrated in a 50/50 mixture of toluene–THF and cooled to −35 °C, yellow crystals are obtained which were analyzed by X-ray crystallography and determined to be the THF adduct (salen′)Y(OAr′)(THF), **4** (Scheme 2, Fig. 1). As expected [7], **2** could be transformed quantitatively to **4** by reaction with HOAr′ in THF, Scheme 3.

2.3. Synthesis of (salen′)Y(hfac)(THF)$_2$, 5

Although **3** was not easily synthesized by ionic metathesis, this synthetic approach did succeed with the chelating oxygen donor ligand hexafluoroacetylacetonate (hfac). **1** reacts with Na(hfac) to form a yellow solution and a white precipitate according to Scheme 4.



Scheme 2.

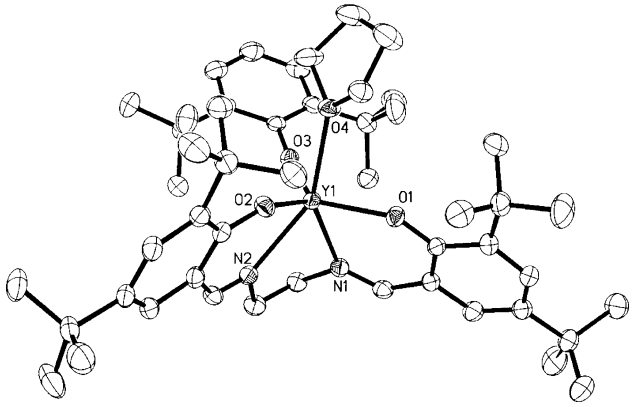


Fig. 1. Thermal ellipsoid plot of [(salen′)Y(OC$_6$H$_3$Bu$_2^t$-2,6)(THF)], **4**, drawn at the 50% probability level with hydrogen atoms omitted for clarity.

The yellow product had a ^{1}H NMR spectrum consistent with the formula (salen′)Y(hfac)(THF)$_2$, **5**, and the IR spectrum contained two strong absorbances at 1660 and 1613 cm^{-1} attributable to [C=O]$_{hfac}$ and [C=N]$'_{salen}$. X-ray diffraction confirmed the identity of this product as (salen′)Y(hfac)(THF)$_2$, **5**, Fig. 2.

2.4. Synthesis of organoyttrium salen′ complexes

In attempt to isolate an organometallic complex of the salen′ yitrium system, the reaction of **1** and KC$_5$Me$_5$ was examined. (salen′)Y(C$_5$Me$_5$), **6** could be isolated in good yields (Scheme 5) and was fully characterized by NMR, IR and X-ray diffraction (Fig. 3). In contrast, when **1** reacts with simple lithium alkyls, LiR (R = Me, CH$_2$SiMe$_3$, CH(SiMe$_3$)$_2$), in toluene at −78 °C, a mixture is indicated by the complicated ^{1}H NMR spectrum. These mixtures could result from attack of the alkyl on the imine portion of the salen′ ligand as has been reported to occur in Group IV systems [16,17]. The susceptibility of the imine bonds to nucleophilic attack could be further enhanced by coordination to the highly electropositive metal.

2.5. Structural comparison of yttrium–salen′ complexes

The Y–O(salen′) distances in **4**, **5**, and **6** range from 2.141(2) to 2.240(2) Å while the Y–N(salen′) interactions range from 2.392(3) to 2.559(3) Å (Table 1). These

$$\underset{\mathbf{2}}{\text{(salen')Y[N(SiMe}_3)_2\text{](THF)}} + \text{HOAr'} \xrightarrow{\text{THF}} \underset{\mathbf{4}}{\text{(salen')Y(OAr')(THF)}} + \text{HN(SiMe}_3)_2$$

Scheme 3.

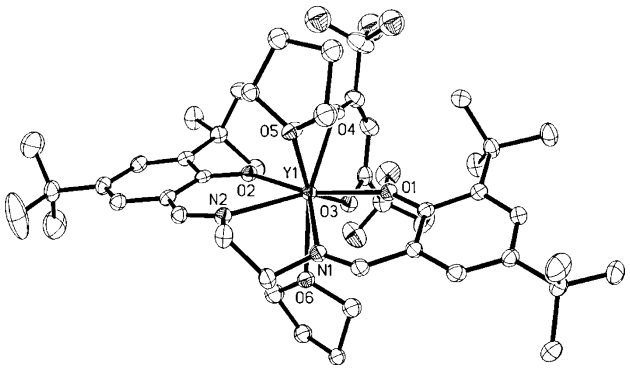


Fig. 2. Thermal ellipsoid plot of (salen′)Y(hfac)(THF)$_2$, **5**, drawn at the 50% probability level with hydrogen atoms omitted for clarity.

distances are consistent with Ln–O and Ln–N salen′ distances in other reported Schiff base complexes when metal sizes are taken in consideration [20] (Ln–O and Ln–N): [(salen′)Y(μ-Cl)(THF)]$_2$ [14], 2.143(2) and 2.492(3) Å; (salen′)Y[N(SiMe$_2$H)$_2$](THF) [7], 2.16 and 2.27 Å; [(*N*-(2,4,6-trimethylphenyl)salicylideneimine)$_2$La(μ-Cl)(THF)] [10], 2.295(11) and 2.659(16) Å; [(*trans*-(±)-*N*,*N*′-bis(salicylidene)-1,2-cyclohexanediamine)Sm(C$_5$H$_5$)]$_2$(μ-THF)(THF)$_2$ [9], 2.30(6) and 2.56(5) Å.

The salen′ moieties in complexes **4**–**6** adopt bent geometries about the yitrium metal center as measured by the dihedral angle between the two phenyl rings. The aryloxide, **4**, which has the largest deviation from planarity, 60.2°, is followed by the pentamethylcyclopentadienyl, complex **6**, with a 44° angle, and the hfac complex, **5**, with a 17° angle. These angles show that the salen′ ethylene backbone is flexible and is able to adopt a preferred orientation with respect to the steric bulk of the second ligand in the complex, i.e. the alkoxide, hfac, or cyclopentadienyl group.

The 2.128(2) Å Y–O(OAr′) distance in **4**, the 2.383(2) and 2.404(2) Å Y–O(hfac) distances in **5**, and the 2.372 Å Y-(C$_5$Me$_5$ ring centroid) length in **6** are similar to analogous bond lengths in other yttrium complexes containing these groups: e.g. 2.096(4) Å, Y–O(OAr′) in (C$_5$Me$_5$)Y(OC$_6$H$_3^t$Bu$_2$-2,6)$_2$ [18]; 2.283(7) and 2.322(6) Å, Y–O(hfac) in [(triglyme)Y(hfac)$_2$]$^+$ [19]; and 2.381 Å, Y-(C$_5$Me$_5$ ring centroid) in (C$_5$Me$_5$)$_2$YCl(THF) [20]. These comparisons suggest that salen′ can provide coordination equivalent to that of (C$_5$Me$_5$)(OC$_6$H$_3^t$Bu$_2$-2,6), (hfac)(triglyme), or (C$_5$Me$_5$)Cl(THF).

3. Conclusion

These studies have shown that the readily obtainable chloride, [(salen′)Y(μ-Cl)(THF)]$_2$ and ionic metathesis reactions are synthetically useful in making yttrium complexes ligated by salen′. Reactions of **1** with KN(SiMe$_3$)$_2$, Na(hfac), and KC$_5$Me$_5$ all form the corresponding products in high yields. Although the chemistry of salen′ as an ancillary ligand is promising, it contains a reactive imine functional group that is prone to nucleophilic attack. This can interfere with the isolation of complexes of reactive alkyl and hydride groups.

4. Experimental

The chemistry described below was performed under nitrogen with rigorous exclusion of air and water by Schlenk, vacuum line, and glovebox techniques. Solvents were purified by distillation over sodium or potassium benzophenone ketyl. KN(SiMe$_3$)$_2$ was purchased from Aldrich and used as received. [(salen′)Y(μ-Cl)(THF)]$_2$ [14] and Y[(OC$_6$H$_3$Bu$_2^t$-2,6)$_2$]$_3$ [15] were prepared by literature methods. NMR spectra were recorded using a Bruker DRX400 or a General Electric GE500 spectrometer. Infrared spectra were recorded on a ReactIR1000 system (Applied System Inc.) as thin films in toluene. X-ray crystallographic data were obtained on a Bruker CCD platform diffractometer. Complexometeric analyses were obtained as previously described [21].

4.1. (Salen′)Y[N(SiMe$_3$)$_2$](THF), 2

In a glovebox KN(SiMe$_3$)$_2$ (52 mg, 0.26 mmol) was added to a slurry of **1** (180 mg, 0.26 mmol) in 5 ml of toluene. After stirring for 12 h, the dark orange–red slurry was centrifuged to remove KCl. The solvent was removed by rotary evaporation and the dark orange–

$$\underset{\mathbf{1}}{\text{[(salen')Y(μ-Cl)(THF)]}_2} + 2\ \text{Na(hfac)} \xrightarrow{\text{THF}} 2\ \underset{\mathbf{5}}{\text{(salen')Y(hfac)(THF)}_2} + 2\ \text{NaCl}$$

Scheme 4.

$$\underset{\mathbf{1}}{[(\text{salen'})\text{Y}(\mu\text{-Cl})(\text{THF})]_2} + 2\ \text{K}(\text{C}_5\text{Me}_5) \xrightarrow{\text{THF}} \underset{\mathbf{6}}{2\ (\text{salen'})\text{Y}(\text{C}_5\text{Me}_5)} + 2\ \text{KCl}$$

Scheme 5.

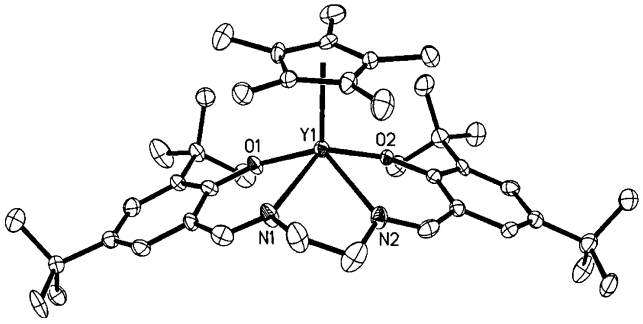


Fig. 3. Thermal ellipsoid plot of (salen′)Y(C_5Me_5), **6**, drawn at the 50% probability level with hydrogen atoms omitted for clarity.

Table 1
Selected bond lengths for [(salen′)Y(μ-Cl)(THF)]$_2$, **1**; (salen′)-Y(OAr′)(THF), **4**; (salen′)Y(hfac)(THF)$_2$, **5**; (salen′)Y(C_5Me_5), **6**

Complex	Y–O(salen′)	Y–N(salen′)	Y–O(THF)
1	2.143(2)	2.492(3)	2.463(3)
	2.143(2)	2.418(3)	
4	2.165(2)	2.430(3)	2.457(2)
	2.179(2)	2.483(3)	
5	2.205(2)	2.511(3)	2.379(2)
	2.240(2)	2.559(3)	2.425(2)
6	2.141(2)	2.392(3)	
	2.148(2)	2.418(3)	

red oil was stirred for 15 min in hexanes. Removal of solvent by rotary evaporation gave a dark orange powder (155 mg, 72%). *Anal*. Calc. for $C_{42}H_{72}N_3O_3Si_2Y$: Y, 10.9. Found: Y, 11.2%. ^{1}H NMR (C_6D_6): δ 7.73 (s, 2H), 7.69 (d, 2H, $J = 2.5$ Hz), 7.03 (d, 2H, $J = 2.5$ Hz), 4.39 (q, 2H, $J = 6.0$ Hz), 4.10 (b, 4H, $\Delta\nu_{1/2} = 125$ Hz), 2.82 (q, 2H, $J = 6.0$ Hz), 1.63 (s, 18H), 1.50 (b, 4H, $\Delta\nu_{1/2} = 120$ Hz), 1.36 (s, 18H), 0.26 (s, 18H). ^{13}C{^{1}H} NMR: δ (C_6D_6) 170.6, 164.4, 139.2, 136.8, 130.0, 129.7, 122.6, 70.2, 59.0, 35.7, 34.1, 31.7, 30.3, 25.4, 5.3. IR 2957vs, 2907s, 2868s, 1617vs, 1536s, 1463s, 1440s, 1413s, 1390s, 1274w, 1235w, 1200w, 1166s, 1054w, 1027w, 980w, 837m cm^{-1}.

4.2. (Salen′)Y($OC_6H_3Bu^t_2$-2,6)(THF)$_{0,1}$, **3**, **4**

Addition of H_2salen′ (111 mg, 0.22 mmol) to a white slurry of Y(OAr′)$_3$ (159 mg, 0.22 mmol) in 5 ml of hexanes immediately generated a yellow solution. Within a few minutes, a yellow precipitate appeared. The reaction was stirred overnight and the slurry was centrifuged to separate a yellow solid and light yellow solution. The yellow solid was isolated and dried by rotary evaporation (151 mg, 85%). X-ray quality crystals were grown from a 50/50 mixture of toluene–THF at −35 °C. *Anal*. Calc. for $C_{50}H_{75}N_2O_4Y$: Y, 10.4. Found: Y, 9.9%. ^{1}H NMR (C_6D_6): δ 7.73 (d, 2H, $J = 2.4$ Hz), 7.65 (s, 2H), 7.31 (d, 2H, $J = 7.7$ Hz), 7.06 (d, 2H, $J = 2.4$ Hz), 6.82 (t, 1H, $J = 7.7$ Hz), 3.73 (q, 2H, $J = 6.5$ Hz), 2.76 (q, 2H, $J = 6.5$ Hz), 1.69 (s, 18H), 1.46 (s, 18H), 1.36 (s, 18H). ^{13}C{^{1}H} NMR (C_6D_6): δ 170.9, 164.1, 139.8, 138.0, 137.8, 130.6, 129.6, 129.3, 124.9, 122.7, 116.7, 58.2, 35.7, 34.7, 34.1, 31.7, 30.6, 30.1. IR 2958vs, 2912s, 2873s, 1614vs, 1537s, 1437m, 1321m, 1259a, 1205w, 1166m, 1097w, 1027w, 841w, 803w cm^{-1}.

4.3. (Salen′)Y(hfac)(THF)$_2$, **5**

Na(hfac) (51 mg, 0.22 mmol) was added to a yellow slurry of **1** (152 mg, 0.22 mmol) in 5 ml of THF. After stirring for 12 h, the yellow slurry was centrifuged and the solvent was removed from the yellow solution under vacuum (169 mg, 82%). X-ray quality crystals were grown from a toluene solution at room temperature (r.t.). *Anal*. Calc. for $C_{45}H_{63}N_2O_6F_6Y$: Y, 9.6. Found: Y, 9.4%. ^{1}H NMR (C_6D_6): δ 7.91 (s, 2H), 7.70 (d, 2H, $J = 2.6$ Hz), 7.11 (d, 2H, $J = 2.6$ Hz), 6.48 (s, 1H), 3.40 (b, 8H, $\Delta\nu_{1/2} = 116$ Hz), 3.28 (s, 4H), 1.64 (s, 18H), 1.37 (s, 18H), 1.14 (b, 8H, $\Delta\nu_{1/2} = 124$ Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 168.6, 165.0, 140.5, 135.7, 129.7, 129.1, 120.8, 91.9, 69.4, 63.3, 35.5, 34.0, 31.8, 29.9, 25.2. IR 2957vs, 2914s, 2868s, 1660vs, 1613s, 1552w, 1498m, 1463w, 1440m, 1413m, 1393w, 1363w, 1339m, 1332s, 1254s, 1200s, 1146s, 1100s, 1023s, 911w, 872w cm^{-1}.

4.4. (Salen′)Y(C_5Me_5), **6**

KC_5Me_5 (33 mg, 0.19 mmol) was added to **1** (133 mg, 0.19 mmol) in 5 ml of THF. The reaction was stirred for 12 h, the yellow slurry was centrifuged, and the solvent was removed from the yellow solution by rotary evaporation to give a yellow oil. Hexanes were added, the mixture was stirred, and solvent was removed from the oil by rotary evaporation to give a yellow solid (103 mg, 75%). X-ray quality crystals were grown from a 50/50 toluene–hexanes mixture at r.t. *Anal*. Calc. for $C_{46}H_{80}N_3O_4Si_2Y$: Y, 12.4. Found: Y, 11.6%. ^{1}H NMR (C_6D_6): δ 7.71 (d, 2H, $J = 2.3$ Hz), 7.70 (s, 2H), 7.07 (d, 2H, $J = 2.3$ Hz), 3.60 (q, 2H, $J = 6.5$ Hz), 2.68 (q, 2H, $J = 6.5$ Hz), 2.00 (s, 15H), 1.75 (s, 18H), 1.36 (s, 18H).

$^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 169.9, 164.9, 140.2, 136.8, 130.0, 129.5, 122.4, 116.7, 58.3, 35.8, 34.1, 31.7, 30.3, 11.1. IR 2957vs, 2907s, 2868s, 1610vs, 1532s, 1463w, 1440m, 1413m, 1390m, 1359w, 1316s, 1274s, 1254s, 1200m, 1166s, 1096w, 1058w, 1027w, 984w, 930w, 911w, 876w, 849m cm^{-1}.

4.5. X-ray data collection, structure determination, and refinement for [(salen′)Y($OC_6H_3Bu^t_2$-2,6)(THF)], 4

A colorless crystal of approximate dimensions 0.16 × 0.19 × 0.25 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART [22] program package was used to determine the unit-cell parameters and for data collection (30 s per frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT [23] and SADABS [24] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL [25] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/n$ which was later determined to be correct. Details are in Table 2.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors [26] for neutral atoms were used throughout the analysis. There were 2.5 molecules of toluene solvent present per formula unit. The half molecule of solvent was modeled as a disorder over an inversion center. Hydrogen atoms were included using a riding model. At convergence, $wR_2 = 0.1788$ and GOF = 0.0631 for 586 variables refined against 15 186 unique data. As a comparison for refinement on *F*, $R_1 = 0.0631$ for those 9780 data with $I > 2.0\sigma(I)$. Subsequent complexes were handled as described for **4**.

4.6. (Salen′)Y(hfac)(THF)$_2$, 5

A yellow crystal of approximate dimensions 0.17 × 0.20 × 0.33 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer (30 s per frame scan time for a hemisphere of diffraction data). The diffraction symmetry was 2/*m* and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/c$ which was later determined to be correct.

Disorder was present in the CF_3 group and both THF molecules. Atoms F(4)–F(5), C(38)–C(40), C(43) and C(44) were disordered and included using multiple components with partial site-occupancy factors. Hydrogen atoms were included using a riding model. At convergence, $wR_2 = 0.1533$ and GOF = 1.032 for 518 variables refined against 10 952 data. As a comparison for refinement on *F*, $R_1 = 0.0576$ for those 8653 data with $I > 2.0\sigma(I)$.

4.7. (Salen′)Y(C_5Me_5), 6

A yellow crystal of approximate dimensions 0.10 × 0.15 × 0.25 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer (30 s per frame scan time for a hemisphere of diffraction data). The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space group $P2_12_12_1$ which was later determined to be correct.

Hydrogen atoms were included using a riding model. At convergence, $wR_2 = 0.0592$ and GOF = 0.934 for 424 variables refined against 9633 data. As a comparison for refinement on *F*, $R_1 = 0.0452$ for those 6021 data with $I > 2.0\sigma(I)$. The absolute structure was assigned by refinement of the Flack parameter [26].

Table 2
X-ray crystallographic data on Y(salen′)($OC_6H_3Bu^t_2$-2,6)(THF), **4**, Y(salen′)hfac$(THF)_2$, **5**, (salen′)Y(C_5Me_5), **6**

Compound	4	5	6
FW	$C_{50}H_{73}N_2O_4Y \cdot 2.5(C_7H_8)$	$C_{45}H_{63}F_6N_2O_6Y$	$C_{42}H_{61}N_2O_2Y$
Temperature (K)	178 (2)	158 (2)	158 (2)
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_1/c$	$P2_12_12_1$
a (Å)	16.5331(7)	13.7169(6)	10.4859(9)
b (Å)	16.0380(6)	21.1351(10)	15.7481(13)
c (Å)	23.5698(9)	16.7430(7)	24.370(2)
α (°)	90	90	90
β (°)	92.4660(10)	109.0750(10)	90
γ (°)	90	90	90
V (Å^3)	6243.9(4)	4587.4(4)	4024.2(6)
Z	4	4	4
ρ_{calc} (Mg m^{-3})	1.157	1.348	1.180
μ (mm^{-1})	0.980	1.343	1.484
Final $R_1[I > 2\sigma(I)]$	0.0631	0.0576	0.0452
Final wR_2 (all data)	0.1788	0.1533	0.0592

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Numbers CCDC 172137–172139 for compounds **4**–**6**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http//www.ccdc.cam.ac.uk).

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