# Halide titanium(IV) Schiff base complexes; fluoride and bromide derivatives and evidence for a new seven-coordinate chloride intermediate

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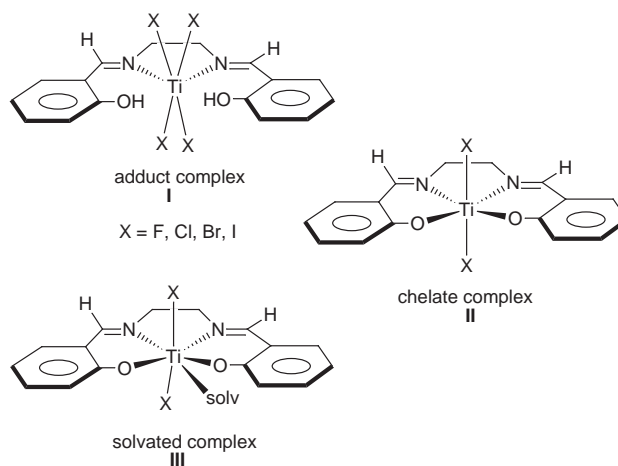
The synthesis of titanium(IV) Schiff base complexes has been investigated using the tetradentate salen ligand and its derivatives [L = salenH$_2$ = $N,N'$-bis(salicylidene)ethylenediamine]. Complexes of the form [TiX$_2$(L)], [(thf)TiX$_2$(L)] and [TiX$_4$(LH$_2$)] have been observed with the nature of these products being dependent on the salen derivative, halide and reaction condition employed. The reaction of [(thf)$_2$TiF$_4$] with salenH$_2$ yields the complex [TiF$_4$(salenH$_2$)] **1** which does not eliminate HF to form [TiF$_2$(salen)] **2** even after toluene reflux. Compound **2** can be obtained in 90% yield using the silylated Schiff base salen(TMS)$_2$ (TMS = Me$_3$Si) and [(thf)$_2$TiF$_4$] in thf. Compound **2** has been characterised by single crystal X-ray diffraction. Refluxing an equimolar ratio of salenH$_2$ and TiCl$_4$ gave the previously prepared [TiCl$_2$(salen)] **3**, while stirring the same reactants at room temperature afforded the seven-coordinate solvent adduct [(thf)TiCl$_2$(salen)] **4** in quantitative yield. TiBr$_4$ reacts similarly with salenH$_2$ or salen(TMS)$_2$ to give [TiBr$_2$(salen)] **5**. The bromide analogue of **4** was identified from its characteristic FAB$^+$ mass spectrum. Reaction of TiI$_4$ with salen(TMS)$_2$ or salenH$_2$ in thf or MeCN gave the μ-oxo bridged species [TiI(salen)]$_2$(μ-O) **6** in preference to the iodide analogue of [TiX$_2$(salen)]. Substituted Schiff bases (MeO)$_2$salenH$_2$, salphenH$_2$ and (MeO)$_2$salphenH$_2$ [salphenH$_2$ = $N,N'$-bis(salicylidene)-1,2-phenylenediamine] react with TiCl$_4$ (1:1) to yield the corresponding dichloride complexes [TiCl$_2$(L)] [L = (MeO)$_2$salen **7**, salphen **8**, (MeO)$_2$salphen **9**] via the elimination of HCl. In contrast, the α-methylated salen derivative dmsalenH$_2$ [$N,N'$-bis(α-methylsalicylidene)-ethylenediamine] reacts in an analogous manner to the TiF$_4$–salen system affording [TiCl$_4$(dmsalenH$_2$)] **10**.

## Introduction

Schiff base ligands have played an integral role in the development of coordination chemistry since the late nineteenth century. That metal complexes of these ligands are ubiquitous is a reflection of their facile synthesis and the accessibility of diverse structural modifications. It is perhaps remarkable then that within Group 4 the many studies of titanium halide complexes have been restricted to the chloride derivatives,[1–5] whilst the few reports of zirconium and hafnium complexes are limited to the same halide.[6–9] More recent studies have focused on the alkylation of such complexes to afford viable olefin polymerisation catalysts.[6,10] Model systems have indicated that metal or ligand alkylation, metal reduction and post-alkylation metal to ligand alkyl migration are all potentially feasible; mixtures of reaction products are often formed and the exact nature of the isolated products appears to be susceptible to the metal, Schiff base ligand, solvent and alkylating agent involved.[6,11–13] There are no reports considering the role of the halide in influencing the formulation of such alkylated derivatives. Thus, as part of our studies of Group 4 alkylation using trimethylaluminium [14,15] we have developed synthetic routes to titanium(IV) Schiff base complexes containing halide counter ions.

Within this work reference will be made to the three classical forms of Schiff base interaction with titanium (see below). Thus the potentially tetradentate salenH$_2$ ligand may act as a bidentate nitrogen donor in adduct **I**, or eliminate HX to form the typical chelate **II**. The formation of solvated derivatives, **III**, of chelated complexes have been reported for zirconium,[9] and are thus also investigated here. The retention of acidic hydrogens in adduct complexes suggests that this type of complex

may be unattractive for subsequent reactivity studies, as organometallics (e.g. RLi, RMgX, AlR$_3$) react with acidic residues in addition to halide ligands. Therefore, as part of our continuing investigations into the activation of Group 4 Schiff base complexes with alkylaluminiums,[14,15] the conditions which favour the isolation of chelate complexes, our preferred precursors, over adduct complexes have been thoroughly investigated and identified.



adduct complex **I**  X = F, Cl, Br, I
chelate complex **II**
solvated complex **III**

## Results and discussion

### Fluoride complexes

The preparation of titanium(IV) chelate complexes containing fully ionised tetradentate Schiff base ligands [MX$_2$(L)] (M = Ti;
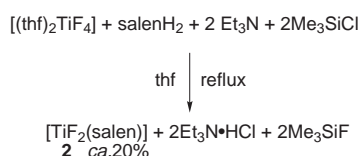
**Table 1** Selected data for titanium(IV) Schiff base complexes

| Complex | Colour | Yield (%) | $^1$H $HC$=N$^a$ $\delta$ (ppm) | $\nu$(C=N)$^d$/cm$^{-1}$ | Elemental analysis | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | N | X |
| [TiF$_4$(salenH$_2$)] **1** | Yellow | 96 | 8.34 | 1633 | 48.1 (48.9) | 4.3 (4.1) | 7.0 (7.1) | |
| [TiF$_2$(salen)] **2** | Yellow | 90 | 8.35 | 1631 | 54.4 (54.5) | 3.8 (4.0) | 8.3 (8.0) | 13.2 (13.6) |
| [TiCl$_2$(salen)] **3** | Red | 75–85 | 8.39$^b$ | 1612 | 49.8 (49.9) | 3.6 (3.6) | 7.2 (7.3) | |
| [(thf)TiCl$_2$(salen)] **4** | Orange | 97 | 8.34 | 1613 | 51.6 (52.5) | 4.7 (4.8) | 6.5 (6.1) | 15.8 (15.5) |
| [TiBr$_2$(salen)] **5** | Red | 95 | 8.45 | 1609 | 40.8 (40.5) | 3.1 (3.0) | 6.0 (6.0) | 33.0 (33.7) |
| [TiI(salen)]$_2$($\mu$-O) **6** | Orange | 46 | insol. | 1618 | 43.7 (42.8) | 3.2 (3.1) | 6.4 (6.2) | |
| [TiCl$_2$\{(MeO)$_2$salen\}] **7** | Black | 80 | 8.40$^c$ | 1622 | 48.6 (48.5) | 4.2 (4.0) | 6.6 (6.3) | |
| [TiCl$_2$(salphen)] **8** | Brown | 96 | insol. | 1610 | 55.6 (55.4) | 3.2 (3.2) | 6.3 (6.5) | |
| [TiCl$_2$\{(MeO)$_2$salphen\}] **9** | Black | 85 | 8.90$^c$ | 1599 | 52.2 (53.5) | 4.1 (3.7) | 5.2 (5.7) | |
| [TiCl$_4$(dmsalenH$_2$)] **10** | Orange | 96 | insol. | 1626 | 44.3 (44.4) | 4.9 (4.1) | 5.8 (5.8) | |

$^a$ In CDCl$_3$. $^b$ Refs. 3 and 4. $^c$ In CD$_2$Cl$_2$. $^d$ Nujol mull.

X = F, Cl, Br, I) cannot always be achieved by the binary combination of metal salt and ligand with the elimination of the corresponding acid, HX. However, as this route has been employed by previous authors in their preparation of type **II** chelates we envisaged this as the obvious route to the fluoride derivative of **II**. Nonetheless, an equimolar mixture of bis-(tetrahydrofuran)titanium(IV) fluoride, necessary for the purification of titanium(IV) fluoride, and salenH$_2$ in thf does not yield the expected chelate. Instead an adduct complex, with the stoichiometry [TiF$_4$(salenH$_2$)] **1**, is isolated as a bright yellow free flowing powder in quantitative yield, Table 1. Furthermore, [TiF$_2$(salen)] **2** could not be prepared from the reaction of [TiCl$_2$(salen)] **3** with sodium fluoride (1:2) despite the propensity of titanium to bond favourably to fluorine; a heterogeneous mixture of **3** and excess sodium fluoride in acetonitrile or thf was recovered unchanged after prolonged reflux (ca. 1 d).

Careful addition of 2 equivalents of anhydrous Me$_3$SiCl to a mixture of [(thf)$_2$TiF$_4$], salenH$_2$ and Et$_3$N (1:1:2) in hot thf gave **2** in low yield (ca. 20%) after work up, Scheme 1. Using the

[(thf)$_2$TiF$_4$] + salenH$_2$ + 2 Et$_3$N + 2Me$_3$SiCl

thf | reflux

[TiF$_2$(salen)] + 2Et$_3$N•HCl + 2Me$_3$SiF
**2** ca.20%

**Scheme 1** Formation of compound **2** from [(thf)$_2$TiF$_4$] and salenH$_2$ in the presence of 2 equivalents of Et$_3$N and 2 equivalents of Me$_3$SiCl.

strategy that the formation of Me$_3$SiF appears to thermodynamically favour titanium–fluorine cleavage the substituted Schiff base salen(TMS)$_2$ (TMS = Me$_3$Si) was prepared. Subsequent addition to [(thf)$_2$TiF$_4$] in thf followed by refluxing afforded, via the elimination of Me$_3$SiF, **2** as a bright yellow crystalline solid. Compound **2** is air stable and soluble in thf, acetonitrile, dichloromethane and chloroform. This contrasts with the chloride derivative, [TiCl$_2$(salen)] **3**, which is only very sparingly soluble in these polar solvents. The preparation of **2** represents the first example of a Group 4 Schiff base complex containing fluoride ligands. The crystal structure of **2** is discussed in the following section.
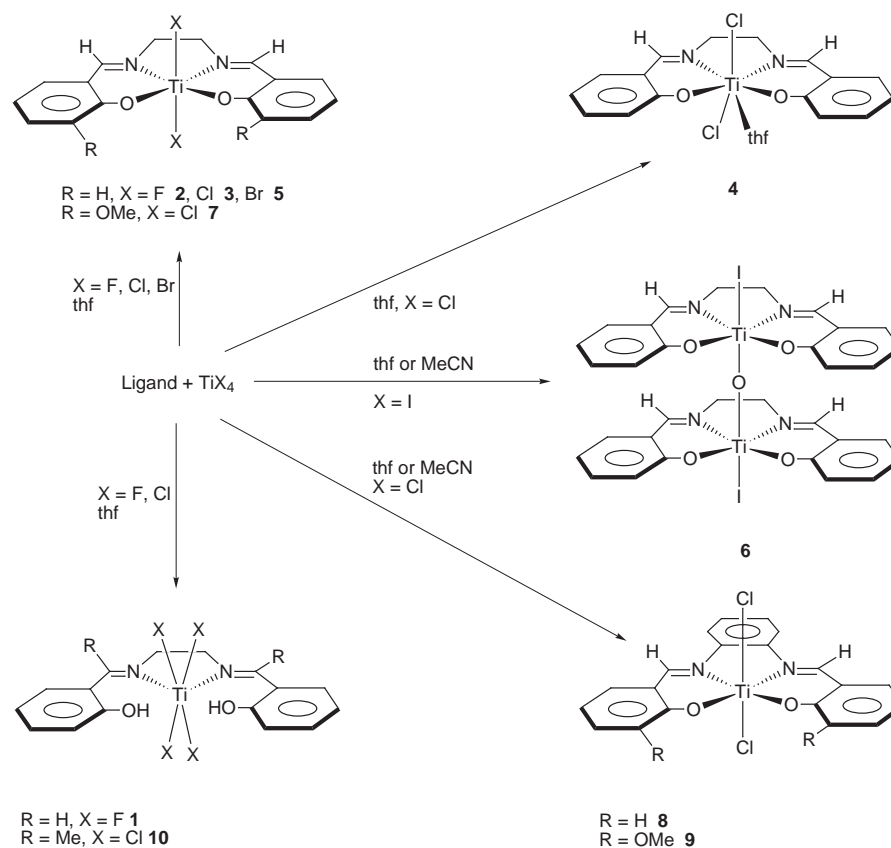
### Chloride complexes

The chloro complex [TiCl$_2$(salen)] **3** has been reported by

several groups and used as a precursor for organometallic derivatives.[4,11,12] Moreover, synthetic procedures have been reported which allow the isolation of **3** or the adduct complex [TiCl$_4$(salenH$_2$)] **Ia** using the same reactants in polar or non-polar reaction media at different temperatures.[16] Compound **3** has been crystallographically characterised as its thf solvate, albeit as the result of oxidation from [(thf)TiCl$_3$(salenH$_2$)].[17] Thus, as expected the reaction of TiCl$_4$ with salenH$_2$ in refluxing thf afforded **3** as a dark red complex in 75–85% yield. However, repeating the reaction in the same solvent at ambient temperature immediately resulted in the precipitation of [(thf)-TiCl$_2$(salen)] **4** as a fine orange precipitate which is sparingly soluble in thf and chlorinated solvents, Table 1. In view of the numerous reported syntheses of **3** it is remarkable that such adduct formation has not been characterised. Furthermore, in the absence of crystallographic data it is essential that **4** can be distinguished from **3**, **Ia** and the crystallographically characterised **3**·thf.

Compound **4** is readily distinguished from **3** and **Ia** on the basis of elemental analysis and $^1$H NMR spectroscopy. Thermogravimetric analysis provides further evidence for the presence of thf in **4**. The complex shows a discrete mass loss of 15.2% in the region 60–90 °C with no further losses below 300 °C. Such a loss compares well with the predicted loss of thf from **4** of 15.7%. Moreover, no comparable loss is observed for **3** below 300 °C. This data provides secondary evidence for the presence of thf, but does not aid in distinguishing between **4** and **3**·thf. Perhaps the strongest evidence here, apart from the obvious differences in colour and solubility, comes from the $^1$H NMR spectra. Coordinated thf appears as poorly resolved resonances at $\delta$ 1.85 and 3.80 in CDCl$_3$. This slight downfield C$_\alpha$ shift and the low resolution of these resonances is indicative of the metal coordination and is a feature which could not occur for thf bound in the solid state only as solvent of crystallisation.

The isolation of solvated salen complexes such as **4** is not without precedent; seven-coordinate complexes of the type [(thf)MCl$_2$(L)] \{M = Zr, Hf; H$_2$L = salenH$_2$, salphenH$_2$ [N,N'-bis(salicylidene)-1,2-phenylenediamine], dmsalenH$_2$ [N,N'-bis-($\alpha$-methylsalicylidene)ethylenediamine], acenH$_2$ [N,N'-bis-(acetylacetone)ethylenediamine]\} have been fully characterised.[9] The latter often require reflux in toluene to displace the coordinated thf, but poor solubility of the unsolvated complexes makes the reverse reaction impossible. At the more sterically hindered titanium(IV) centre it is not surprising that

R = H, X = F **2**, Cl **3**, Br **5**
R = OMe, X = Cl **7**

**4**

**6**

R = H, X = F **1**
R = Me, X = Cl **10**

R = H **8**
R = OMe **9**

X = F, Cl, Br
thf

thf, X = Cl

thf or MeCN
X = I

thf or MeCN
X = Cl

Ligand + TiX$_4$

X = F, Cl
thf

**Scheme 2** Preparation of titanium(IV) Schiff base complexes.

the solvent is more easily liberated. Indeed on prolonged standing at ambient temperatures solutions of **4** slowly convert to **3**. In other respects all the Group 4 solvated complexes show similar behaviour; attempts to convert **3** to **4** have failed presumably as a result of the poor solubility of **3**.

**Bromide complexes**

Refluxing an equimolar mixture of TiBr$_4$ and salenH$_2$ in thf for *ca*. 45 min yields, after work up, analytically pure **5** in high yield. Compound **5**, like **3**, is a deep red, air stable microcrystalline solid. Preceding the formation of **5** a pale orange solid is observed in the reaction vessel on mixing the reactants at room temperature. The EI$^+$ MS (70 eV) of this compound identified an ion fragment corresponding to the adduct complex, [(thf)-TiBr$_2$(salen)]$^+$ (*m/z* 546), and in addition the fragments [TiBr$_2$-(salen)]$^+$ (*m/z* 474) and [TiBr(salen)]$^+$ (*m/z* 393). This implies that the adduct complex [(thf)TiBr$_2$(salen)] is formed as an intermediate in the formation of **5** in the same manner as [TiCl$_2$(salen)] **3** is formed from [(thf)TiCl$_2$(salen)] **4**. Solvent lability precluded full characterisation of this complex. The $^1$H NMR spectrum of **5** in CDCl$_3$ is almost identical to those of [TiF$_2$(salen)] **2** and [TiCl$_2$(salen)] **3**. The spectra of these complexes only differ in the position of the chemical shift of the imino protons of the coordinated Schiff base, a result of the changes in electron density in the coordination sphere which is controlled by the nature of the halide ligand.

**Iodide complexes**

If an equimolar mixture of TiI$_4$ and salenH$_2$ in acetonitrile is heated at reflux for *ca*. 1 h an intense red-brown solution is observed containing an appreciable quantity of insoluble material. If this hot solution is filtered in air a microcrystalline orange solid precipitates after standing for *ca*. 2 min. Washing this precipitate with water–acetone and drying *in vacuo* gave [TiI(salen)]$_2$(μ-O) **6**. The preparation of [TiCl(salen)]$_2$(μ-O) *via*

the oxidation of [(thf)Ti(salen)Cl] in thf has been noted by Floriani and co-workers.[18] The hydrolysis of monoalkylated titanium(IV) Schiff base complexes affords similar dimeric oxo-bridged species in high yield.[15] The molecular ion was not observed in the FAB$^+$ mass spectrum (nitrobenzyl alcohol matrix) of **6** but a peak at *m/z* 771 corresponds to the loss of a single iodide ligand from **6**.

**Salen derivatives**

If an equimolar mixture of (MeO)$_2$salenH$_2$, salphenH$_2$ or (MeO)$_2$salphenH$_2$ and titanium(IV) chloride are refluxed in thf or acetonitrile [TiCl$_2${(MeO)$_2$salen}] **7**, [TiCl$_2$(salphen)] **8** and [TiCl$_2${(MeO)$_2$salphen}] **9** are isolated respectively as air stable, dark coloured microcrystalline solids. However, the latter displays some degree of impurity, possibly due to solvent retention. Biradar and Kulkarni[4] have previously reported the synthesis of **7** from salphenH$_2$ and titanium(IV) chloride (1:1) in absolute ethanol under extreme conditions *i.e.* reflux for 3–4 h followed by complete vapourisation of the solvent and heating the solid at 120 °C for *ca*. 2 h. Compounds **6–8** are characterised on the basis of their $^1$H NMR (except insoluble **7**), IR and FAB$^+$ (nitrobenzyl alcohol matrix) spectra and elemental analyses, Table 1.

The addition of titanium(IV) chloride, in toluene, to a toluene slurry of dmsalenH$_2$ at room temperature affords, after stirring for 3 h, [TiCl$_4$(dmsalenH$_2$)] **10** in quantitative yield. Compound **10**, insoluble in common organic solvents, is moisture sensitive but indefinitely stable under an atmosphere of dry nitrogen. The IR spectrum of **10** confirms the retention of the hydroxy protons (3358 cm$^{-1}$) and the presence of an imino group (1626 cm$^{-1}$). A possible structure for **10**, similar to that proposed for [TiF$_4$(salenH$_2$)] **1**, Scheme 2, illustrates the influence of ligand structure in determining the reaction product. Similar adduct complexes have been described in detail by Biradar and Kulkarni.[16] Here it is proposed that the steric interaction between the α-methyl and the *ortho*-hydrogen of the ligand is

**Table 2** Comparison of the average metal–oxygen (M–O$_{av}$), metal–nitrogen (M–N$_{av}$) and metal–halide (M–X$_{av}$) bond lengths (Å) in titanium Schiff base complexes

| Complex | M–O$_{av}$/Å | M–N$_{av}$/Å | M–X$_{av}$/Å |
|---|---|---|---|
| [TiF$_2$(salen)] **2** | 1.867 | 2.142 | 1.8494 |
| [TiCl$_2$(salen)]·thf[a] | 1.835 | 2.141 | 2.346 |
| [TiCl$_2$(acen)][b] | 1.863 | 2.127 | 2.347 |
| [Ti(py)Cl(salen)]·thf[c] | 1.910 | 2.138 | 2.148 |
| [Ti(thf)Cl(acen)][b] | 1.941 | 2.123 | 2.415 |

[a] Ref. 17. [b] Ref. 2. [c] Ref. 1.
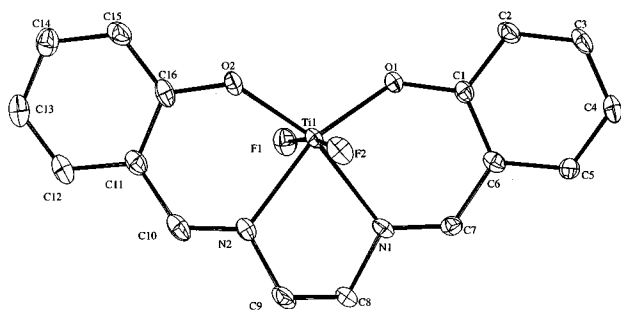


**Fig. 1** The molecular structure of [TiF$_2$(salen)] **2**. Selected bond lengths (Å) and angles (°): Ti(1)–F(1) 1.8438(13), Ti(1)–F(2) 1.8550(13), Ti(1)–O(1) 1.858(2), Ti(1)–O(2) 1.876(2), Ti(1)–N(1) 2.163(2), Ti(1)–N(2) 2.147(2); F(1)–Ti(1)–F(2) 170.48(6), N(2)–Ti(1)–N(1) 75.95(7), O(1)–Ti(1)–O(2) 112.95(7).

sufficient to distort the Schiff base from its ideal planar configuration, this in turn appears to be sufficient to prevent coordination and deprotonation of the hydroxyl group.

### Solid state structure of [TiF$_2$(salen)] 2

The molecular structure of **2** showing the atomic numbering scheme is shown in Fig. 1. Although the titanium centre is pseudo-octahedral considerable distortion is evident, with metal centred bond angles varying from 75.95 to 94.94°. The equatorial plane of the octahedron is provided by the N$_2$O$_2$ core of the Schiff base ligand. The apices are occupied by the two fluoride atoms which are skewed from the equatorial plane defined by the ligand by symmetrical orientation towards the nitrogen atoms [F(1)–Ti–F(2) 170.48(6)°]. The Ti–F bond lengths of 1.8438(13) Å and 1.8550(13) Å are comparable with the non-bridging Ti–F average bond lengths (Ti–F$_{av}$) in the dimeric six-coordinate complexes [Cp*TiF$_2$(OCOCF$_3$)]$_2$ (Ti–F$_{av}$, 1.822 Å) and [Cp*TiF$_2$(OCOC$_6$F$_5$)]$_2$ (Ti–F$_{av}$, 1.829 Å) [OCOCF$_3$ = trifluoroacetate; OCOC$_6$F$_5$ = pentafluorobenzoate] reported by Roesky and co-workers.[19]

Table 2 compares average metal–oxygen (M–O$_{av}$), metal–nitrogen (M–N$_{av}$) and metal–halide (M–X$_{av}$) bond lengths (Å) in Group 4 Schiff base complexes. The Ti–O bond lengths of 1.858(2) Å and 1.876(2) Å in **2** are comparable to the average Ti–O bond length of 1.835(5) Å reported for [TiCl$_2$(salen)]·thf.[17] Similarly, Ti–N bond lengths of 2.147(2) Å and 2.163(2) Å in **2** are in close agreement with the average Ti–N bond length, 2.141(5) Å, reported for [TiCl$_2$(salen)]·thf.[17]

The O(1)–Ti–O(2) [112.95(7)°] angle in **2** is as expected much smaller than the corresponding angle in the seven-coordinate *trans*-[(thf)ZrCl$_2$(salphen)][9] [137.6(1)°] and *trans*-[(thf)HfCl$_2$(salphen)][9] [137.0(1)°], but is in close agreement with that in [TiCl$_2$(salen)]·thf.[17] Similarly, the N(1)–Ti–N(2) angle [75.95(7)°] is in close agreement with that found in [TiCl$_2$(salen)]·thf[17] [76.1(2)°].

## Conclusions

The primary objective of this study has been to produce complexes of the type **II**, for the purpose of further reaction studies

with organometallic reagents. However, it is evident that these systems are highly sensitive to small changes in reactants and conditions. In the present work, the choice of solvent, reaction temperature and the nature of both the metal salt and Schiff base ligand are crucial to the formation of adducts **I**, chelates **II** or solvated chelates **III**, Scheme 2. The direct interaction of Lewis acids and bases is not always adequate for the formation of chelates **II** and **III**. Fully protonated intermediates, **I**, may be isolated as a consequence of thermodynamic or steric/electronic factors. Thus the formation of **1** appears to be thermodynamically favoured with respect to **2** when HF is the elimination product rather than Me$_3$SiF. Addition of α-methyl groups to salen also appears sufficient to prevent HCl elimination.

The exclusion of solvent from type **III** chelates appears a facile process, and the transformation from sterically hindered seven-coordinate species can be followed by TGA analysis. However, the favourability of solvent coordination appears to follow the trend F < Cl < Br, since no solvated species can be formed for the fluoride salt, that of the chloride shows significant lability, whilst the bromide adduct is sufficiently stable to be detected by mass spectrometry.

## Experimental

### Crystal structure determination of 2

Recrystallisation of **2** by CH$_2$Cl$_2$ diffusion into thf produced crystals (0.215 × 0.14 × 0.14 mm) suitable for X-ray diffraction. Intensity data were recorded on a FAST TV area detector diffractometer at 150 K following previously described procedures.[20] The structure was solved by direct methods (SHELXS)[21] and refined by full matrix least squares on $F^2$ (SHELX-93).[22] Data were corrected for absorption effects using DIFABS.[23]

**Crystal data.** C$_{16}$H$_{14}$F$_2$N$_2$O$_2$Ti, $M = 352.19$, monoclinic, $a = 14.285(2)$, $b = 8.881(3)$, $c = 12.3799(11)$ Å, $\beta = 109.733(9)°$, $U = 1478.3(6)$ Å$^3$, $D_c = 1.582$ g cm$^{-3}$, $T = 150(2)$ K, space group $P2_1/c$ (no. 14), $Z = 4$, $\mu$(Mo-Kα) $= 6.11$ mm$^{-1}$, unique total no. of data $= 2139$, unique no. of observed data $= 1746$ [$I > 2\sigma(I)$], $R = 0.0310$, $R_w = 0.0705$.

CCDC reference number 186/1148.

See http://www.rsc.org/suppdata/dt/1998/3489/ for crystallographic files in .cif format.

### Synthetic procedures

Inert atmosphere glovebox and Schlenk-line techniques were used throughout the preparative procedures unless otherwise indicated. Solvents were dried under nitrogen using standard reagents.[15] Salen and its derivatives were prepared by published routes and characterised by elemental analysis and $^1$H NMR spectroscopy.[24] NMR spectra were recorded at 270 MHz. Elemental analysis and important characterisation data for **1**–**10** are given in Table 1.

### Syntheses

**[TiF$_4$(salenH$_2$)] 1.** [(thf)$_2$TiF$_4$] was prepared *in situ* by adding an excess of thf to a cooled suspension of TiF$_4$ (4.0 g, 32 mmol). After filtration, the [(thf)$_2$TiF$_4$] was added to a thf solution of salenH$_2$ (8.65 g, 32.3 mmol) and the resulting bright yellow suspension was heated at 60–65 °C for *ca.* 2 h with no observed changes. The solvent was removed by filtration, toluene (*ca.* 150 cm$^3$) added and the suspension heated at *ca.* 110 °C for 3 h. After removing the solvent by filtration the remaining solid was dried *in vacuo* for *ca.* 6 h to give 12.0 g of **1** (96%) as a bright yellow, free-flowing powder. $^1$H NMR (CDCl$_3$): $\delta$ 4.12 (s, 4H, CH$_2$), 6.83–6.97 (m, 4H, Ph), 7.42–7.51 (m, 4H, Ph), 8.34 (s, 2H, CH), 9.89 (s, 1H, OH) and 11.01 (s, 1H, OH). FAB$^+$ MS: $m/z$ 333 (35%, [TiF(salen)]$^+$), 352 (5, [TiF$_2$(salen)]$^+$), 392 (20, [TiF$_4$(salenH$_2$)]$^+$).

**[TiF₂(salen)] 2.** A 30 cm³ aliquot of anhydrous CH₂Cl₂ was deaerated with argon for *ca.* 15 min and then added to freshly sublimed TiF₄ (1.50 g, 12.1 mmol). This suspension was then treated, with stirring, with thf (4.0 cm³, *ca.* 50 mmol) at −20 °C over a period of *ca.* 5 min. Immediately, the TiF₄ was consumed resulting in a colourless solution after the addition was complete. The solution was warmed to room temperature over *ca.* 30 min and filtered to remove the small amount of undissolved impurities. An additional 75 cm³ of thf was added to aid stirring during the subsequent reaction. A thf solution of salen(TMS)₂ (5.03 g, 12.2 mmol) was added to the [(thf)₂TiF₄] and a yellow-orange solid precipitated. The mixture was heated at 60–65 °C for *ca.* 1 h to give first a clear yellow solution then a bright yellow microcrystalline solid precipitate. The mother-liquor was then removed by filtration, the solid was washed with hexane (2 × 20 cm³) to remove any unreacted ligand, and dried *in vacuo*. This yielded 3.5 g of [TiF₂(salen)] **2** with a further 0.40 g (90% overall) of **2** crystallised as yellow cubes from the filtrate in air at room temperature. ¹H NMR (CDCl₃): $\delta$ 4.13 (s, 4H, CH₂), 6.98–6.83 (m, 4H, Ph), 7.52–7.43 (m, 4H, Ph) and 8.35 (s, 2H, CH). ¹⁹F NMR (CDCl₃): $\delta$ 145.49 (s, 2F). FAB⁺ MS: *m/z* 333 (100%, [TiF(salen)]⁺), 352 (10, [TiF₂(salen)]⁺).

**[TiCl₂(salen)] 3.** In a typical preparation salenH₂ (10.0 g, 37.3 mmol) in thf was treated dropwise with titanium(IV) chloride (1.0 M, 37.3 cm³, 37.3 mmol) with vigorous stirring. At once orange [(thf)TiCl₂(salen)] **4** precipitated from solution. This mixture was then heated at reflux for *ca.* 45 min until all of the orange solid, **4**, was replaced by the dark red microcrystalline **3**. Solvent was then removed and the solid washed with acetone–water (50:50) and then acetone and subsequently dried *in vacuo*. The yield of **3** varies from 75–85%. ¹H NMR (CDCl₃): $\delta$ 4.25 (s, 4H, CH₂), 6.85–7.13 (m, 4H, Ph), 7.33–7.61 (m, 4H, Ph) and 8.39 (s, 2H, CH). FAB⁺ MS: *m/z* 330 (10%, [Ti(=O)-(salen)]⁺), 349 (15%, [TiCl(salen)]⁺).

**[(thf)TiCl₂(salen)] 4.** Titanium(IV) chloride (1.0 M, 7.5 cm³, 7.5 mmol) was added to a yellow thf solution of salenH₂ (2.01 g, 7.46 mmol) to immediately give an orange solid. The mixture was then stirred at room temperature for *ca.* 3 h without any further changes. The very pale orange supernatant was then removed by filtration, the solid washed with thf and then dried *in vacuo* to yield **4** (*ca.* 3.2 g) in quantitative yield. ¹H NMR (CDCl₃): $\delta$ 1.85 (m, 4H, CH₂), 3.80 (m, 4H, C$_\alpha$H₂), 4.25 (s, 4H, CH₂), 6.80–7.20 (m, 4H, Ph), 7.40–7.60 (m, 4H, Ph) and 8.34 (s, 2H, C$_\beta$H). FAB⁺ MS: *m/z* 330 (10%, [Ti(=O)(salen)]⁺), 349 (15%, [TiCl(salen)]⁺).

**[TiBr₂(salen)] 5.** *Method A.* Titanium(IV) bromide (8.1 g, 22 mmol) was dissolved in toluene and the red solution was filtered to remove a small amount of undissolved material. This was then added, over a period of *ca.* 30 min, to salenH₂ (5.9 g, 22 mmol) in thf giving a red-orange solid precipitate. The mixture was then heated for 45 min at 70 °C resulting in the precipitation of a deep red microcrystalline solid. The mother-liquor was removed by filtration and the solid washed thoroughly with cold acetone and dried to yield 8.5 g of **5**. The mother-liquor was allowed to stand in the air at room temperature giving a further 0.7 g (90% overall) of **5** as long, deep red needles.

*Method B.* TiBr₄ (4.01 g, 10.9 mmol) was dissolved in toluene and was added, over a period of *ca.* 15 min, to a solution of salen(TMS)₂ (4.50 g, 10.9 mmol) in thf. At once, an orange-red precipitate formed. With continued stirring the reactants were then heated at 65 °C for *ca.* 30 min, a deep red solution and a microcrystalline deep red solid quickly precipitated. The mother-liquor was then decanted from the solid which was washed with toluene (3 × 30 cm³) to remove any unreacted starting materials and the concomitant Me₃SiBr. After drying *in vacuo* and washing with cold acetone **5** was dried in an oven overnight at 75 °C. This gave a yield of 4.85 g (95%). ¹H NMR

(CDCl₃): $\delta$ 4.25 (s, 4H, CH₂), 6.85–7.13 (m, 4H, Ph), 7.33–7.61 (m, 4H, Ph) and 8.45 (s, 2H, CH). EI⁺ MS (70 eV): *m/z* 393 (100%, [TiBr(salen)]⁺), 474 (10, [TiBr₂(salen)]⁺).

**[TiI(salen)]₂(μ-O) 6.** *Method A.* Titanium(IV) iodide (2.7 g, 4.9 mmol) was washed with toluene until the extracts were colourless to remove any iodine impurities and dried *in vacuo*. A suspension of the metal salt was then treated with salen(TMS)₂ (2.1 g, 5.1 mmol) and slowly yielded an orange-red solution. The mixture was then refluxed for 45 min whereupon an intense red coloured solution was observed and was quickly followed by the precipitation of a reddish-brown solid with some contamination by unreacted titanium(IV) iodide. The mixture was allowed to cool and the solvent was removed *in vacuo* to give a red-brown solid. This was then extracted with hot toluene (2 × 30 cm³) to remove the concomitant Me₃SiI (not isolated). The resulting brown solid was dried *in vacuo* and subsequently washed with acetone to immediately give **6** as a bright orange solid (Found: C, 43.7; H, 3.2; N, 6.4. Calc. for **6**, C₃₂H₂₈N₄O₅I₂Ti₂: C, 42.8; H, 3.1; N, 6.2%).

*Method B.* Titanium(IV) iodide (4.05 g, 7.29 mmol) was washed with hexane until the extracts were colourless to remove traces of iodine and dried *in vacuo*. This was then added in two portions to an acetonitrile solution (*ca.* 300 cm³) of salenH₂ (1.95 g, 7.29 mmol) to immediately give an orange solution as the metal salt dissolved. Within *ca.* 10 min the solution had become dark brown in colour and a small quantity of brown precipitate was seen. After refluxing for *ca.* 1 h the supernatant was filtered in the air and after *ca.* 2 min **6** precipitated from the solute as a bright orange microcrystalline solid. Washing the brown filtrate with acetone immediately gave further **6**. The yield of **6** was *ca.* 3.0 g (46%) *via* method B.

**[TiCl₂{(MeO)₂salen}] 7.** To a yellow acetonitrile solution of (MeO)₂salenH₂ (3.0 g, 9.2 mmol) was added a toluene solution of titanium(IV) chloride (1.0 M, 9.2 cm³, 9.2 mmol). The red solution was heated to *ca.* 80 °C for 1 h and on cooling resulted in the precipitation of a black solid, **7**. The supernatant red solution was decanted and yielded *ca.* 0.20 g of **7** at −20 °C. The solid residue was washed with an acetone–water (50:50) mixture and dried *in vacuo*. The combined yield of **7** was 3.1 g (*ca.* 80%). ¹H NMR (CD₂Cl₂): $\delta$ 4.00 (s, 6H, MeO), 4.20 (s, 4H, CH₂), 7.00–7.20 (m, 6H, Ph) and 8.40 (s, 2H, CH).

**[TiCl₂(salphen)] 8.** A thf solution of salphenH₂ (10.0 g, 31.6 mmol) was treated with titanium(IV) chloride (1.0 M, 32 cm³, 32 mmol) to immediately yield a light brown solid. This suspension was then refluxed for *ca.* 45 min. After cooling the solid was filtered off and washed with copious quantities of acetone and dried at 75 °C. The yield of **8** (13.6 g) was quantitative. FAB⁺ MS: *m/z* 413 (15%, [Ti(=O)Cl(salphen)]⁺.

**[TiCl₂{(MeO)₂salphen}] 9.** To an orange thf solution of (MeO)₂salphenH₂ (3.0 g, 8.0 mmol) was added a toluene solution of titanium(IV) chloride (1.0 M, 8.0 cm³, 8.0 mmol). During the addition a black solid precipitated. The mixture was refluxed for 1 h and subsequently cooled overnight to yield a black microcrystalline solid and a dark red solution. Decanting the supernatant, washing the solid with cold acetone (3 × 50 cm³) and drying at 75 °C gave 3.2 g of impure **9**. A further 200 mg of the complex was recovered from the filtrate (85% overall). ¹H NMR (CD₂Cl₂): $\delta$ 4.00 (s, 6H, MeO), 7.10–7.70 (m, 10H, Ph) and 8.90 (s, 2H, CH). FAB⁺ MS: *m/z* 423 (10%, [Ti{(MeO)₂salphen}]⁺, protonated).

**[TiCl₄(dmsalenH₂)] 10.** A toluene slurry of dmsalenH₂ (2.0 g, 6.8 mmol) was treated with a toluene solution of titanium(IV) chloride (1.0 M, 7.0 cm³, 7.0 mmol) to instantly give a red-orange solid. The mixture was then stirred for a further 3 h with no further changes. The colourless solvent was then removed by

decantation and the precipitated solid was washed with toluene ($3 \times 30$ cm$^3$) and dried *in vacuo* to give **10** (*ca.* 3.2 g) in quantitative yield. FAB$^+$ MS: *m/z* 450 (15%, [(dmsalenH$_2$)TiCl$_3$]$^+$) and 638 (5, [(dmsalenH$_2$)TiCl$_4$]$^+$ + nitrobenzyl alcohol). IR (Nujol mull): $\nu$(O–H) 3358 cm$^{-1}$.

## References

1 M. Pasquali, F. Marchetti, A. Landi and C. Floriani, *J. Chem. Soc.*, *Dalton Trans.*, 1978, 545.

2 M. Mazzanti, J. Rosset, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc.*, *Dalton Trans.*, 1989, 953.

3 F. L. Bowden and D. Ferguson, *J. Chem. Soc.*, *Dalton Trans.*, 1974, 460.

4 N. S. Biradar and V. H. Kulkarni, *J. Inorg. Nucl. Chem.*, 1971, **33**, 3847.

5 M. Mazzanti, C. Floriani, A. Chiesi-Villa and C. Guastini, *Inorg. Chem.*, 1986, **25**, 4158.

6 E. B. Tjaden, D. C. Swenson, R. F. Jordan and J. L. Petersen, *Organometallics*, 1995, **14**, 371.

7 R. D. Archer, R. O. Day and M. L. Illingworth, *Inorg. Chem.*, 1979, **18**, 2908.

8 N. S. Biradar and A. L. Locker, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1308.

9 F. Corazza, E. Solari, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc.*, *Dalton Trans.*, 1990, 1335.

10 T. Repo, M. Klinga, P. Pietikainen, M. Leskela, A. M. Uusitalo, T. Pakkanen, K. Hakala, P. Aaltonen and B. Lofgren, *Macromolecules*, 1997, **30**, 171.

11 C. Floriani, E. Solari, F. Corazza, A. Chiesi-Villa and C. Guastini, *Angew. Chem.*, *Int. Ed. Engl.*, 1989, **28**, 64.

12 E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 367.

13 J.-M. Rosset, C. Floriani, M. Mazzanti, A. Chiesi-Villa and C. Guastini, *Inorg. Chem.*, 1990, **29**, 3991.

14 D. G. Kelly, A. J. Toner, N. M. Walker, S. J. Coles and M. B. Hursthouse, *Polyhedron*, 1996, **15**, 4307.

15 S. J. Coles, M. B. Hursthouse D. G. Kelly, A. J. Toner and N. M. Walker, submitted.

16 N. S. Biradar and V. H. Kulkarni, *Rev. Roum. Chim.*, 1970, **15**, 1993.

17 G. Gilli, D. W. J. Cruickshank, R. L. Beddoes and O. S. Mills, *Acta Crystallogr.*, *Sect. B*, 1972, **28**, 1889.

18 E. Gallo, E. Solari, F. Franceschi, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Inorg. Chem.*, 1995, **34**, 2495.

19 J. Gindl, F.-Q. Liu, M. Noltemeyer, H.-G. Schmidt and H. W. Roesky, *Inorg. Chem.*, 1995, **34**, 5711.

20 J. A. Darr, S. R. Drake, M. B. Hursthouse and K. M. A. Malik, *Inorg. Chem.*, 1993, **32**, 5704.

21 G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A*, 1990, **46**, 467.

22 G. M. Sheldrick, SHELX-93. University of Göttingen, 1993.

23 N. P. C. Walker and D. Stuart, *Acta Crystallogr.*, *Sect. A*, 1983, **39**, 158, adapted for FAST geometry by A. Karaulov, University of Wales, Cardiff, 1991.

24 M. Calligaris and L. Randaccio, *Comprehensive Co-ordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 2, ch. 20.1.

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