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Titanium(IV) complexes of the crystallographically characterised fluorene-Schiff base *N*-2-fluorenyl(salicylideneimine) and related bi- and tetradentate ligands

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Abstract

Schiff base ligands have been prepared by the condensation of 2-aminofluorene with salicylaldehyde (**1**, flusalH) or 3-methoxy-2-hydroxybenzaldehyde (**2**, MeOflusalH). Compound **1** reacts with $TiCl_4$ in a 1:1 stoichiometry to afford [$TiCl_3$(flusal)] (**3**) and in a 2:1 ratio to yield [$TiCl_4$(flusalH)$_2$] (**4**). The reaction of excess $TiBz_4$ with compound **1** results in the isolation of the octahedral Ti(IV) complex [Ti(flusal)$_2$(flusalaBz)$_2$] (**5**). Crystallographic and spectroscopic data for the latter indicate a complex containing two Schiff base ligands present as conventional N,O chelates and a further two ligands in which the C=N function is reduced by the addition of benzyl and hydrogen moieties producing an O-bound species with pendant amine. The single crystal X-ray diffraction structure of compound **1** has been obtained and compared with the published data for compound **5**. Similar ligand alkylation to that observed in compound **5** is also achieved by the reaction of organolithium reagents with compounds **1** and **2**; the reaction of PhLi and compound **2** followed by aqueous hydrolysis affords MeOflusalaPhH (**6**). Although reactivity does occur between $TiCl_4$ and compound **6**, the products could not be fully characterised. Thus tetradentate reduced Schiff base ligands were synthesised by the reaction of salenH_2 with MeLi or PhLi, giving salenaMe_2H_2 (**7**) and salenaPh_2H_2 (**8**), respectively. Reaction of compound **8** and $TiCl_4$ affords the quadruply deprotonated amido complex [Ti(salenamidoPh_2)] (**9**), which hydrolyses in air to the μ-oxo amine complex [Ti(salenaPh_2)O] (**10**).

Keywords: Additions; Alkylation; Insertions; Nucleophilic; Schiff bases; Titanium

1. Introduction

The recent interest in group 4 complexes incorporating the fluorenyl ligand stems from the discovery that *ansa*-metallocene zirconium complexes containing linked fluorenyl-cyclopentadienyl ligands are involved in the syndiospecific polymerisation of α-olefins [1–11]. Examples of unsupported fluorenyl coordination to group 4 metals are far less numerous than the corresponding indenyl and cyclopentadienyl moieties [12]; the preparation of [(η^5-$C_{13}H_9$)$_2$-$TiCl_2$], from sodium fluorenyl and titanium(IV) chloride, and of [(η^5-$C_{13}H_9$)(η^5-C_5H_5)$TiCl_2$], from thallium fluorenyl and [$CpTiCl_3$], are the only examples of titanium(IV) metallocene precursors containing the fluorenyl moiety [13,14], although a large number of monodithiocarbamate derivatives have been synthesised from [(η^5-$C_{13}H_9$)$_2TiCl_2$] [15]. Recently bis-fluorenyltitanium(0) has also been formed by metal vapour deposition (MVD) methods [16]. In the present work the relative coordination affinities of Schiff base and fluorenyl moieties contained within potentially chelating ligands are assessed. Part of this work has previously been the subject of a brief communication [17].

2. Results and discussion

2.1. Titanium(IV) complexes of flusalH and derivatives

Schiff base ligands can be readily formed by the condensation of 2-aminofluorene and salicylaldehyde (**1**, flusalH) or 3-methoxy-2-hydroxybenzaldehyde (**2**, MeOflusalH) (Table 1). The synthetic route, outlined in Scheme 1, is conventional and employs published methods [18]. Although compounds **1** and **2** appear visually very different in colour, visible reflectance spectra display similar features, with a shift in absorbance to higher wavelength occurring as

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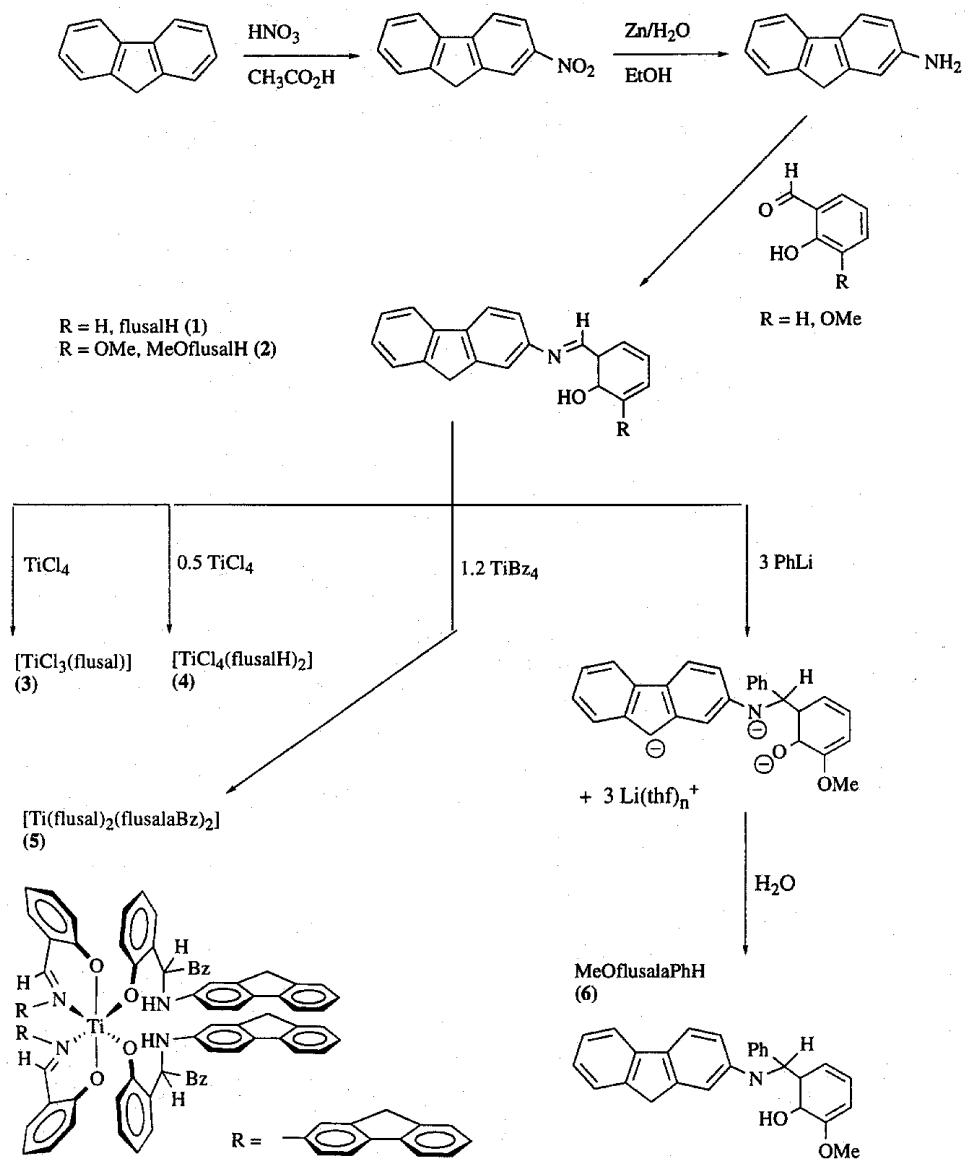
Table 1
Analytical and spectroscopic data for compounds **1**–**10**

Compound	Colour	Yield (%)	^{1}H NMR (δ, ppm)		IR [a] (cm^{-1})		Elemental analysis			
			*H*C=N	*H*CR–NH	ν(C=N)	ν(N–H)	C	H	N	Cl
FlusalH (**1**)	yellow	80	8.70		1618		84.6 (84.2)	5.2 (5.3)	4.9 (4.9)	
MeOflusalH (**2**)	orange	75	8.71		1618		80.0 (80.0)	5.8 (5.4)	4.4 (4.4)	
$TiCl_3$(flusal) (**3**)	red	95	insoluble		1612		54.4 (54.7)	3.5 (3.2)	3.1 (3.2)	23.7 (24.3)
$TiCl_4$(flusalH)$_2$ (**4**)	red	99	insoluble		1620 [b]		62.6 (63.0)	4.6 (4.4)	3.7 (3.4)	17.8 (17.4)
[Ti(flusal)$_2$(flusalaBz)$_2$] (**5**)	orange	25	8.75	4.10	1612	3376, 3389	82.2 (82.5)	5.6 (5.3)	3.8 (4.1)	
MeOflusalaPhH (**6**)	cream	96		3.95		3414, 3475	82.7 (82.4)	6.3 (5.9)	3.2 (3.6)	
$SalenaMe_2H_2$ (**7**)	white	45		3.88		3299	72.1 (72.0)	8.2 (8.0)	9.2 (9.3)	
$SalenaPh_2H_2$ (**8**)	white	80		3.88		3303	80.0 (79.2)	6.8 (6.6)	6.2 (6.6)	
[Ti(salenamidoPh_2)] (**9**)	brown	90		not obsvd.	Abs		70.4 (71.8)	5.8 (5.1)	6.0 (6.0)	
[Ti(salenaPh_2)O] (**10**)	yellow	93		insoluble	[c]	3255, 3374	69.2 (69.2)	5.4 (5.4)	5.6 (5.8)	

[a] Nujol mull.
[b] Also C=O 1645 cm^{-1}.
[c] Also Ti–O 756 cm^{-1}.



Scheme 1. Synthesis and reactivity of compounds **1** and **2**.

a consequence of the electron donating methoxy substituent in compound **2** (Fig. 1). Considering the coordination potential of compounds **1** and **2**, it is of note that the pK_a of fluorene is significantly larger than that of indene or cyclopentadiene [19]. Moreover, the extended delocalisation of charge within the deprotonated fluorene results in far lower coordination affinities than either indenyl or cyclopentadienyl moieties. Thus, the stoichiometric reaction of titanium(IV) chloride and compound **1** in dichloromethane yields the deep red complex [$TiCl_3$(flusal)] (**3**), which on the basis of IR evidence displays ligand bonding through the Schiff base moiety by chelation of nitrogen and the deprotonated oxygen centre. The significant change in colour from compound **1** to compound **3** is common in Schiff base systems and does not imply more complex interactions or processes (Fig. 1). Although the formation of compound **3** is entirely normal, it is of note that compound **3** is nominally five coordinate . The fact that this compound strongly retains solvent, and affords an insoluble high melting solid once dried, suggests six coordinate geometry is achieved by the formation of halide bridged dimers. Molecular weight measurements for related 1:1 complexes have been indicative of such behaviour [20]. Reaction of titanium(IV) chloride with two equivalents of compound **1** in tetrahydrofuran (THF) yields a red sticky and intractable solid which retains solvent. After suspension in dry, deaerated acetone, [$TiCl_4$(flusalH)$_2$]·$(Me)_2CO$ (**4**) is isolated as a free-flowing powder from which acetone is not liberated even at elevated temperatures in vacuo. The insolubility of compound **4** limits the extent of its characterisation (Table 1); however, the various forms of Schiff base denticity and deprotonation have been explored in detail for both titanium(IV) and zirconium(IV) [20–24]. By analogy with this work it is possible to suggest that compound **4** exists as a six coordinate complex containing N-bound ligands in which acetone hydrogen bonds to the phenolic protons of the pendant OH functionalities. It is the presence of the latter and their interactions with solvents which are likely to cause the difficulties in handling and drying the complex [25–27].

Complexes **3** and **4** are typical Schiff base complexes in which the fluorenyl moiety is entirely passive. To induce reactivity at this centre, interaction with organometallic reagents was examined. Since considerable problems are associated with the alkylation of group 4 Schiff base complexes using alkyllithium and Grignard reagents [28,29], compound **1** was reacted directly with $TiBz_4$ [17]. Thus, the addition of compound **1** to a hexane solution of $TiBz_4$ (1:1.2) at −20°C affords, after work-up, the complex [Ti(flusal)$_2$(flusalaBz$_2$)$_2$] (**5**) (Scheme 1). ^{1}H NMR data are consistent with the crystallographic characterisation of the complex [17], which indicates the presence of two chelating flusal ligands in the octahedral titanium(IV) coordination sphere. The remaining sites are occupied by reduced Schiff base ligands, reduction having occurred as a consequence of benzyl and hydrogen addition to the C=N moieties to afford pendant amine functions. IR data are also consistent with amine and imine absorbances being observed. Once again there is no

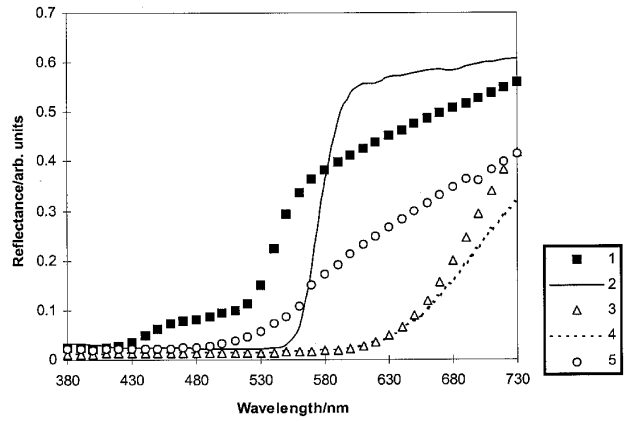


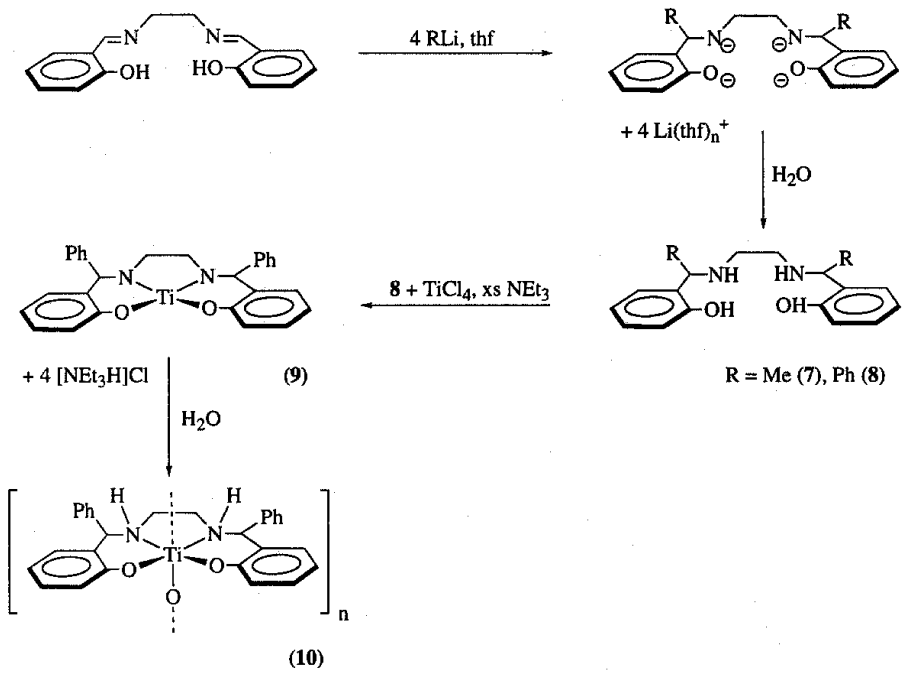
Fig. 1. Diffuse reflectance visible spectra of compounds **1–5**.

evidence for reactivity at the fluorene moiety. However, these extended aromatic systems do appear to influence the overall structure; π–π interaction of the fluorene groups of the two reduced ligands inducing a *cis* orientation of the monodentate donors.

A mechanistic appreciation of the formation of compound **5** is difficult to obtain, although several groups have considered the reactivity of systems containing alkyl functionalities, Schiff base ligands and group(4) metals [28–32]. Although direct interaction of metal and alkyl groups can occur, reactivity is complicated by the potential for metal reduction and/or nucleophilic attack of the alkyl at the Schiff base C=N group resulting in amide formation. The isolation of compound **5** extends the latter reactivity, with imine reduction to amines resulting from the effective addition of benzyl and hydrogen moieties to the C=N group. It has not proved possible to follow this process stepwise, although Bz migration to the coordinate d flusalH ligand followed by intramolecular proton transfer is clearly realistic. Such a mechanism has been explored using the reactivity of compounds **1** and **2** with organolithium reagents.

2.2. Reactivity of organolithium reagents with flusalH and derivatives

Three equivalents of organolithium reagent are consumed in the reaction of compound **1** with PhLi or n-BuLi and of compound **2** with MeLi or t-BuLi. Reaction stoichiometry suggests that highly air-sensitive intermediates are formed as a consequence of the deprotonation at hydroxyl and 9-fluorenyl protons, and nucleophilic alkyl attack at the imine centre (Scheme 1). Aqueous hydrolysis protonates all three basic sites leaving imine reduction by R-addition as the single permanent change. The formation of amines is confirmed in each reaction by the observation of parent ions in the respective mass spectra, with additional characterisation of the product obtained from the reaction of compound **2** and PhLi, i.e. MeOflusalaPhH (**6**) (Table 1). Since reducing the reaction stoichiometry to a 2:1 RLi/ligand ratio results in the complete recovery of compounds **1** and **2**, it can be assumed that the relative pK_a of the three acidic sites is OH < 9-fluorenyl



Scheme 2. Synthesis and reactivity of compounds **7** and **8**.

<HC=N. This view is supported by the reactivity observed between compound **1** or **2** and $Li[N(SiMe_3)_2]$. Addition of excess $Li[N(SiMe_3)_2]$, followed by hydrolysis, results in the quantitative recovery of compounds **1** and **2**. Although steric control cannot be ignored, this behaviour suggests that this less basic reagent is not capable of nucleophilic attack at the imine moiety.

The reactivity of compounds **1** and **2** with organolithium reagents demonstrates the general principle that nucleophilic alkyl attack at the imine function, followed by protonation, can afford amines. However, clear differences in selectivity are apparent. The 1:1.2 **1**/$TiBz_4$ reaction stoichiometry which affords compound **5** provides an excess of alkylating agent, but titanium coordination and stoichiometric availability of phenolic protons moderate reactivity. As a consequence, it can be proposed that the initial N,O coordination of the Schiff base ligand enhances intramolecular nucleophilic attack of the Bz moiety and facilitates intramolecular proton transfer. That imine alkylation remains marginal is demonstrated by the 50:50 ratio of amine and imine moieties in compound **5**. However, it is evident that in the formation of compound **5** imine reactivity is preferred to that of the fluorene function, a clear contrast to the reactivity observed with organolithium reagents.

The reactivity of compound **6** and $TiCl_4$ also provides a useful contrast to the formation of compound **5**. It is apparent that reactivity occurs between compound **6** and $TiCl_4$; however, the insolubility of the products precludes the separation and characterisation of what appears to be several metal-containing complexes. The elimination of HCl from the reaction $TiCl_4$ with ammine and amine ligands is well established, and such reactivity may be the source of multiple products here [33]. To increase the potential to form a single characterisable product, quadradentate reduced Schiff base ligands were prepared by the reaction of $salenH_2$ with organolithium reagents.

2.3. Synthesis and reactivity of reduced salenH_2 ligands

In an analogous manner to the reaction of flusalH and organolithium reagents, the reaction of MeLi or PhLi, followed by aqueous hydrolysis, affords $salenaMe_2H_2$ (**7**) and $salenaPh_2H_2$ (**8**), respectively (Scheme 2). Stoichiometric reaction of compound **8** and $TiCl_4$ in the presence of NEt_3 results in complete deprotonation of the N_2O_2 donor set and the isolation of [Ti(salenamidoPh_2)] (**9**). Similar tetra-anionic species have been synthesised using reduced Schiff base ligands and zirconium(IV) [34]. In the latter, the octahedral geometry is completed by pyridine coordination. Although compound **9** is nominally four coordinate, the classical octahedral geometry may be completed by intermolecular dative bonding by the oxygen centres. Such behaviour is well established in the corresponding titanium Schiff base chemistry [31,32,35,36]. Compound **9** is unstable in moist air, undergoing rapid hydrolysis to the polymeric μ-oxo diamine complex [Ti($salenaPh_2$)O] (**10**). Once again the relative stability of such μ-oxo species has been demonstrated by the formation of a number of dimeric, oligomeric and polymeric complexes in which the μ-oxo group is readily identified by a strong ν(Ti–O) IR vibration [32,37,38].

2.4. Crystallographic characterisation of N-2-fluorenyl-(salicylideneimine) (1)

Crystallographic characterisation of *N*-2-fluorenyl-(salicylideneimine) allows direct structural comparison with

the titanium complex **5**. Structural elucidation of compound **1** indicates similarities with the bond lengths and angles that are observed in single crystal X-ray diffraction studies of the fluorene and simple Schiff base ligands such as salenH_2 [39,40], Fig. 2. Comparison of geometries in the deprotonated flusal and reduced flusala ligands of compound **5** with compound **1** demonstrates the effects of both coordination and reduction (Table 2). The imine flusalH bond, N(1)–C(14), is slightly elongated in the coordinate d Schiff base of compound **5**, although it must be noted that the O(1)···H···N(1) hydrogen bond of flusalH is replaced by metal coordination in compound **5**. Thus, the relatively modest elongation on titanium coordination must be viewed in the context of substituting one Lewis acid interaction at N(1) with another. More significantly, lengthening of the same bond occurs by reduction in the pendant amine of the same complex — clearly a direct consequence of changing bond order. The corresponding nitrogen–fluorene linkages, N(1)–C(12), shorten in both metal-bound forms. Perhaps most notably, little change in the C(12)–N(1)–C(14) bond angle occurs between the hydrogen bonded free Schiff base and the reduced flusala moiety of compound **5**, despite the change from sp^2 to sp^3 hybridisation. In contrast, the coordinated imine moiety displays a shift towards sp character — a feature which may optimise a Ti(dπ)–N(pπ) interaction. Moreover, the significant structural changes which occur on coordination help to rationalise the differing functional group selectivity observed for the reactivity of RLi or $TiBz_4$ with compound **1**.

3. Conclusion

Titanium(IV) complexes containing Schiff base ligands and their reduced analogues may be synthesised by direct reaction of metal salt and ligand. More complex reactivity occurs between Schiff base ligands and the organotitanium reagent $TiBz_4$, involving partial imine alkylation and reduction. Reduced ligands can react with $TiCl_4$ to afford amido functionalities, which may themselves be hydrolysed to regenerate coordinate d amines. Thus by manipulation of reagents and conditions a range of ligand-centred transformations involving imine, amine and amido functionalities may occur within the group 4 metal coordination sphere.

4. Experimental

4.1. Crystallographic characterisation

Recrystallisation of compound **1** from THF–Et_2O using vapour diffusion techniques gave yellow-brown crystals ($0.07\times0.07\times0.11$ mm) suitable for single crystal X-ray analysis. Data collection and structure solution of compound **1** was performed using previously described methods, resulting in the following crystal data [41–44].

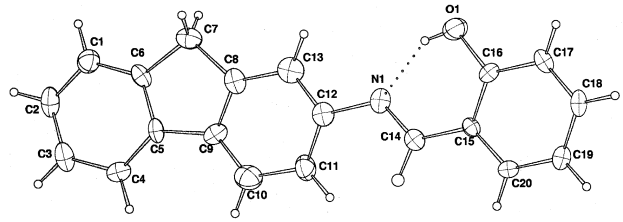


Fig. 2. Single crystal X-ray structure of compound **1**.

Table 2
Bond lengths and angles in **1** and **5**

Molecular dimensions	**1**	**5** [a]	
		Flusal moiety	Flusala moiety
Bond lengths (Å)			
N(1)–C(12)	1.469(5)	1.409(10)	1.379(12)
N(1)–C(14)	1.272(5)	1.317(10)	1.449(10)
C(14)–C(15)	1.449(5)	1.419(11)	1.507(11)
O(1)–C(16)	1.362(4)	1.318(10)	1.370(9)
O(1)–H	0.820(1)		
N(1)–H	1.805(4)		
O(1)–N(1)	2.528(4)		
Bond angles (°)			
C(13)–C(12)–N(1)	113.9(5)	120.9(9)	119.3(11)
C(12)–N(1)–C(14)	119.3(4)	128.7(9)	118.8(8)
C(14)–C(15)–C(16)	120.6(4)	121.7(10)	114.2(8)
C(15)–C(16)–O(1)	122.0(4)	119.7(10)	115.3(9)
O(1)–H–N(1)	146.2(2)		

[a] From [17].

Crystal data for $C_{18}H_{15}NO$ (**1**): $M=285.33$; monoclinic; space group $P2_1a$, $a=11.048(42)$, $b=7.936(15)$, $c=15.899(35)$ Å; $\beta=97.39(8)°$; $U<1478.3(6)$ Å^3; $D_c=1.371$ g cm^{-3}; $Z=4$; $T=145(2)$ K; $\mu=0.084$ mm^{-1}; $F(000)=600$; λ(Mo Kα) = 0.71069 nm; $2.58<\theta<25.07$; total observed reflections = 2124; observed reflections [$I>2\sigma(I)$] 734; $R=0.0489$; $R_w=0.0958$ (observed data).

4.2. Data collection and structure solution

Collection, FAST TV area detector; absorption correction, DIFFABS (min./max. factors 0.748 and 1.324, respectively); solution, direct methods (SHELXS-86); refinement, full matrix least squares on F^2 (SHELX-92), non-hydrogen atoms anisotropic, hydrogen atoms riding.

4.3. Synthetic procedures

Solvents were dried using standard methods. All titanium reactions were performed under nitrogen [32]. RLi reagents [R = Me, Ph, n-Bu, t-Bu, N(SiMe$_3$)$_2$] were purchased from Aldrich. 2-Aminofluorene, lithiumfluorenyl and $TiBz_4$, were prepared using published methods [18,45–47]. ^{1}H NMR spectra were obtained at 270 MHz in $CDCl_3$ unless stated otherwise. Elemental analysis and important characterisation data are given in Table 1.

*4.3.1. N-2-Fluorenyl(salicylideneimine), flusalH (**1**)*

The ligand was prepared by the dropwise addition of one equivalent of 2-aminofluorene in THF to an ethanolic solution of freshly distilled salicylaldehyde. After refluxing for 1 h the solution was cooled to afford crude compound **1**, which was washed in Et_2O and dried in vacuo. Recrystallisation of the crude material from ethanol–chloroform gave compound **1** as a yellow-brown crystalline solid (80%). ^{1}H NMR: δ 3.95 (s, 2H, CH_2), 6.92–7.84 (m, 11H, aromatic), 8.70 (s, 1H, CH), 13.30 (s, 1H, OH). EI^+ MS: *m/z* 285 (100%, $[\mathbf{1}]^+$). IR (Nujol) (cm^{-1}): ν(C=N) 1618, ν(O–H) 3460.

*4.3.2. N-2-Fluorenyl(3-methoxysalicylideneimine) (**2**)*

Compound **2** was prepared by the same method as compound **1** and recrystallised from ethanol (75% yield). ^{1}H NMR ($CDCl_3$): δ 3.94 (s, 3H, MeO) and (s, 2H, CH_2) (methylene protons obscured by the methoxy resonance), 6.84–7.83 (m, 11H, Ph), 8.71 (s, 1H, CH), 13.83 (s, 1H, OH). EI^+ MS: *m/z* 316 (100%, $[2+H]^+$). IR (Nujol) (cm^{-1}): ν(C=N) 1618, ν(O–H) 3460.

*4.3.3. [$TiCl_3$(flusal)] (**3**)*

A toluene solution of titanium(IV) chloride (1.0 M, 3.15 cm^3, 3.15 mmol) was added dropwise to compound **1** (0.9 g, 3.2 mmol) in CH_2Cl_2 (approx. 30 cm^3). A deep red precipitate immediately formed. The solution was refluxed for 1 h, after which the solid was separated by filtration, washed with hexane (5×10 cm^3) and dried in vacuo to afford compound **3** as a maroon free-flowing solid. Yield: 1.3 g (95%). Compound **3** is insufficiently soluble to obtain ^{1}H NMR spectroscopic data. FAB^+ MS: *m/z* 437 (15%, $[\mathbf{3}]^+$). M.p. dec.: 306–310°C.

*4.3.4. [$TiCl_4$(flusalH)$_2$] (**4**)*

Compound **1** (2.0 g 7.0 mmol) in THF (approx. 50 cm^3) was treated with titanium(IV) chloride (1.0 M, 3.5 cm^3, 3.5 mmol). A deep red solid precipitated, after which the solution was refluxed for 1 h. The colourless solvent was then decanted from the solid which was washed with THF (2×30 cm^3), also resulting in colourless extracts. The solid was slurried in acetone and cooled to −20°C. After 1 day, decantation of the solvent and drying in vacuo gave 2.8 g of [$TiCl_4$(flusalH)$_2$]·Me_2CO (**4**) as a deep red, air-stable solid in quantitative yield. Insolubility precluded ^{1}H NMR spectroscopic characterisation. FAB^+ MS: *m/z* 286 (100%, $[1+H^+]$), 348 (40%, [Ti(=O)(flusal)]$^+$). IR (Nujol) (cm^{-1}): ν(C=O) 1645, ν(C=N) 1620, ν(O–H) 3361.

*4.3.5. [Ti(flusal)$_2$(flusalaBz$_2$)$_2$] (**5**)*

Compound **1** (0.50 g, 1.8 mmol) was added in a single portion to a hexane solution (20 cm^3) of $TiBz_4$ (0.87 g, 2.1 mmol) at −20°C. The dark brown precipitate which formed over 0.5 h was filtered, washed with hexane and extracted with toluene. The resultant brown solution becomes progressively pale orange. Addition of hexane and storage at −20°C affords toluene solvated compound **5** over about 3 days. ^{1}H NMR: δ 3.22 (m, 4H, Ph*CH*$_2$CHNH), 3.72 (s, 2H, 9-fluorene CH_2), 3.96 (s, 2H, 9-fluorene CH_2), 4.18 (s, 2H, PhCH$_2$CH*NH*), 4.60 (m, 2H, PhCH$_2$*CH*NH), 6.67–7.86 (m, 54H, aromatic), 8.75 (s, 2H, *CH*). FAB^+ MS: *m/z* 268 (100%, $[\mathbf{1}]^+$), 1368 (10%, $[\mathbf{5}]^+$). IR (Nujol) (cm^{-1}): ν(C=N) 1612(s), ν(N–H) 3376(s), 3389(s).

*4.3.6. N-2-Fluorenyl(α-phenyl-3-methoxysalicylideneamine) (**6**)*

Compound **2** (3.0 g, 9.5 mmol) in THF (approx. 40 cm^3) was cooled to −20°C and PhLi (1.8 M, 15.9 cm^3, 28.6 mmol) was added dropwise. During addition the solution developed a deep red colour. After stirring for 1 h, deaerated distilled water was added. The mixture was diluted with Et_2O and the organic layer was separated. The aqueous layer was shaken with two portions of Et_2O (approx. 2×30 cm^3) and the combined organic fractions were dried over magnesium sulfate. Following filtration the solvent was removed under reduced pressure to yield crude compound **6** (3.7 g, ≈96%) as a gelatinous, off-white solid. Recrystallisation from THF–Et_2O afforded cream, crystalline material. ^{1}H NMR: δ 1.18 (s br, 1H, *NH*), 3.68 (s, 2H, *CH*$_2$), 3.83 (s, 3H, *CH*$_3$O), 4.40 (s br, 1H, *OH*), 5.82 (s, 1H, CH), 6.73–6.83, 7.07–7.35 (m, Ph). FAB^+ MS: *m/z* 393 (55%, $[\mathbf{6}]^+$). IR (Nujol) (cm^{-1}): ν(N–H) 3414, 3475 (vs), ν(O–H) 1375.

Similar reactions carried out using compounds **1** and **2** with other organolithium reagents afforded products analogous to compound **6**. These products did not lend themselves to crystallisation and thus produced ^{1}H NMR spectra containing residual solvent, and tolerable but somewhat variable elemental analysis. However, molecular ions of significant intensity could be recorded in each case. Thus *N*-2-fluorenyl(α-phenyl-salicylideneamine) [EI MS: *m/z* 363, 85%] and *N*-2-fluorenyl(α-n-butyl-salicylideneamine) [FAB^+ MS: *m/z* 344, 100%] were recovered from the reaction of compound **1** with phenyllithium and butyllithium, respectively. The methoxyl derivatives *N*-2-fluorenyl(α-methyl-3-methoxysalicylideneamine) [FAB^+ MS: *m/z* 331, 20%] and *N*-2-fluorenyl(α-t-butyl-3-methoxysalicylideneamine) [FAB^+ MS: *m/z* 374, 100%] were also isolated from the reaction of compound **2** with methyllithium and t-butyllithium.

*4.3.7. N,N′-(1,2-Ethlyenebis(α-methylsalicylaldamine)] (**7**)*

An ET_2O solution of methyllithium (1.4 M, 21.3 cm^3, 29.9 mmol) was added dropwise to a THF solution of salenH_2 (2.0 g, 7.46 mmol) at −20°C. The resultant colourless solution was stirred for 1 h before deaerated, distilled water was added (approx. 20 cm^3). Addition of Et_2O produced two layers. After separation, the aqueous layer was washed with ether (3×30 cm^3). The combined organic phases were concentrated, dried with $MgSO_4$ and further reduced to produce a paste which was recrystallised from THF–Et_2O to afford compound **7** (1.0 g, 45%). ^{1}H NMR (CD_2Cl_2): δ 1.38 (s, 3H, *Me*), 1.41 (s, 3H, *Me*), 1.53 (b s, *NH*), 2.66 (m, 2H,

CH_2), 2.79 (m, 2H, CH_2), 3.88 (q, 2H, *CH*), 6.70–7.13 (m, 8H, *Ph*), 11.03 (bs *OH*). EI MS: m/z 300 (100%, $[\mathbf{7}]^+$).

*4.3.8. N,N′-(1,2-Ethylenebis(α-phenylsalicylaldamine)] (**8**)*

The compound was prepared by the same route as compound **7**, giving a white solid in 80% yield. ^{1}H NMR: δ 1.42 (b s, *NH*), 2.93 (m, 4H, CH_2), 4.88 (s, 2H, *CH*), 6.72–7.31 (m, 18H, *Ph*), 11.50 (bs *OH*). FAB$^+$ MS: m/z 425 (30%, $[\mathbf{8}]^+$).

*4.3.9. [Ti(salenamidoPh$_2$)] (**9**)*

A toluene solution of compound **8** (1.76 g, 4.15 mmol) and triethylamine (3.5 cm^3, 25 mmol) was treated dropwise with $TiCl_4$ (1.0 M toluene, 4.15 cm^3, 4.15 mmol). After stirring for 12 h, an orange solution was filtered from the precipitated $[NEt_3H]Cl$, and after concentration and addition of hexane afforded compound **9** as a brown crystalline solid (1.8 g, 90%). FAB$^+$ MS: m/z 468 (50%, $[\mathbf{9}]^+$).

*4.3.10. [Ti(salenaPh$_2$)O] (**10**)*

An orange toluene solution of compound **9** (1.0 g, 2.14 mmol) was filtered in air and rapidly formed a pale yellow precipitate. After 0.5 h the precipitate was filtered and washed with dry hexane to afford compound **10** (1.8 g, 93%). Compound **10** could be crystallised from CH_2Cl_2–Et_2O as an analytically pure microcrystalline solid. FAB$^+$ MS: m/z 955 (100%, $[\mathbf{10}_2 - O]^+$).

5. Supplementary data

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC, No. 127639. Copies of this information can be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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