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Reactivity of $AlMe_3$ with titanium(IV) Schiff base complexes: X-ray structure of $[Ti\{(\mu\text{-}Br)(AlMe_2)\}\{(\mu\text{-}Br)(AlMe_2X)\}(salen)] \cdot C_7H_8$ (X = Me or Br) and reactivity studies of mono-alkylated [Ti(Me)X(L)] complexes

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Abstract

$[TiCl_2(salen)]$ (**1**) reacts with $AlMe_3$ (1:2) to give the heterometallic Ti(III) and Ti(IV) complexes $[Ti\{(\mu\text{-}Cl)(AlMe_2)\}\{(\mu\text{-}Cl)(AlMe_2X)\}(salen)]$ (X = Me or Cl) (**2**) and $[TiMe\{(\mu\text{-}Cl)(AlCl_2Me)\}(salen)]$ (**3**). Addition of diethyl ether to **3** affords [Ti(Me)Cl(salen)] (**4**). The analogous reaction of $[TiBr_2(salen)]$ (**5**) gives the crystallographically characterised $[Ti\{(\mu\text{-}Br)(AlMe_2)\}\{(\mu\text{-}Br)(AlMe_2X)\}(salen)]$ (X = Me or Br) (**6**) and [Ti(Me)Br(salen)] (**7**) in a single step, whilst the comparable reaction of $[TiCl_2\{(3\text{-}MeO)_2salen\}]$ (**8**) with $AlMe_3$ yields $[Ti(Me)Cl\{(3\text{-}MeO)_2salen\}]$ (**9**) with no evidence of titanium(III) species. Reactivity of both halide and methyl groups of **4** has been probed using magnesium reduction, $SbCl_5$ and $AgBF_4$ halide abstraction and SO_2 insertion reactions. Hydrolysis of [Ti(Me)X(L)] complexes affords μ-oxo species $[TiX(L)]_2(\mu\text{-}O)$ [X = Cl, L = salen (**13**); X = Br, L = salen (**14**); X = Cl, L = $(3\text{-}MeO)_2$salen (**15**)].

Keywords: Titanium; Alkylation; Schiff base

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1. Introduction

The structure and reactivity of Group 4 metal complexes containing Schiff base ligands and alkyl groups has been explored in several publications. Two general approaches have been applied to such syntheses; viz the alkylation of Schiff base/chloride complexes with Group 1 and 2 metal alkyls [1–3] and the direct reaction of Schiff base ligands with Group 4 organometallics, such as tetrabenzylzirconium [4]. Whilst simple alkylated species can result from such reactions, reduced metal complexes, ligand-alkylated complexes and partially characterised fluxional species have also been observed. Continued interest in the area stems from the apparent dependence of product distribution on both reaction constituents and conditions. Our own studies have considered the complexes obtained by trimethylaluminium alkylation. In a preliminary communication we noted the formation of trimetallic $Al/Ti^{III}/Al$ and bimetallic Al/Ti^{IV} complexes from the reaction of $[TiCl_2(salen)]$ and $AlMe_3$ [5]. This work has been expanded to consider the reactivity of structurally related titanium(IV) Schiff base complexes with $AlMe_3$, and the products derived from reaction of the novel mono-alkylated [Ti(Me)Cl(salen)] with a series of substrates.

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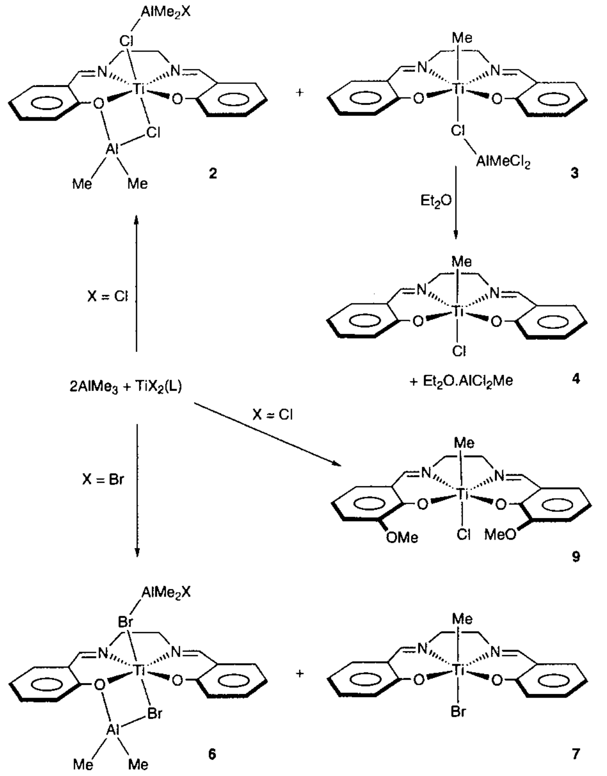


Scheme 1. The activation of Group 4 Schiff base complexes with trimethylaluminium.

2. Results and discussion

2.1. Reaction of [TiX$_2$(L)] and AlMe$_3$

The reaction of [TiCl$_2$(salen)] (**1**) [6] with AlMe$_3$ (1:2) in toluene/hexane affords the trimetallic titanium (III) species [Ti{(μ-Cl)(AlMe$_2$)}{(μ-Cl)(AlMe$_2$X)}(salen)] (X = Me or Cl) (**2**), and the bimetallic titanium(IV) complex [TiMe{(μ-Cl) (AlCl$_2$Me)}(salen)] (**3**), Scheme 1. Whilst the isolation of **2** and **3** has been previously reported [5], the importance of reaction stoichiometry and conditions is elaborated here. Thus, increasing the reaction time to ca. 14 h at ambient temperature provided access to the reduced complex **2** in quantitative yield. Conditions cannot be modified to afford **3** as the sole product since reducing the reaction temperature to ca. −78°C produced **2** and **3** at lower rates, whilst using an equimolar ratio of AlMe$_3$ produced the same product distribution together with ca. 45% unreacted **1**. Increasing the Al:Ti stoichiometry does not affect the distribution of **2** and **3**. **2** is stable under inert atmospheres in the solid state and at −20°C in non-polar solvents, but reacts with THF or Et$_2$O, producing an immediate purple to blue colour change followed by rapid decomposition. Crystallographic characterisation [5] confirms the structure of **2** and indicates the presence of a substitutionally disordered site on the AlMe$_2$X moiety; crystallographic refinement being optimised by a 0.65:0.35 Me:Cl distribution. Paramagnetism of **2** is confirmed by magnetic susceptibility measurements, Table 1. ESR spectra (77 K, dichloromethane) are indicative of a d^1 configuration, although no hyperfine structure could be observed.

[TiMe{(μ-Cl)(AlCl$_2$Me)}(salen)] (**3**), which is insoluble in hexanes and only moderately soluble in toluene, is readily separated from **2**. ^{1}H-NMR is in accord with the assignment of methyl moieties to titanium and aluminium centres on the basis of resonances at δ 0.98 and δ −0.36, respectively [7,8]. Further evidence for this formulation is derived from the reaction of **3** with Et$_2$O; on treatment of **3** with Et$_2$O, the pendant AlMeCl$_2$ group is lost as its highly reactive solvent adduct, Et$_2$O · AlMeCl$_2$, to afford [Ti(Me)Cl(salen)] (**4**) in high yield (95%), Scheme 1. Et$_2$O · AlMeCl$_2$ can be purified by distillation, 101–105°C at 0.1 mmHg [9] to yield a colourless, highly pyrophoric, viscous liquid,

Table 1
Analytical and physical data for products of the reaction TiX$_2$(L) + 2AlMe$_3$

Complex	Colour	ν(C=N)[a] (cm^{-1})	^{1}H-NMR (Ti–CH$_3$)/δ	μ_{eff}/μ_B	Analysis (%)			
					C	H	N	Cl
2	Purple	1624, 1598		1.84	48.1 (47.7)	4.6 (5.2)	4.9 (5.4)	
3	Orange–brown	1615	−0.36, 0.98		45.8 (45.2)	4.5 (4.5)	6.1 (5.9)	
4	Red–brown	1616	0.67		55.3 (55.9)	4.5 (4.7)	7.6 (7.6)	9.8 (9.7)
6	Purple	1628, 1598		1.89	39.4 (40.2)	4.7 (4.6)	4.6 (4.5)	
7 · 0.5CH$_2$Cl$_2$	Red	1612	0.79		46.8 (46.5)	3.7 (4.0)	6.4 (6.2)	
9 · 0.5CH$_2$Cl$_2$	Red		0.78		50.9 (50.2)	4.5 (4.7)	5.7 (6.0)	

[a] Nujol mull.

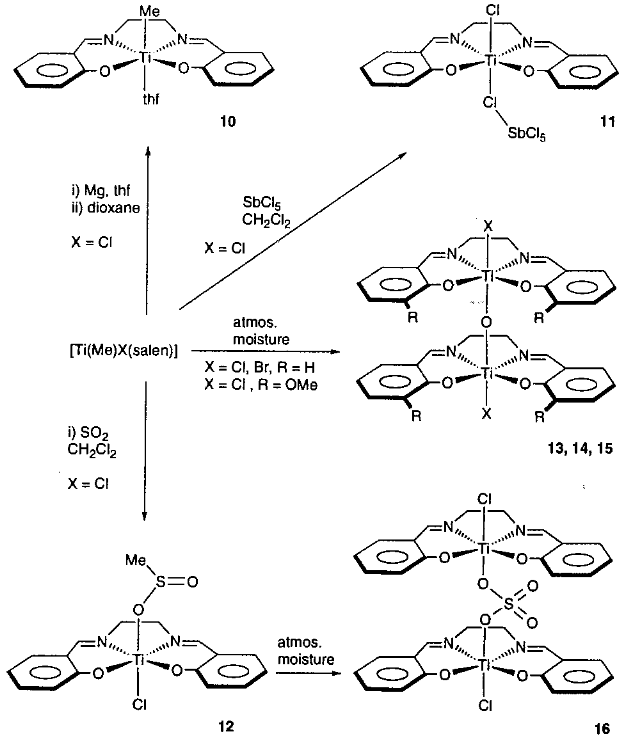
which is authenticated by comparison with the published ^{1}H-NMR data [10]. The presence of a single methyl group in **4** is confirmed by the δ 0.67 ^{1}H-NMR resonance. **4** shows remarkable thermal stability displaying no propensity for alkyl migration to the Schiff base ligand even after prolonged reflux in toluene or dichloromethane. This behaviour contrasts markedly with the rapid alkyl migration at ambient temperature reported for the corresponding dimethyl complex [1].

The reaction of [TiBr$_2$(salen)] (**5**) [6] with trimethylaluminium (1:2) in toluene:hexane (50:50) at ambient temperature for ca. 12 h affords, after work-up, [Ti{(μ-Br)(AlMe$_2$)}{(μ-Br)(AlMe$_2$X)}(salen)] (X = Me or Br) (**6**) and [Ti(Me)Br(salen)] (**7**) in yields of 10 and 60%, respectively, Scheme 1. Elemental analysis supports the formulation of both complexes, whilst respective magnetic susceptibility and ^{1}H-NMR data are consistent with these structures, Table 1. Although representing single crystal rather than bulk analysis, the formulation is also consistent with the X-ray structure of **6** discussed in Section 2.3. The latter refines the structural disorder in the AlMe$_2$X moiety as 0.74:0.26 Me:Br.

Recrystallisation of **7** from dichloromethane at −20°C yielded solvated [Ti(Me)Br(salen)] as deep red needles. Spectroscopic and physical properties of **7** are entirely consistent with its chloride analogue, Table 1. Even crude materials show no ^{1}H-NMR evidence of high-field resonances indicative of terminal or bridging aluminium methyl groups. Moreover, washing **7** with diethyl ether does not result in the isolation of the reactive adduct Et$_2$O · AlMeBr$_2$. Thus, the formation of **5** occurs either entirely without the formation of [TiMe{(μ-Br)(AlMeBr$_2$)}(salen)] or with the latter representing only a transient solution intermediate.

Qualitatively it is apparent that a reaction does occur between [TiF$_2$(salen)] [6] and trimethylaluminium under analogous conditions to those used for the chloro and bromo derivatives. The formation of an initial red–orange solution from the yellow fluoride complex and the absence of a deep purple product is suggestive of the formation of titanium(IV) complex(es). Storage of the filtered mother liquor at −20°C consistently gives a deep blue solution and an intractable oily blue residue after several days, perhaps indicative of slow reduction to Ti(III). However, purification and acceptable characterisation of these materials has thus far not proved possible.

Adding trimethylaluminium (two equivalents) to a toluene:hexane (50:50) suspension of [TiCl$_2${(MeO)$_2$salen}] (one equivalent) (**8**) [6] at ambient temperature immediately gave a red–orange precipitate, but no coloured solutions diagnostic of a titanium(III) analogue to **2** and **6**. Removal of the solvent in vacuo and addition of THF to the dried solid immediately resulted in a red–brown slurry. The mother liquor was removed after ca. 10 min and the remaining red–brown solid recrystallised from dichloromethane to give solvated [Ti(Me)Cl{(MeO)$_2$salen}] (**9**).



Scheme 2. Examples of the reactivity of [Ti(Me)Cl(salen)] (**4**).

2.2. *Reactivity of [Ti(Me)Cl(salen)]*

Other workers have observed considerable instability for Group 4 alkyls in the presence of co-ordinated Schiff bases, often resulting in complex mixtures of paramagnetic/fluxional species. The unprecedented thermal stability **4** provides the opportunity to investigate its reactivity without the complications of intramolecular reactivity.

Stirring a heterogeneous mixture of **4** and magnesium powder in THF for ca. 4 h gave a dark green coloured solution, Scheme 2. Following purification, [Ti(THF)Me(salen)] (**10**) is isolated as a green microcrystalline solid in ca. 55% yield, Table 1. The complex is stable at ambient temperature under an inert atmosphere but is extremely susceptible to oxidation and/or hydrolysis both in solution and the solid state. The corresponding phenyl complex has been isolated from the direct alkylation/reduction of **1** with PhLi [2].

Since ethylene polymerisation is believed to be catalysed by cationic Group 4 complexes, synthetic strategies have been developed to generate cationic metallocenes [11]. It has also been possible to synthesise cationic Schiff base complexes of zirconium, although the latter are not catalytically active [4]. In an attempt to abstract the chloride ligand from **4** and prepare the first base-free cationic alkyl–titanium(IV) complex containing a Schiff base ligand, one equivalent of antimony(V) chloride was added to a dichloromethane solution of **4**. This method of chloride abstraction has been utilised by Willey et al. in sequential halide abstractions from $TiCl_4$, $[Cp_2TiCl_2]$ and $[CpTiCl_3]$ in acetonitrile [12], and it was anticipated that such a system, incorporating the non-coordinating $SbCl_6^-$ counterion would allow direct investigation of the chemistry of the key $[TiMe(salen)]^+$ cation. However, the reaction leads to the immediate precipitation of $[Ti\{(\mu\text{-}Cl)(SbCl_5)\}Cl(salen)]$ (**11**), a unique antimony–titanium complex, Scheme 2. The structure of **11**, which is based on analytical and spectroscopic data, can be considered as the $[TiCl_2(salen)]$ (**1**) unit acting as a Lewis base through a chloride bridge to a pendant antimony pentachloride moiety, Table 2. This type of bonding is observed in **2** and **6** and has been postulated for **3**. Allowing a CH_2Cl_2 solution of **11** to stand in air results in the precipitation of a reddish solid and an unidentified white solid. Washing the former with acetone:water (50:50) gave analytically pure **1**. **1** is also isolated from the reaction of **4** with $AgBF_4$ (1:1) after reaction in the absence of light.

Sulfur dioxide insertion into metal-alkyls represents an extensively investigated form of reactivity [13]. Thus, when a deep red CH_2Cl_2 solution of **4** is exposed to an atmosphere of sulphur dioxide at ambient temperature the solution gradually becomes a pale red–orange in colour, Scheme 2. Work-up and storage at −20°C affords $[Ti(SO_2Me)Cl(salen)]\cdot 0.5CH_2Cl_2$ (**12**) as pale red crystals. ^1H-NMR of **12** displays a singlet at δ 2.26 that is typically diagnostic of a sulphur bound methyl group and is comparable with others reported for titanium methanesulphinate complexes, e.g. $[Cp_2Ti(O_2SMe)_2]$ at δ 2.48 and $[CpTiMe_2(O_2SMe)_2]$ at δ 2.55 [14,15]. However, the oxophilicity of titanium and its inclination to coordinate to hard ligands would suggest the preferential insertion of SO_2 to form an *O*-sulphinate complex. Such reactivity can be inferred from the IR spectrum of **12**; of the three bands not attributable to the Schiff base ligand at 853, 975 and 1032 cm^{-1}; the lowest stretch suggests the presence of a new titanium–oxygen bond in **12**. Such an assignment is in agreement with those reported previously [15,16], and indicative of partial multiple bond character [17]. The bands at 975 and 1032 cm^{-1} can be assigned to ν_s(S–O) and ν_{as}(S–O), respectively, which confirms **12** as an η^1-*O*-sulphinate complex [18].

Oxo-bridged dimeric and polymeric complexes based on Group 4 Schiff base complexes have previously been obtained by the partial hydrolysis of titanium(IV) halides [19] or the oxidation of titanium(III) halides [20]. The asymmetric halide/methyl substitution offers a rational and high yield route to dimeric complexes. Thus, if a CH_2Cl_2 solution of **4** is allowed to stand in the air, $[TiCl(salen)]_2(\mu\text{-}O)$ (**13**) is isolated as a bright red crystalline solid in quantitative yield. Similarly, $[TiBr(salen)]_2(\mu\text{-}O)$ (**14**) and $[TiCl\{(MeO)_2salen\}]_2(\mu\text{-}O)$ (**15**) are isolated from solutions of **7** and **9**, respectively. Over several hours, a CH_2Cl_2 solution of **12** also undergoes hydrolysis, which results in the precipitation of $[TiCl(salen)]_2(\mu\text{-}SO_4)$ (**16**) as an air stable solid. A structure for **16** is tentatively proposed in Scheme 2. The chemistry of titanium(IV) with the sulphate ion is limited to polymeric species, e.g. $TiOSO_4\cdot H_2O$. There has been a single report of a titanium complex containing SO_4^{2-} but the bonding mode of the sulphate ion in polymeric $[CpTi(\mu\text{-}O)(SO_4)_{0.5}(H_2O)]_n$ was not established [21].

Table 2
Analytical and physical data for products of the reactions of [Ti(Me)Cl(salen)]

Complex	Colour	ν(C=N)[a] (cm^{-1})	ν(Ti–O) (cm^{-1})	μ_{eff}/μ_B	Analysis (%)			
					C	H	N	Cl
10	Green	1608		1.76	63.1	6.4	7.3	
					(62.8)	(6.2)	(7.0)	
11	Orange	1631			27.6	2.0	4.1	35.9
					(27.9)	(2.0)	(4.1)	(36.1)
12 $\cdot 0.5CH_2Cl_2$	Pale red	1619	853		44.6	3.5	6.3	
					(44.6)	(3.8)	(6.0)	
13	Red	1633	760		53.5	4.0	7.6	
					(53.7)	(3.9)	(7.8)	
14 $\cdot CH_2Cl_2$	Red	1620	735		44.1	3.4	6.2	
					(44.5)	(3.4)	(6.3)	
15	Red	1624	754		50.9	4.3	7.3	
					(51.7)	(4.3)	(6.8)	
16	Orange	1630[b]			48.7	3.4	7.2	
					(48.3)	(3.5)	(7.0)	

[a] Nujol mull.

[b] ν(S–O) 971, 1044 and 1090 cm^{-1}.

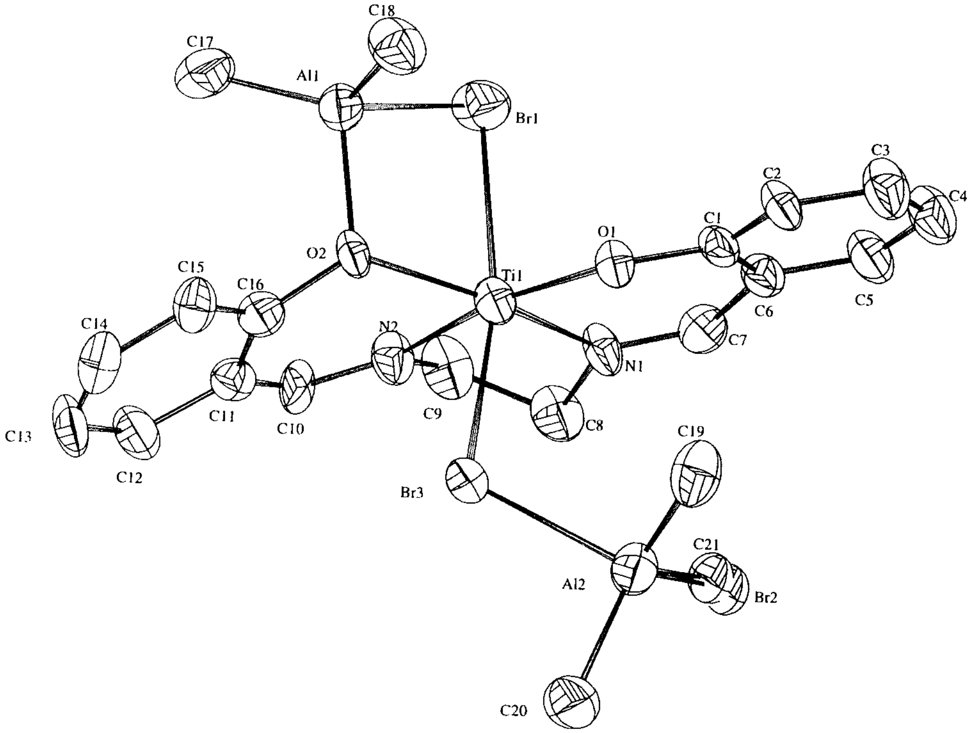


Fig. 1. The molecular structure of **6** showing the atomic numbering scheme.

Treatment of **4** in toluene at −78°C with phenyllithium gave a dark brown solution, which after filtration and standing at −20°C overnight, yielded dark brown crystals. The ^{1}H-NMR spectrum (C_6D_6) of this material indicated complex solution state chemistry similar to that observed from the reaction of **1** with alkylating agents [22]. The absence of an imino proton resonance and the disappearance of the C=N IR stretching vibration indicates a transformation involving alkyl migration(s) and reduction of the imino groups of the Schiff base. Evidently, the *trans* chloride in **4** more effectively stabilises the single methyl present more readily than a second alkyl/aryl group.

*2.3. Solid state structures of **2** and **6***

2 and **6** can be recrystallised from toluene/hexane to produce crystals suitable for X-ray diffraction. The structure of **2** has been briefly reported [5]; however, full data for **6** are presented with detailed comparisons between the two structures. The structure of **6** indicates a formulation of [Ti{(μ-Br)($AlMe_2$)}{(μ-Br)($AlMe_2X$)}-(salen)], Fig. 1, which can be considered as aluminium(III)–titanium(III)–aluminium(III) moieties of [Me_2-Al(1)], [Ti(salen)] and [Al(2)Me_2X (X = Br/Me)]. These substructures are linked by μ^2-bromide ions that bond into the apical positions of the central titanium atom. The group X contains disordered methyl and bromide groups modelled on an occupancy of 0.26 (Br) and 0.74 (Me). It is notable that this structure is completely isostructural with **2**; being demonstrated by the comparable bond lengths and angles within the two complexes that only differ significantly as a consequence of the inclusion of the larger bromide ion, Table 3. Initial characterisation of **2** might have suggested that such a trimetallic species was one of several possible titanium(III) species. Moreover, the single disordered site might have again been indicative of crystal packing selection rather than bulk properties. However, since **6** is also trimetallic and exhibits the same single site of disorder, it must be postulated that **2** and **6** represent stable and structurally representative samples of their bulk. Furthermore, it must be speculated that the mechanism or stoichiometry of complex formation or post-formation reactivity limits exchange of aluminium substituents to a single site. Since the Al(1) moiety is conformationally locked by the halide bridge and the O(2)–Al(1), interaction substitution exchange should be mechanistically difficult. In contrast, the Al(2) containing group, whilst also four-coordinate, can undergo free rotation and presumably associative or dissociate exchange.

The distortion resulting from aluminium–oxygen dative bonding is crucial to the anomalous bond lengths observed with **2** and **6** and to the significant distortions from the idealised octahedral bonding for titanium. Within both complexes, the μ^2-bonded oxygen shows elongation of the Ti–O(2) bond beyond that reported in simple Ti(III) and Ti(IV) Schiff base complexes, Table 3. Shortening of the *trans* Ti–N(1) is a natural and obvious consequence of this elongation. The asymmetry in the N_2O_2 salen ligand is also reflected in the significantly different C=N distances observed in both **2** and **6**, although both distances show the increased bond distance from the free salen ligand [26]. The aluminium–oxygen interactions in both complexes should not be considered trivial since both lie between the Al–O distances reported in the reduced Schiff base complex [(AlMe)salphan(AlMe$_2$)$_2$] [salphan = *N*,*N*′-bis(*o*-hydroxybenzyl)-1,3-diaminopropane] [27] and those of [Al(salen)Et] [28]. The ability of coordinated Schiff base ligands to act as Lewis bases with a second metal is not without precedent. This facility has been observed with both iron(III) and nickel(II), although similar reactivity was not recorded with titanium(III) or (IV) [29,30].

3. Conclusion

All the titanium(IV) complexes considered appear to react with $AlMe_3$, although characterisable products have not been obtained in every case. Product distribution is dependent on both the halide and Schiff base ligand present in the titanium(IV) precursor. Reduction appears to occur less readily for the fluoride analogue, [TiF$_2$(salen)], and is not observed for [TiCl$_2${(MeO)$_2$-salen}]; reactivity that may relate to the greater electron density afforded to the Ti^{IV} centre by the π-donating fluoride or the electron donating MeO groups. Probing the reactivity of mono-methylated titanium(IV) complexes using **4**, produced a series of conventional products from zinc reduction and sulphur dioxide insertion. Attempts to produce cationic Schiff base complexes leads to the regeneration of [TiCl$_2$(salen)]. Hydrolysis of [Ti(Me)X(salen)] complexes occurs specifically at the methyl group affording the dimeric μ-oxo complexes. Such reactivity affords a high yield route to dimeric complexes and potentially through further alkylation to the rational synthesis of oligomeric complexes.

4. Experimental

4.1. Crystal structure determination of **6**

Recrystallisation of **6** from toluene:hexane (50:50) produced at −20°C over ca. 4 weeks air-sensitive crystals of **6**·C_7H_8. Crystal dimensions 0.07 × 0.14 × 0.14 mm^3. Intensity data were recorded on a FAST TV area detector diffractometer at 150 K following previously described procedures [31]. The structure was solved by direct methods (SHELXS) [32] and refined by

Table 3
Important bond lengths and angles in complexes **2** and **6**

Bonding feature[a]	Complex **2**	Complex **6**	Literature comparisons[b]
Bond lengths (Å)			
Ti–X(1)	2.579(5)	2.670(3)	
Ti–X(3)	2.512(5)	2.589(3)	2.148 in [Ti(py)Cl(salen)][c]
Ti–O(1)	1.849(4)	1.849(4)	1.835 in [TiCl$_2$(acen)][d]
Ti–O(2)	2.057(3)	2.045(3)	1.867 in [TiF$_2$(salen)][e]
Ti–N(1)	2.127(4)	2.106(4)	2.138 in [Ti(py)Cl(salen)][c]
Ti–N(2)	2.174(5)	2.186(5)	2.141 in [TiCl$_2$(salen)] · THF[f]
Al(1)–O(2)	1.914(4)	1.872(4)	
Al(1)–X(1)	2.287(3)	2.421(2)	
Al(2)–X(3)	2.359(4)	2.530(3)	
Bond angles (°):			
Ti-centered pseudo-O_h angles			
Minimum	N(2)–Ti–N(1) = 76.6(2)	N(2)–Ti–N(1) = 76.9(2)	
Maximum	O(2)–Ti–O(1) = 118.25(13)	O(2)–Ti–O(1) = 117.4(2)	
Al(1)-centered pseudo-T_d angles			
Minimum	O(2)–Al(1)–Cl(1) = 90.0(2)	O(2)–Al(1)–Br(1) = 89.49(14)	
Maximum	C(21)–Al(1)–C(20) = 123.9(3)	C(17)–Al(1)–Br(1) = 112.8(2)	
Metal bridging halide angles			
Ti–X(1)–Al(1)	82.17(11)	77.82 (8)	
Ti–X(3)–Al(2)	119.46(13)	114.72(7)	

[a] X = Cl (**2**), X = Br (**6**).

[b] Average bond lengths (Å).

[c] [23].

[d] [24].

[e] [6].

[f] [25].

full-matrix least-squares on F^2 (SHELX-93), with all non-hydrogen atoms being refined anisotropically [33]. Data were corrected for absorption effects using DIFABS with maximum and minimum correction factors of 1.08 and 0.93, respectively [34].

Crystal data. $C_{27.74}H_{36.21}Al_2Br_{2.26}N_2O_2Ti$, $M = 712.30$, monclinic, $a = 10.186(9)$, $b = 14.936(2)$, $c = 21.044(3)$ Å, $\beta = 95.05(11)°$, $V = 3188.9(30)$ Å^3, $D_{calc.} = 1.484$ g cm^{-3}, $T = 150(2)$ K, space group $P2_1/c$, $Z = 4$, μ(Mo–K$_\alpha$) = 31.85 mm^{-1}, unique total number of data = 6995, unique number of observed data = 1916 [$I > 2\sigma(I)$], $R_1 = 0.0454$, $wR = 0.1031$.

4.2. Synthetic procedures

Inert atmosphere glovebox and Schlenk-line techniques were used throughout the preparative procedures unless otherwise indicated. Nitrogen and argon were purified prior to use by passage through two columns containing MnO and 4 Å molecular sieves, respectively. Solvents were pre-dried, then refluxed over the appropriate drying agent, and subsequently distilled under nitrogen or argon. Benzene-d_6 was pre-dried over 4 Å molecular sieves, degassed, and stored over sodium–potassium alloy. Dichloromethane-d_2 and chloroform-d_1 were refluxed over calcium hydride or phosphorus pentoxide and stored in ampoules over 4 Å molecular sieves. NMR spectra were recorded at 270 MHz. Magnetic susceptibility measurements were made in sealed tubes using a Johnson Matthey Faraday balance. Elemental analysis and important characterisation data are given in Table 1. Syntheses of **1**, **5**, **8** and [TiF$_2$(salen)] are previously reported [6].

4.3. [Ti{(μ-Cl)(AlMe$_2$)}{μ-Cl)(AlMe$_2$X)}(salen)] (2) (X = Me or Cl) and [TiMe{(μCl)(AlCl$_2$Me)}(salen)] (3)

A toluene:hexane (1:1) suspension of **1** (7.0 g, 18 mmol) was treated with a toluene solution of AlMe$_3$ (2.0 M, 18.2 cm^3, 36 mmol) over a period of ca. 20 min. Immediately, a red–purple solution was observed. The reactants were stirred for a further 30 min at ambient temperature and an orange–brown solid precipitated from solution. The deep purple solution was filtered and the solid residue was then washed successively with hexane (ca. 6 × 30 cm^3) and these extracts were added to the original supernatant until they were colourless. After storage at −20°C, 500 mg (13%) of **2** · C_7H_8 were collected as large purple pyrophoric crystals. Solvent-free **2** was isolated from less polar toluene–hexane mixtures (25:75) as purple needles. The remaining orange–brown solid was dried in vacuo for ca. 6 h to give 3.2 g (55%) of the air- and moisture-sensitive **3**. Recrystallisation of **3** from a dilute toluene solution at −20°C gave an analytically pure orange–brown microcrystalline solid.

3: ^{1}H-NMR (C_6D_6): δ −0.36 (s, 3H, Al–Me), 0.98 (s, 3H, Ti–Me), 3.08 (dd, 2H, CH$_2$) 3.70 (dd, 2H, CH$_2$), 6.60 (m, 4H, Ph), 7.00 (m, 4H, Ph) and 7.70 (s, 2H, CH).

4.4. [Ti(Me)Cl(salen)] (4)

Diethyl ether (ca. 30 cm^3) was decanted onto **3** and immediately the solid darkened to a red–brown. After stirring for 10 min, the almost colourless Et$_2$O was decanted from the solid. After washing with Et$_2$O and drying in vacuo, 2.2 g (95%) of analytically pure **4** was collected. Removing the solvent from the filtrate in vacuo yielded an oily residue that was distilled, 101–105°C at 0.1 mmHg, to give Et$_2$O · AlCl$_2$Me as a highly pyrophoric, colourless liquid.

Et$_2$O · AlCl$_2$Me: ^{1}H-NMR (C_6D_6): δ −0.58 (s, 3H, Al–Me), 0.64 (t, 6H, Me) and 3.26 (q, 4H, CH$_2$).

[Ti(Me)Cl(salen)] (**4**): ^{1}H-NMR (CH$_2$Cl$_2$): δ 0.67 (s, 3H, Me), 4.00 (dd, 2H, CH$_2$), 4.37 (dd, 2H, CH$_2$), 6.90–7.10 (m, 4H, Ph), 7.50–7.70 (m, 4H, Ph) and 8.50 (s, 2H, CH). ^{1}H-NMR (C_6D_6): δ 1.07 (s, 3H, Me), 3.08 (dd, 2H, CH$_2$), 3.76 (dd, 2H, CH$_2$), 6.60–6.85 (m, 4H, Ph), 7.03–7.30 (m, 4H, Ph) and 7.78 (s, 2H, CH). EI$^+$ MS (70 eV): m/z 365 (10%, [Ti(Me)Cl(salen)]$^+$, protonated).

4.5. [Ti{(μ-Br)(AlMe$_2$)}{(μ-Br)(AlMe$_2$X)}(salen)] (X = Me or Br) (6) and [Ti(Me)Br(salen)] (7)

In a similar preparation to **3**, [TiBr$_2$(salen)] (**5**) was treated with a toluene solution of AlMe$_3$ over ca. 10 min, and stirred for a further 12 h until all **5** was consumed. The resulting purple solution was filtered from a brown precipitate. The solid residue was then washed successively with hexane (3 × 20 cm^3) and these extracts were added to the original mother liquor until they were colourless. This was placed at −20°C and over a period of ca. 4 weeks gave **6** · C_7H_8 (ca. 10%) as deep purple pyrophoric crystals. Following an identical preparative procedure, the purple toluene solution of **6** was removed by filtration, layered with hexane and allowed to stand at −20°C overnight to give analytically pure **6**. The remaining solid was dried in vacuo for ca. 4 h to give crude [Ti(Me)Br(salen)] (**7**) (ca. 60%). Several recrystallisations from dichloromethane gave [Ti(Me)Br(salen)] · 0.5CH$_2$Cl$_2$ as dark red moisture-sensitive needles.

(**7**): ^{1}H-NMR (CDCl$_3$): δ 0.79 (s, 3H, Me), 4.11 (dd, 2H, CH$_2$), 4.30 (dd, 2H, CH$_2$) 6.87–7.10 (m, 4H, Ph) 7.50–7.80 (m, 4H, Ph) and 8.51 (s, 2H, CH). FAB$^+$ MS (NOBAH matrix): m/z 394 (5%, [TiBr(salen)]$^+$).

4.6. [Ti(Me)Cl{(MeO)$_2$salen}] (**9**)

In a similar preparation to **3**, AlMe$_3$ and [TiCl$_2${(MeO)$_2$salen}] (**8**) yielded a light red–orange solution and a red–orange precipitate within ca. 5 min. After stirring for a further 30 min, the mother liquor was removed by decantation. The solid was dried in vacuo and THF added, resulting in the formation of a red–brown solid. The solvent was removed after ca. 10 min and the residue was extracted into CH_2Cl_2 (ca. 3 × 20 cm^3), filtered and stored at −20°C to give **9**·0.5CH_2Cl_2 (2.0 g, 52%).

9: ^{1}H-NMR ($CDCl_3$): δ 0.78 (s, Me), 3.45 (m, CH_2), 4.00 (s, MeO), (m, CH_2), 6.95–7.15 (m, Ph) and 8.45 (s, CH).

4.7. [Ti(THF)Me(salen)] (**10**)

A CH_2Cl_2 solution (40 cm^3) of **4** (0.5 g, 1.4 mmol) was added to an excess of magnesium powder at room temperature and the resulting heterogeneous mixture was stirred vigorously. After ca. 30 min, a dark green solution was apparent, stirring was continued for a further ca. 3.5 h. The solution was filtered, anhydrous 1,4-dioxane was added, and the mixture cooled to −20°C. The green mother liquor was then filtered from a small quantity of insoluble material, the volume reduced to ca. 20 cm^3 in vacuo. **10** (0.30g, 55%) was collected as a green microcrystalline solid and dried in vacuo.

4.8. [TiCl{(μ-Cl)(SbCl$_5$)}(salen)] (**11**)

A CH_2Cl_2 solution of antimony pentachloride (1.0 M, 2.74 cm^3, 2.74 mmol) was added, with stirring, to a CH_2Cl_2 solution of **4** (1.0 g, 2.74 mmol). Instantly, a tan solid precipitated from solution to leave a very pale orange supernatant. Stirring was continued for a further 20 min with no observed changes. The supernatant was then removed by filtration and the solid residue was washed with CH_2Cl_2 (ca. 3 × 20 cm^3). The solid was then dried in vacuo to give ca. 1.2 g (60%) of analytically pure **11**. The combined CH_2Cl_2 extracts were filtered and layered with toluene. After standing at −20°C overnight **11**·1.5C_7H_8 was collected as an orange crystalline material (ca. 300 mg).

[TiCl{(μ-Cl)(SbCl$_5$)}(salen)] (**11**): ^{1}H-NMR (CD_2Cl_2): δ 4.57 (s, 4H, CH_2), 7.11–7.42 (m, Ph), 7.45–7.54 (m, Ph) and 8.90 (s, 2H, CH). Some phenyl resonances are obscured due to the presence of co-crystallised toluene. Removal of the solvent in vacuo gave an analytical sample.

4.9. Hydrolysis of **11**

11 was prepared (1.0 g scale) and the resulting pale orange supernatant was decanted. Precipitated **11** was then washed successively with copious quantities of dry CH_2Cl_2 (ca. 250 cm^3) and these extracts were added to the original. After standing in air for 12 h a white insoluble material was removed by filtration. The solvent was removed in vacuo to yield [TiCl$_2$(salen)] (**1**) (0.8 g, 85%).

1: ^{1}H-NMR ($CDCl_3$): δ 4.25 (s, 4H, CH_2), 6.85–7.13 (m, 4H, Ph), 7.33–7.61 (m, 4H, Ph) and 8.39 (s, 2H, CH). Found: C, 49.8; H, 3.6; N, 7.5. Calc. for **1**, $C_{16}H_{14}N_2O_2Cl_2Ti$: C, 49.8; H, 3.6; N, 7.3. ν(C=N) 1612 cm^{-1}.

4.10. [Ti(SO$_2$Me)Cl(salen)] (**12**)

A CH_2Cl_2 solution (ca. 50 cm^3) of **4** (500 mg, 1.4 mmol) was exposed to SO_2 and over a period of ca. 10 min and the solution turned a red–orange in colour. Solvent was reduced to ca. 20 cm^3 and placed at −20°C. [Ti(SO$_2$Me)Cl(salen)]·0.5CH_2Cl_2 (400 mg, 70%) was collected by filtration and dried in vacuo.

12: ^{1}H-NMR ($CDCl_3$): δ 2.26 (s, 3H, Me), 3.87 (dd, 2H, CH_2), 4.32 (dd, 2H, CH_2), 6.59–7.05 (m, 4H, Ph), 7.41–7.67 (m, 4H, Ph) and 8.16 (s, 2H, CH).

4.11. [TiX(salen)]$_2$(μ-O) (**13**) (**14**) (**15**) (**16**)

A CH_2Cl_2 solution of **4** (200 mg, 5.49 mmol) was allowed to stand in air and after 12 h yielded red crystalline **13** (200 mg, ca. 96%), which was collected, washed with sodium dried Et_2O and dried in vacuo. A similar preparation yielded **14**·CH_2Cl_2, **15** and **16**.

14·CH_2Cl_2: ^{1}H-NMR ($CDCl_3$) δ 4.30 (s, 4H, CH_2), 6.85–7.20 (m, 4H, Ph), 7.45–7.70 (m, 4H, Ph) and 8.46 (s, 2H, CH).

15: ^{1}H-NMR ($CDCl_3$): δ 3.90 (s, 6H, MeO), 4.23 (s, 4H, CH_2), 7.07 and 7.11 (m, 6H, Ph) and 8.36 (s, 2H, CH).

16: ^{1}H-NMR could not be obtained as a consequence of the insolubility of **16** in all common solvents.

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