Articles

Titanium Imido Complexes with Tetradentate Schiff Base Ligands

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New mono- and binuclear titanium imido complexes supported by tetradentate, dianionic N_2O_2-donor Schiff base ligands were prepared in good yield from the readily available [Ti(NBu^t)Cl_2(py)$_3$] (**1a**). Thus treatment of **1a** with Na_2[substituted-salen] gave monomeric [Ti(NBu^t)(substituted-salen)] where substituted-salen = Et_2salen (**2**) or Bu$^t_4$salen (**4**). In contrast, the binuclear complex [Ti(NBu^t){μ-(MeO)$_2$salen}]$_2$ (**5**) was obtained from **1a** and Na_2[(MeO)$_2$salen]. The less sterically crowded compounds **2** and **5** undergo *tert*-butyl imide/arylamine exchange reactions to form [Ti(N-2,6-$C_6H_3Me_2$)(Et_2salen)] (**3**) and [Ti(N-2,6-$C_6H_3Me_2$){μ-(MeO)$_2$salen}]$_2$ (**6**), respectively, whereas **4** does not exhibit this kind of reactivity. The compound **3** can also be obtained directly from Na_2[Et_2salen] and [Ti(N-2,6-$C_6H_3Me_2$)Cl_2(py)$_3$] (**1b**). Crystal data for **3**: triclinic, $P\bar{1}$, $a = 12.216(4)$ Å, $b = 12.312(11)$ Å, $c = 17.246(2)$ Å, $\alpha = 90.352(12)°$, $\beta = 102.59(2)°$, $\gamma = 104.96(2)°$, $V = 2440.3(8)$ Å^3, $Z = 4$, $R = 0.051$, $R_w = 0.066$ for 7011 data with $I > 2\sigma(I)$. Crystal data for **5·CH$_2$Cl$_2$**: orthorhombic, *Pbca*, $a = 14.747(4)$ Å, $b = 17.042(4)$ Å, $c = 20.545(3)$ Å, $V = 5163.5(13)$ Å^3, $Z = 4$, $R_1 = 0.096$, $wR_2 = 0.086$ for 3765 data with $I > 2\sigma(I)$. Crystal data for **6**: monoclinic, $C2/c$, $a = 17.902(5)$ Å, $b = 12.411(4)$ Å, $c = 21.068(5)$ Å, $\beta = 90.27(2)°$, $V = 4681(2)$ Å^3, $Z = 4$, $R = 0.034$, $R_w = 0.039$ for 3633 data with $I > 2\sigma(I)$.

Introduction

Transition metal imido chemistry has attracted considerable interest, and a wide range of ancilliary ligand environments for the M═NR functional group has been explored.[1−4] As part of an ongoing research program in early transition metal imido chemistry,[5−8] we reported the mono- and binuclear tetraazamacrocycle-supported group 4 imido complexes [Ti(NR)(Me$_n$taa)] (R = Bu^t or aryl; $n = 4$ or 8; H$_2$Me$_n$taa = tetra- or octamethyldibenzotetraaza[14]annulene, respectively),[9,10] [Zr(N-2,6-C_6H_3-Pr$^i_2$)(py)(Me$_4$taa)],[11] and [(Me$_4$taa)Zr(μ-NR)$_2$Zr(NHR)$_2$] (R = Bu^t or 2,6-$C_6H_3Me_2$).[7] These were the first macrocyclic group 4 imido complexes, further examples of which have since been reported.[12−14] The Me$_n$taa-supported imido complexes show a potentially rich chemistry of the Ti═NR linkage including cycloaddition reactions and reversible C−N bond formation.[11] Since no other macrocyclic group 4 imido complexes have been reported to show comparable reactivity, we were interested to explore the suitability of other tetradentate, dianionic supporting ligands for titanium imido chemistry, and it is these studies that form the basis of this contribution.

A class of ligand that has enjoyed widespread use across a range of transition metal chemistry are “salen”-type Schiff bases of the type shown in Figure 1.[15−19] The peripheral substituents (i.e., R^1, R^2, R^3) of these N_2O_2-donor ligands are readily modified, and their syntheses from diamines and salicylaldehydes are typically straightforward. A wide range of transition metal terminal and bridging oxo complexes of these and related ligands have been structurally characterized.[20] Salen ligands, however, have been little used in transition metal imido

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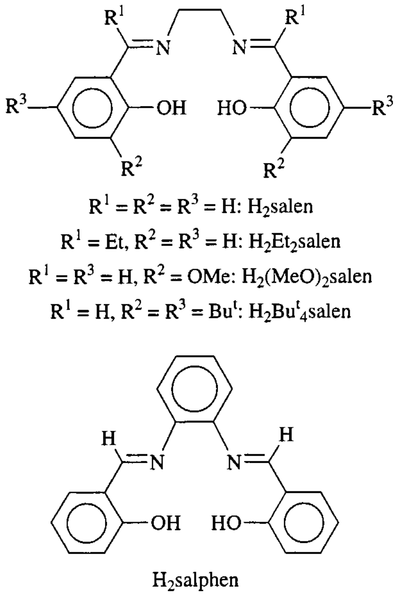

Figure 1. Neutral forms of the Schiff base ligands and abbreviations used.

chemistry,[21−24] and there are no structurally characterized terminal imido complexes containing these moieties. The binuclear compound $[Fe_2(salen)_2(\mu\text{-N-4-}C_6H_4Me)]$ has been structurally characterized and possesses a bridging tolylimido group.[22] Two rhenium tolylimido compounds with bidentate *N*-R-salicylaldiminato (R = Me, Ph) Schiff bases ligands have been also structurally characterized.[25] Furthermore, no salen-supported imido compounds from group 4 have been described at all, despite the well-established literature for other classes of N_2O_2-donor Schiff base complex incorporating these metals.[26−30] Oxotitanium salen complexes are either structurally ill-defined,[31,32] or are polynuclear, typically aggregating through μ-oxo linkages.[33−35] Since the oxo and imido ligands are valence isoelectronic and isolobal with each other, we considered it worthwhile also in this context to explore the synthesis and structures of salen ligand-supported titanium imido complexes. We therefore describe herein new mono- and binuclear titanium imido complexes containing tetradentate, dianionic N_2O_2-donor Schiff bases in which the differing positions and degrees of substitution in the ligand peripheries lead to substantially different solid-state structures and reactivity. Note that although for ease of representation all titanium-imido linkages are drawn "Ti═NR", the formal Ti−N bond order in the complexes $[Ti(NR)(\text{substituted-salen})_n]$ (R = Bu^t, aryl, $n = 1, 2$) described herein is generally best thought of as 3 (pseudo-σ^2 π^4 triple bond) rather than as 2.[1,36]

Experimental Section

General Methods and Instrumentation. Manipulations were carried out under an atmosphere of dinitrogen or argon using either standard Schlenk-line or drybox techniques. Solvents were predried over molecular sieves and refluxed over potassium (tetrahydrofuran, hexane), sodium−potassium alloy (pentane) or calcium hydride (dichloromethane) under an atmosphere of dinitrogen and collected by distillation. $CDCl_3$ and CD_2Cl_2 were dried over calcium hydride at room temperature, and C_6D_6 was dried over potassium at 70 °C. All deuterated solvents were distilled under reduced pressure and stored under N_2 in Young's ampules in a drybox. NMR samples were prepared in a drybox in Teflon valve (Young's) 5 mm tubes.

^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer at ambient temperature unless stated otherwise. The spectra were referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in Hertz. Assignments were supported by DEPT-135 and DEPT-90, homo- and heteronuclear, one- and two-dimensional, and NOE experiments as appropriate. Elemental analyses were carried out by the analysis laboratory of this department.

Literature Preparations. $[Ti(NBu^t)Cl_2(py)_3]$, $[Ti(N\text{-}2,6\text{-}C_6H_3Me_2)Cl_2(py)_3]$, H_2Et_2salen, $H_2Bu^t_4salen$, and $H_2(MeO)_2salen$ were prepared according to literature methods.[37−40] Disodium salts of the Schiff bases were prepared from the neutral ligands and NaH in THF and were used without further purification.

$[Ti(NBu^t)(Et_2salen)]$ (2). To a solution of $[Ti(NBu^t)Cl_2(py)_3]$ (0.580 g, 1.36 mmol) in THF (30 mL) was added dropwise $Na_2[Et_2salen]$ (0.500 g, 1.36 mmol) in THF (30 mL) at 0 °C. The solution immediately turned red and was allowed to warm to room temperature. A fine white solid formed, and the mixture was stirred for 24 h. The volatiles were removed under reduced pressure, and the residue extracted into CH_2Cl_2 (30 mL) and filtered. Hexane (20 mL) was added and the solution cooled to −25 °C overnight to give **2** as an orange solid which was washed with hexane (2 × 10 mL) and dried in vacuo. Yield: 0.530 g (89%). The product contained ca. 0.1 equiv of residual CH_2Cl_2 (by ^1H NMR and elemental analysis) even after prolonged drying.

The following NMR assignments have the O- and C(Et)═N-substituents of the Et_2salen ligand in the ring 1- and 6-positions, respectively. ^1H NMR ($CDCl_3$, 300.1 MHz): 7.60 (d, $J = 8.1$ Hz, 2 H, 5-C_6H_4), 7.31 (apparent t, apparent $J = 7.6$ Hz, 2 H, 3-C_6H_4), 7.06 (d, $J = 8.2$ Hz, 2 H, 2-C_6H_4), 6.70 (apparent t, apparent $J = 7.6$ Hz, 4-C_6H_4), 4.48, 4.15 (2 × m, 2 × 2 H, NCH_2), 3.06 (q, $J = 7.8$ Hz, 4 H, CH_2CH_3), 1.40 (t, $J = 7.8$ Hz, 6 H, CH_2CH_3), 0.48 (s, 9 H, $NCMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): 175.6 (C═N), 166.9 (1-C_6H_4), 133.1 (3-C_6H_4), 129.1 (5-C_6H_4), 124.0 (6-C_6H_4), 121.4 (2-C_6H_4), 116.0 (4-C_6H_4), 68.3 ($NCMe_3$), 52.0 (NCH_2), 31.4 ($NCMe_3$), 24.8 (CH_2CH_3), 12.3 (CH_2CH_3). Anal. Found (calcd) for $C_{24}H_{31}N_3O_2Ti\cdot 0.1CH_2Cl_2$: C, 64.1 (64.3); H, 6.9 (7.0); N, 9.1 (9.3).

$[Ti(N\text{-}2,6\text{-}C_6H_3Me_2)(Et_2salen)]$ (3). Method a: From $[Ti(N\text{-}2,6\text{-}C_6H_3Me_2)\ Cl_2(py)_3]$ and $Na_2[Et_2salen]$. To a cold (0 °C) solution of $Na_2[Et_2salen]$ (0.20 g, 0.54 mmol) in THF (20 mL) was added $[Ti(N\text{-}2,6\text{-}C_6H_3Me_2)Cl_2(py)_3]$ (0.27 g, 0.055 mmol) in cold THF (20 mL). The mixture was allowed to warm to room temperature, and after

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stirring for 48 h, the volatiles were removed under reduced pressure. The red-orange product was extracted with CH_2Cl_2, filtered through a pad of Celite, and recrystallized from CH_2Cl_2 and hexane to afford **3** as a red-orange microcrystalline powder. Yield: 0.15 g (55%).

Method b: From [Ti(NBu^t)(Et$_2$salen)] (2) and 2,6-Dimethylaniline. To a stirred solution of [Ti(NBu^t)(Et$_2$salen)] (**2**) (1.20 g, 2.7 mmol) in CH_2Cl_2 (15 mL) was added 2,6-dimethylaniline (400 μL, 3.2 mmol = 1.2 equiv). The solution was heated in a sealed ampule at 50 °C for 24 h, after which the volatiles were removed under reduced pressure. The residue was recrystallized from CH_2Cl_2 and hexane at room temperature to afford **3** as a red-orange microcrystalline powder which was washed with hexane and dried *in vacuo*. Yield: 1.21 g (90%).

Diffraction-quality crystals of **3** were grown overnight at room temperature from a saturated CH_2Cl_2 solution of **3** layered with hexane. The following NMR assignments have the O- and C(Et)═N-substituents of the Et$_2$salen ligand in the ring 1- and 6-positions, respectively. ^{1}H NMR ($CDCl_3$, 300.1 MHz): 7.74 (d, $J = 8.1$ Hz, 2 H, 5-C_6H_4), 7.43 (apparent t, apparent $J = 7.5$ Hz, 2 H, 3-C_6H_4), 7.22 (d, $J = 7.1$ Hz, 2 H, 2-C_6H_4), 6.85 (apparent t, apparent $J = 7.5$ Hz, 4-C_6H_4), 6.62 (d, $J = 7.3$ Hz, 2 H, *m*-H), 6.30 (t, $J = 7.3$ Hz, 1 H, p−H), 4.58, 4.09 (2 × m, 2 × 2 H, NCH_2), 3.10 (m, 4 H, $C\mathit{H}_2CH_3$), 1.91 (s, 6H, Me), 1.41 (t, $J = 7.6$ Hz, 6 H, $CH_2C\mathit{H}_3$), $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): 177.2 (C═N), 166.1 (1-C_6H_4), 160.1 (i-$\mathit{C}_6H_3Me_2$) 134.1 (3-C_6H_4), 130.2 (*o*-$\mathit{C}_6H_3Me_2$) 129.5 (5-C_6H_4), 126.4 (6-C_6H_4), 123.0 (*m*-$\mathit{C}_6H_3Me_2$), 121.6 (2-C_6H_4), 118.9 (*p*-$\mathit{C}_6H_3Me_2$), 117.3 (4-C_6H_4), 52.3 ($N\mathit{C}H_2$), 24.9 ($\mathit{C}H_2CH_3$), 18.8 (Me of $C_6H_3Me_2$), 12.3 ($CH_2\mathit{C}H_3$). Anal. Found (calcd) for $C_{28}H_{31}N_3O_2Ti$): C, 68.7 (69.1); N, 6.4 (6.5); N, 8.6 (8.4).

[Ti(NBu^t)(Bu$^t_4$salen)] (4). A cold (0 °C) solution of Na$_2$[Bu$^t_4$salen] (1.00 g, 1.86 mmol) in THF (40 mL) was added to a cold solution of [Ti(NBu^t)Cl$_2$(py)$_3$] (0.160 g, 1.86 mmol) in THF (20 mL). The mixture was warmed to room temperature and then stirred for 24 h during which the solution changed from a light to dark orange color, and a fine white precipitate formed. The volatiles were removed under reduced pressure to yield an orange oil which was extracted into pentane (30 mL), filtered, and concentrated. After 48 h at −25 °C, **4** formed an orange solid, which was washed with a minimum amount of cold pentane and dried *in vacuo*. Yield: 0.750 g (66%).

The following NMR assignments have the O- and C(H)═N-substituents of the Bu$^t_4$salen ligand in the ring 1- and 6-positions, respectively. ^{1}H NMR (C_6D_6, 300.1 MHz): 7.83 (d, $J = 2.5$ Hz, 2 H, 3-$C_6\mathit{H}_2Bu^t_2$), 7.75 (s, 2 H, N═CH), 7.14 (d, $J = 2.5$ Hz, 2 H, 5-$C_6\mathit{H}_2$-Bu^t_2), 3.91 and 3.87 (2 × apparent q, app $J = 6.6$ Hz, 2 × 2 H, NCH_2), 1.93 (s, 18 H, 2-$C_6H_2\mathit{Bu}^t_2$), 1.39 (s, 18 H, 4-$C_6H_2\mathit{Bu}^t_2$), 1.00 (s, 9 H, $NC\mathit{Me}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz): 166.6 (C═N), 165.0 (1-$\mathit{C}_6H_2Bu^t_2$) 139.7, 137.8 (2 × 2- or 4-$\mathit{C}_6H_2Bu^t_2$), 129.7 (3-$\mathit{C}_6H_2Bu^t_2$), 127.8 (5-$\mathit{C}_6H_2Bu^t_2$), 122.2 (6-$\mathit{C}_6H_2Bu^t_2$), 69.1 ($N\mathit{C}Me_3$), 58.9 (NCH_2), 35.9, 34.1 (2 × $C_6H_2(\mathit{C}Me_3)_2$), 32.3 ($NC\mathit{Me}_3$), 31.6, 29.7 (2 × C_6H_2-$(C\mathit{Me}_3)_2$); Anal. Found (calcd) for $C_{36}H_{55}O_2N_3Ti$): C, 70.3 (70.9); H, 9.1 (9.1); N, 6.4 (6.9).

[Ti(NBu^t){μ-(MeO)$_2$salen}]$_2$ (5). To a cold (0 °C) solution of Na$_2$[(MeO)$_2$salen] (0.522 g, 1.40 mmol) in THF (30 mL) was added [Ti(NBu^t)Cl$_2$(py)$_3$] (0.63 g, 1.48 mmol) in THF (30 mL). After a short period the solution turned yellow and a white precipitate formed. The mixture was allowed to warm to room temperature and was stirred for 4 h. The volatiles were removed under reduced pressure, and the product extracted into CH_2Cl_2 (30 mL) and filtered through a pad of Celite to remove NaCl. The volatiles were removed under reduced pressure and the resulting orange/yellow powder was recrystallized at −25 °C overnight from a CH_2Cl_2 solution layered with hexane to afford **5** as an orange solid which was washed with hexane (2 × 10 mL) and dried in vacuo. Yield: 0.46 g (75%). Diffraction-quality crystals of **5·CH$_2$Cl$_2$** were grown by layering a dichloromethane solution with hexane at room temperature.

The following NMR assignments have the O-, MeO-, and C(H)═N-substituents of the (MeO)$_2$salen ligand in the ring 1-, 2-, and 6-positions, respectively. ^{1}H NMR (CD_2Cl_2, 300.1 MHz): 8.51 (s, 2H, C(*H*)═N), 7.01 (d, $J = 7.7$ Hz, 4H, 3-C_6H_3(OMe) and 5-C_6H_3(OMe)), 6.71 (t, $J = 7.7$ Hz, 2H, 4-C_6H_3(OMe)), 4.62 and 4.00 (2 × m, 2 × 2H, $N\mathit{C}H_2$), 3.99 (s, 6H, OMe), 0.66 (s, 9H, $NC\mathit{Me}_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): 165.7 (C(H)═N), 157.0 and 150.7 (1-C_6H_3(OMe)) and 2-C_6H_3(OMe)), 125.0 and 115.1 (CH, 3-C_6H_3(OMe) and 5-C_6H_3-(OMe), 122.4 (6-C_6H_3(OMe)), 115.7 (CH, 4-C_6H_3(OMe)), 69.3 ($N\mathit{C}$-Me_3), 59.5 ($N\mathit{C}H_2$), 56.0 (OMe), 31.1 ($NC\mathit{Me}_3$). Anal. Found (calcd) for $C_{22}H_{27}N_3O_4Ti$: C, 59.3 (59.1); H, 6.1 (6.0); N, 9.4 (9.1).

Table 1. X-ray Data Collection and Processing Parameters for [Ti(N-2,6-$C_6H_3Me_2$)(Et$_2$Salen)] (**3**), [Ti(NBu^t){μ-(MeO)$_2$Salen}]$_2$·CH_2Cl_2 (**5·CH$_2$Cl$_2$**) and [Ti(N-2,6-$C_6H_3Me_2$){μ-(MeO)$_2$Salen}]$_2$ (**6**)

	3	**5·CH$_2$Cl$_2$**	**6**
empirical formula	$C_{28}H_{31}N_3O_2Ti$	$C_{44}H_{54}N_6O_8Ti_2\cdot CH_2Cl_2$	$C_{52}H_{54}N_6O_8Ti_2$
fw	489.46	975.68	986.86
temp/°C	−123(2)	−53(2)	−123(2)
space group	$P\bar{1}$	*Pbca*	*C*2/*c*
a/Å	12.216(4)	14.747(4)	17.902(5)
b/Å	12.312(11)	17.042(4)	12.411(4)
c/Å	17.246(2)	20.545(3)	21.068(5)
α/deg	90.352(12)		
β/deg	102.59(2)		90.27(2)
γ/deg	104.96(2)		
V/Å^3	2440.3(8)	5163.5(13)	4681(2)
Z	4	4	4
d(calcd)/Mg m^{-3}	1.33	1.26	1.40
abs coeff/mm^{-1}	0.381	0.460	0.400
R indices [$I > 2\sigma(I)$]$^{a-c}$	$R = 0.051$, $R_w = 0.066$	$R_1 = 0.096$, $wR_2 = 0.086$	$R = 0.034$, $R_w = 0.039$
R indices (all data)	−	$R_1 = 0.103$, $wR_2 = 0.092$	−

^{a} $R = R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2 = \sqrt{\{\Sigma w(F_o^2 - F_c^2)^2/\Sigma(w(F_o^2)^2\}}$. ^{c} $R_w = \sqrt{\{\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2\}}$.

[Ti(N-2,6-$C_6H_3Me_2$){μ-(MeO)$_2$salen}]$_2$ (6). To a stirred solution of [Ti(NBu^t){μ-(MeO)$_2$salen}]$_2$ (0.20 g, 0.22 mmol) in CH_2Cl_2 (20 mL) was added 2,6-dimethylaniline (160 μL, 0.71 mmol = 3.2 equiv). The solution was stirred in a sealed ampule at 45 °C for 5 days, after which the volatiles were removed under reduced pressure. After the residue was dissolved in CH_2Cl_2 and filtered, the volume was reduced to ca. 7 mL and pentane added at room temperature to give **6** as a red-orange microcrystalline powder which was washed with hexane and dried in vacuo. Yield: 0.15 g (68%). Diffraction-quality crystals of **6** were grown by layering a dichloromethane solution with hexane at room temperature.

The following NMR assignments have the O-, MeO-, and C(H)═N-substituents of the (MeO)$_2$salen ligand in the ring 1-, 2-, and 6-positions, respectively. ^{1}H NMR (CD_2Cl_2, 300.1 MHz): 8.56 (s, 2H, C(*H*)═N), 7.20 (dq, $J = 7.8$, $J = 1.6$, 4H, 3-$C_6\mathit{H}_3$(OMe) and 5-$C_6\mathit{H}_3$-(OMe)), 6.86 (t, $J = 7.8$, 2H, 4-$C_6\mathit{H}_3$(OMe)), 6.60 (d, $J = 7.4$, 2H, m−$C_6\mathit{H}_3Me_2$), 6.38 (t, $J = 7.4$, 1H, p−$C_6\mathit{H}_3Me_2$), 4.64 (m, 2H, $N\mathit{CH}_2$), 4.05 and 4.02 (m, 8H, $N\mathit{CH}_2$ and O*Me*), 1.94 (s, 6H, $C_6H_3\mathit{Me}_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): 166.6 (C(H)═N), 156.9 and 150.5 (1-C_6H_3(OMe)) and 2-C_6H_3(OMe)), 144.8 (i-$\mathit{C}_6H_3Me_2$), 129.6 (*o*-C_6H_3-Me_2), 126.5 (CH, *m*-$\mathit{C}_6H_3Me_2$), 125.1 and 115.6 (CH, 3-C_6H_3(OMe) and 5-C_6H_3(OMe)), 122.4 (6-C_6H_3(OMe)), 119.7 (CH, p-$\mathit{C}_6H_3Me_2$), 116.9 (CH, 4-C_6H_3(OMe)), 59.6 ($N\mathit{C}H_2$), 58.6 (O*Me*), 18.4 ($C_6H_3\mathit{Me}_2$). Anal. Found (calcd) for $C_{26}H_{27}N_3O_4Ti$: C, 63.3 (63.3); H, 5.9 (5.5); N, 8.6 (8.5).

Crystal Structure Determination of [Ti(N-2,6-$C_6H_3Me_2$)(Et$_2$salen)] (3), [Ti(NBu^t){μ-(MeO)$_2$salen}]$_2$·CH_2Cl_2 (5·CH$_2$Cl$_2$), and [Ti(N-2,6-$C_6H_3Me_2$){μ-(MeO)$_2$salen}]$_2$ (6). Crystal data collection and processing parameters are given in Table 1. Crystals were mounted in a film of RS3000 perfluoropolyether oil (Hoechst) on a glass fiber and transferred to a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device.[41] Data were collected using $\omega-\theta$ scans with Mo Kα radiation ($\lambda = 0.710\,73$ Å), and absorption corrections were applied to the data. Equivalent reflections were merged and the structures were solved by direct methods (SIR92[42]). Subsequent difference Fourier syntheses revealed the

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positions of all other non-hydrogen atoms. There are two crystallographically independent molecules of **3** in the asymmetric unit, and molecules of **5** and **6** lie across crystallographic inverson centers. Residual electron density for **5·CH$_2$Cl$_2$** was modeled as a dichloromethane molecule solvent (in a general position) with an estimated chemical site occupancy factor of 0.5 based on satisfactory resultant values for the carbon and chlorine atom displacement parameters. All non-H atoms were refined anisotropically. For **3** and **6**, all the hydrogen atoms were located from Fourier difference syntheses. For **5** the methyl group and CH$_2$Cl$_2$ hydrogen atoms were placed geometrically and the others could be located from difference maps. For **3** and **5** the hydrogen atoms were refined in a riding model with fixed isotropic displacement parameters; attempted refinement of the CH$_2$CH$_2$ linkage hydrogen atoms of **5** was unsuccessful. For **6** free isotropic refinement of the (MeO)$_2$salen CH$_2$CH$_2$ hydrogen atoms was possible and all others were refined in a riding model; common isotropic displacement parameters for groups of similar H atoms were refined. A Chebychev weighting scheme[43] was applied toward the end of the refinements. Examination of the refined secondary extinction parameter[44] and an agreement analysis suggested that no extinction correction was required for any of the structures. For **3** and **6**, F-refinement on $I > 2\sigma(I)$ data gave the most satisfactory refinement; for **5**, F^2-refinement on all but the weakest data gave the better results (as judged by esds of derived parameters, goodness of fit and conventional $I > 2\sigma(I)$ R values). The largest residual electron density peak for **5·CH$_2$Cl$_2$** lies 0.43 Å from Cl(1) in the fractional occupancy dichloromethane molecule.

All crystallographic calculations were performed using SIR92[42] and CRYSTALS-PC.[45] A full listing of atomic coordinates, bond lengths and angles, and displacement parameters for **3**, **5·CH$_2$Cl$_2$**, and **6** have been deposited with the Cambridge Crystallographic Data Centre; see Notice to Authors in Issue No. 1 (*Inorg. Chem.* **1998**, *37*(1)).

Results and Discussion

The neutral forms of the ligands used in this study, and the abbreviations used herein, are illustrated in Figure 1. They are all readily converted to the corresponding disodium salts by reaction with sodium hydride in THF. Filtration and evaporation of volatiles gave products suitable for use without the need for additional purification. We have previously shown that the readily prepared complexes [Ti(NR)Cl$_2$(py)$_3$] (R = Bu^t (**1a**) or 2,6-C$_6$H$_3$Me$_2$ (**1b**))[37] are excellent starting materials in titanium imido chemistry since the pyridine and chloride ligands are usually easily substituted.[5] The compounds **1** were therefore used as the source of titanium imide fragment.

Initial attempts to prepare Schiff base titanium imido complexes starting from Na$_2$[salen] or Na$_2$[salphen] and **1a** gave poorly soluble, apparent mixtures of products. However, use of the substituted salen ligands, Et$_2$salen, Bu$^t_4$salen, and (MeO)$_2$salen (Figure 1), gave access to soluble, well-defined products. The new chemistry is summarized in Scheme 1, and full spectroscopic and analytical data are listed in the Experimental Section.

Reaction of [Ti(NBu^t)Cl$_2$(py)$_3$] (**1a**) with Na$_2$[Et$_2$salen] in THF at 0 °C gave an orange solution. Standard workup and crystallization from dichloromethane/hexane at −25 °C afforded [Ti(NBu^t)(Et$_2$salen)] (**2**) in 89% yield. The NMR spectra for **2** in CDCl$_3$ are consistent with the C_s symmetric structure shown in Scheme 1 and remain unchanged at −60 °C. For example, the hydrogen atoms of the Et$_2$salen ethylene linkage appear as a pair of mutually coupled multiplets, whereas the carbon atoms give rise to only one signal as expected for the proposed structure.

In a similar fashion, reaction of [Ti(N-2,6-C$_6$H$_3$Me$_2$)Cl$_2$(py)$_3$] (**1b**) with Na$_2$[Et$_2$salen] in THF gave the arylimido analogue, namely [Ti(N-2,6-C$_6$H$_3$Me$_2$)(Et$_2$salen)] (**3**) in 55% recrystallized yield. The NMR data for Et$_2$salen in **3** are very similar to those for this ligand in **2**, suggesting that they have analogous structures. Diffraction-quality crystals of **3** were grown at room temperature from a saturated CH$_2$Cl$_2$ solution carefully layered with hexane. These crystals contain two crystallographically independent molecules of **3** in the asymmetric unit; there are no significant differences between their metrical parameters. A displacement ellipsoid plot of one of them is shown in Figure 2, and selected bond distances and angles are presented in Table 2.

[Ti(N-2,6-C$_6$H$_3$Me$_2$)(Et$_2$salen)] (**3**) has the metal in a square base pyramidal geometry with the near-linear arylimido ligand occupying the axial coordination site. Such a coordination geometry is well-established in titanium imido chemistry.[1,5] The Ti=N$_{\text{imide}}$ bond lengths [1.725(2) and 1.729(2) Å] are at the longer end of the range for this linkage (range ca. 1.66−1.74 Å)[1,5] but still imply a formal Ti=N$_{\text{imide}}$ triple bond. The Ti atoms lie 0.57 Å out of the Et$_2$salen N$_2$O$_2$ donor atom plane, and the maximum deviation of these donor atoms from the least-squares plane is 0.03 Å. The least-squares planes of the aryl rings of the Et$_2$salen ligand are inclined “up” and “down” (with respect to the arylimide) by ca. 9 and 24°, respectively, from the N$_2$O$_2$ plane; this is a typical feature of coordinated salen ligands.[15,16]

The compound **3** is the first structurally characterized salen group 4 imido complex and its geometry may be contrasted with those of the bis(aryloxide) complexes [Ti(NR)(OAr)$_2$(L)$_2$].[46−51] These also have Ti=NR moieties supported by a dianionic “N$_2$O$_2$” donor ligand set but typically have a trigonal bipyramidal geometry for titanium, with the imido and near-linear aryloxide ligands in the equatorial coordination sites. Of the structurally characterized bis(aryloxide) compounds the 2,6-dimethylphenylimido homologue [Ti(NAr)(OAr)$_2$(py)$_2$] (Ar = 2,6-C$_6$H$_3$Me$_2$)[51] is most appropriate to compare with **3**. The Ti=N$_{\text{imide}}$ [1.734(4) Å)] and Ti−O [1.884(2) Å] bond lengths are respectively slightly longer and shorter than those in **3**. This might reflect better O−Ti p$_\pi$−d$_\pi$ bonding in the case of [Ti(NAr)(OAr)$_2$(py)$_2$], but more examples are required before firm conclusions can be drawn.

The Et$_2$salen ligand in **3** has the ethyl substituents outside the aryl rings; we were interested to probe also the effects of changing the salen aryl ring substituents on the properties of titanium imido derivatives. Thus reaction of Na$_2$[Bu$^t_4$salen] with [Ti(NBu^t)Cl$_2$(py)$_3$] (**1a**) in THF gave orange, pentane-soluble [Ti(NBu^t)(Bu$^t_4$salen)] (**4**) in 66% recrystallized yield. The compound **4** is proposed to have a monomeric structure analogous to those of the Et$_2$salen derivatives **2** and **3**. Reaction of **1a** with the methoxy-substituted Na$_2$[(MeO)$_2$salen], however, gave 75% yield of orange/yellow [Ti(NBu^t){μ-(MeO)$_2$salen}]$_2$ (**5**) which has considerably lower solubility than **2**−**4**, consistent with its binuclear solid-state structure (see below).

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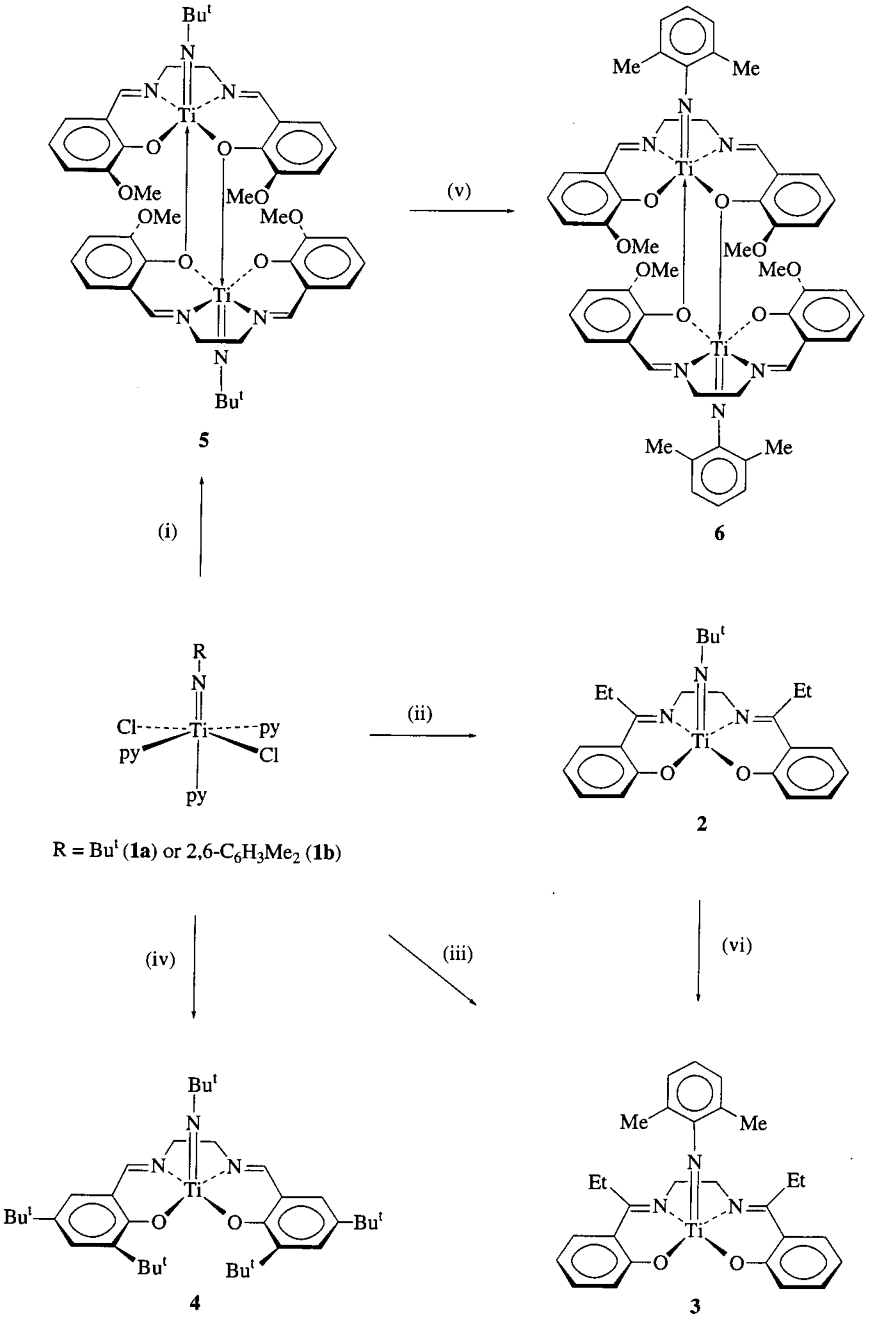
Scheme 1. Synthesis of Titanium Imido Complexes Supported by Tetradentate Schiff Base Ligands[a]



[a] Reagents and conditions: (i) $Na_2[(MeO)_2salen]$, THF, 0 °C then RT, 4 h, 75%; (ii) $Na_2[Et_2salen]$, THF, 0 °C then RT, 24 h, 89%; (iii) $Na_2[Et_2salen]$, THF, 0 °C then RT, 48 h, 55%; (iv) $Na_2[Bu^t_4salen]$, THF, 0 °C then RT, 24 h, 66%; (v) 2,6-dimethylaniline (3.2 equiv), CH_2Cl_2, 45 °C, 5 days, 68%; (vi) 2,6-dimethylaniline (1.2 equiv), CH_2Cl_2, 50 °C, 24 h, 90%.

In previous work we[37,52] and others[53−57] found that arylimido complexes $[M(NAr)L_n]$ may be obtained from the *tert*-butylimido homologues $[M(NBu^t)L_n]$ via metal imide/arylamine exchange reactions. Thus heating a dichloromethane solution of $[Ti(NBu^t)(Et_2salen)]$ (**2**) with 1.2 equiv of 2,6-dimethylaniline at 50 °C for 24 h gave $[Ti(N\text{-}2,6\text{-}C_6H_3Me_2)(Et_2salen)]$ (**3**) in 90% recrystallized yield. Similarly, addition of 2,6-dimethylaniline to dichloromethane solutions of **5** gave $[Ti(N\text{-}2,6\text{-}C_6H_4\text{-}Me_2)\{(MeO)_2salen\}]_2$ (**6**). Interestingly $[Ti(NBu^t)(Bu^t_4salen)]$ (**4**) does not undergo imide/arylamine exchange even after extended reaction times. It may be the more sterically crowded nature of the compound that inhibits reaction in this case.

Diffraction-quality crystals of $[Ti(NBu^t)\{\mu\text{-}(MeO)_2salen\}]_2\cdot CH_2Cl_2$ (**5·CH₂Cl₂**) were grown by layering a dichloromethane solution with hexane; the molecular structure is shown in Figure 3, and selected bond lengths and angles are given in Table 3.

The compound **5** exists as $(MeO)_2salen$-O-bridged dimers in the solid state with the two $Ti(NBu^t)\{(MeO)_2salen\}$ fragments

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Table 2. Selected Distances (Å) and Angles (deg) for [Ti(N-2,6-$C_6H_3Me_2$)(Et_2salen)] (**3**); Values in Brackets Are Those for the Second Molecule in the Asymmetric Unit

Bond Distances					
Ti(1)−N(1)	1.725(2)	[1.729(2)]	Ti(1)−O(1)	1.906(2)	[1.899(2)]
Ti(1)−N(2)	2.157(2)	[2.145(2)]	Ti(1)−O(2)	1.903(2)	[1.913(2)]
Ti(1)−N(3)	2.149(2)	[2.157(2)]	N(1)−C(1)	1.376(3)	[1.367(4)]
			Ti(1)···(N_2O_2 plane)	0.57	[0.57]
Bond Angles					
N(1)−Ti(1)−N(2)	98.9(1)	[100.6(1)]	N(1)−Ti(1)−O(2)	111.3(1)	[113.0(1)]
N(1)−Ti(1)−N(3)	100.7(1)	[99.5(1)]	N(2)−Ti(1)−O(2)	146.73(9)	[143.83(9)]
N(2)−Ti(1)−N(3)	77.97(9)	[78.34(9)]	N(3)−Ti(1)−O(2)	82.83(9)	[83.06(8)]
N(1)−Ti(1)−O(1)	111.9(1)	[110.3(1)]	O(1)−Ti(1)−O(2)	97.17(8)	[96.79(9)]
N(2)−Ti(1)−O(1)	83.68(8)	[83.26(9)]	Ti(1)−N(1)−C(1)	175.3(2)	[177.0(2)]
N(3)−Ti(1)−O(1)	144.62(8)	[147.33(9)]			

Angles Between Least-Squares Mean Planes	
[C(18), C(19), C(20), C(21), C(22), C(23)] to [N(2), N(3), O(1), O(2)]	9.1 [8.3]
[C(9), C(10), C(11), C(12), C(13), C(14)] to [N(2), N(3), O(1), O(2)]	26.8 [22.0]
[C(9), C(10), C(11), C(12), C(13), C(14)] to [C(18), C(19), C(20), C(21), C(22), C(23)]	21.4 [14.8]

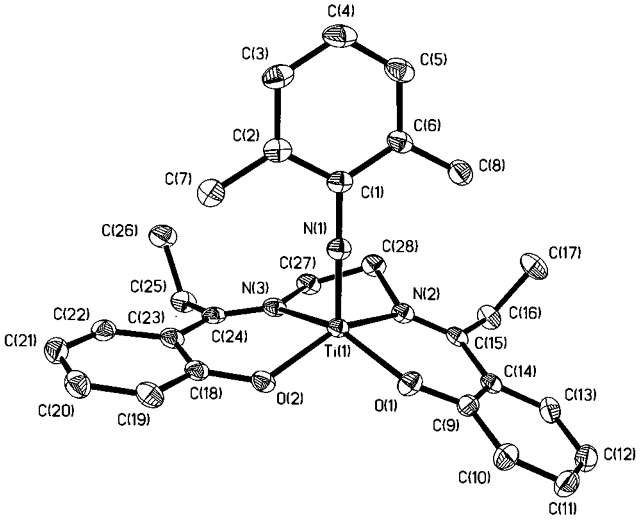

Figure 2. Displacement ellipsoid plot of one of the two crystallographically independent molecules of [Ti(N-2,6-$C_6H_3Me_2$)(Et_2salen)] (**3**) in the asymmetric unit. Hydrogen atoms are omitted and displacement ellipsoids are drawn at the 35% probability level.

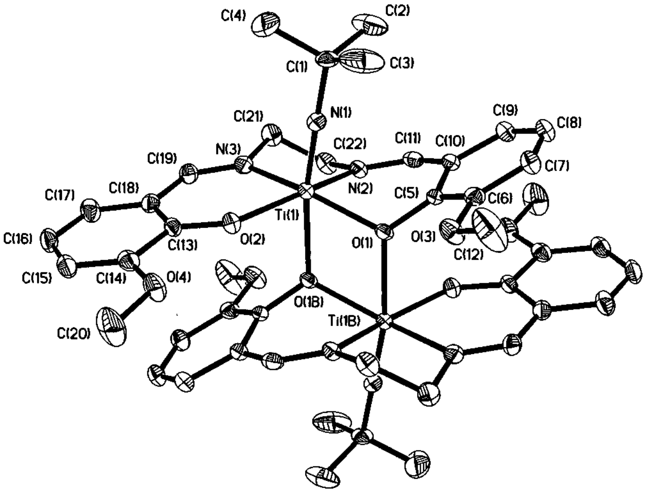

Figure 3. Displacement ellipsoid plot of [Ti(NBu^t){μ-$(MeO)_2$salen}]$_2$·CH_2Cl_2 (**5**). Atoms carrying the suffix "B" are related to their counterparts by the symmetry operator [1 − x, −y, 1 − z]. Hydrogen atoms and dichloromethane molecule of crystallization are omitted. Displacement ellipsoids are drawn at the 35% probability level.

being related by a crystallographic inversion center. The titanium atoms in **5** are six-coordinate with an approximately octahedral geometry. The N_2O_2 atoms of $(MeO)_2$salen make up the equatorial donor set and the axial positions comprise a near-linear NBu^t ligand and a bridging oxygen atom. The methoxy substituent oxygen atoms are not involved in the primary coordination sphere of titanium (but see below).

The $Ti{=}N_{imide}$ bond length [1.705(3) Å] in **5** is identical to that of **1a** and implies a formal $Ti{=}N_{imide}$ triple bond. The equatorial $Ti{-}N_{imine}$ distances (av 2.175 Å) are slightly longer than those in Ti(N-2,6-$C_6H_3Me_2$)(Et_2salen)] (**3**, av 2.152 Å) consistent with both the greater labilizing effect of NBu^t compared with that of NAr,[37] and also the higher coordination number of Ti in **5**. The $Ti{-}O_{cis}$ distances [2.015(2) and 1.978(2) Å] are also longer than those for **3** (av 1.905 Å), with the longer bond length being to the bridging oxygen O(1B), as expected. The trans Ti−O bond length of 2.313(2) Å is longer that those to the *cis*-oxygens. This is consistent with the well-known trans influence of the imido ligand in d^0 systems,[2,37,58−60] and implies that the Ti(1)−O(1B) interaction is effectively dative in nature. The Ti atom lies 0.33 Å out of the $(MeO)_2$salen N_2O_2 donor atom plane, and the maximum deviation of these atoms from the equatorial plane is 0.03 Å. The smaller displacement of Ti in **5** (as compared to that in **3**) is probably a consequence of the additional axial donor. The least squares planes of the aryl rings of $(MeO)_2$salen are inclined "up" and "down" (with respect to the imido ligand) by ca. 36.3 and 15.9° from the N_2O_2 plane; the larger tilting up of the C(5)−C(10) aryl ring (as compared to ca. 9° for the equivalent ring in **3**) presumably reduces steric interactions with the other $(MeO)_2$salen ligand and so facilitates the bridging of O(1) to Ti(1B).

It is interesting that **5** exists as a dimer in the solid state, whereas **3** (and also **2** and **4** by solution NMR spectroscopy) adopt mononuclear forms. In **5** there is a potential O···H−C hydrogen bonding contact with O···H = 2.42 Å (and an associated O···H−C angle of 142.3°) between the O(3) methoxy oxygen of one $(MeO)_2$salen ligand and an ethylene C−H bond of C(22) of the other. This O···H contact is 0.30 Å less than the sum of the O and H atoms' van der Waals radii (1.52 and 1.20 Å, respectively).[61] Such O···H−C (and indeed also

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Table 3. Selected Distances (Å) and Angles (deg) for $[Ti(NBu^t)\{\mu\text{-}(MeO)_2Salen\}]_2$ (**5**); Atoms Carrying the Suffix "B" are Related To Their Counterparts by the Symmetry Operator [1 − *x*, −*y*, 1 − *z*]

Distances			
Ti(1)−N(1)	1.705(3)	Ti(1)−O(2)	1.978(2)
Ti(1)−N(2)	2.172(3)	Ti(1)−O(1B)	2.313(2)
Ti(1)−N(3)	2.178(3)	N(1)−C(1)	1.442(4)
Ti(1)−O(1)	2.015(2)		
Ti(1)···(N_2O_2 plane)	0.33		

Bond Angles			
N(1)−Ti(1)−N(2)	93.9(1)	O(1)−Ti(1)−O(1B)	72.92(9)
N(1)−Ti(1)−N(3)	98.9(1)	O(2)−Ti(1)−O(1B)	84.80(9)
N(2)−Ti(1)−N(3)	75.4(1)	N(1)−Ti(1)−O(2)	102.6(1)
N(1)−Ti(1)−O(1)	99.2(1)	N(2)−Ti(1)−O(2)	155.1(1)
N(2)−Ti(1)−O(1)	81.3(1)	N(3)−Ti(1)−O(2)	83.7(1)
N(3)−Ti(1)−O(1)	151.3(1)	O(1)−Ti(1)−O(2)	113.70(9)
N(1)−Ti(1)−O(1B)	171.0(1)	Ti(1)−N(1)−C(1)	176.7(3)
N(2)−Ti(1)−O(1B)	80.83(9)	Ti(1)−O(1)−Ti(1B)	107.08(9)
N(3)−Ti(1)−O(1B)	86.93(9)		

Angles between Least-Squares Mean Planes	
[C(5), C(6), C(7), C(8), C(9), C(10)] to [N(2), N(3), O(1), O(2)]	36.3
[C(13), C(14), C(15), C(16), C(17), C(18)] to [N(2), N(3), O(1), O(2)]	15.9
[C(5), C(6), C(7), C(8), C(9), C(10)] to [C(13), C(14), C(15), C(16), C(17), C(18)]	20.7

N···H−C[62]) hydrogen bonds are well-established in the literature.[63,64] The O···H−C interaction in **5** results in reasonable Me−O···H and C_{aryl}−O···H angles of 111.0 and 130.4°, respectively, with the sum of the angles at oxygen O(3) being 358.3°. Because hydrogen atoms positions are poorly defined by X-ray diffraction techniques the associated O···C distances are also usually reported: in **5** this distance [O(3)···C(22B)] is 3.38 Å, well within the accepted range.[63]

Since the imido ligand substituents in **3** (Bu^t) and **5** (2,6-$C_6H_3Me_2$) are different we also determined the solid-state structure of $[Ti(N\text{-}2,6\text{-}C_6H_3Me_2)\{\mu\text{-}(MeO)_2salen\}]_2$ (**6**) to probe further the two different types of structure. Selected bond lengths and angles for **6** are given in Table 4, and a view of the molecular structure is shown in Figure 4.

Like **5**, the compound **6** exists as a μ-$(MeO)_2$salen-bridged dimer in the solid state and the molecules lie across crystallographic inversion centers. The structure of **6** is broadly analogous to that of **5** although the dimers of **6** appear to possess considerably weaker bridging titanium−oxygen interactions as judged by Ti(1)−O(1B) bond distances [2.313(2) Å in **5** but 2.490(1) Å in **6**]. Almost all of the previously reported dative Ti^{IV}−O interactions lie in the range ca. 2.0−2.3 Å,[20] the longest dative Ti^{IV}−O distances [2.455(2) and 2.535(2) Å] to date were found for the bridging THF ligand in $[Ti_2(\eta^5\text{-}C_5H_4Me)_2F_4(\mu\text{-}F)_2(\mu\text{-}THF)]$.[65] The unusually long Ti(1)−O(1B) distance in **6** may be related to the reduced tilting up (29°) of the C(9)−C(14) ring (with respect to the N_2O_2 plane) compared to the equivalent ring in **5** (36.3°). Consequently, steric limitations to forming stronger Ti−μ-O linkages may be more severe in **6** than in **5**. A possible cause of the reduced tiliting of the C(9)−C(14) ring may be the different imido N-substituent, the 2,6-dimethylphenylimido ligand presumably being more sterically demanding than *tert*-butylimide.[1]

Because of the better quality of the crystals of **6**, it was possible to locate from Fourier difference maps and freely refine the H atoms of the $(MeO)_2$salen CH_2CH_2 linkage. As for **5**, a less than van der Waals O···H−C contact exists [O···H = 2.51(2) Å with associated angle subtended at H of 142.3(14)°] between the salen methoxy substituent oxygen atom O(3) and a hydrogen atom of the CH_2CH_2 linkage of the neighboring $(MeO)_2$salen ligand. The O···H distance in **6** is somewhat longer than that in **5** (2.42 Å), although for the latter the data quality did not permit refinement of the hydrogen coordinates. Once again the usual caveats concerning the accuracy of hydrogen atom location with X-ray data must be held in mind. However, the O···C distance associated with the proposed

Table 4. Selected Distances (Å) and Angles (deg) for $[Ti(N\text{-}2,6\text{-}C_6H_3Me_2)\{\mu\text{-}(MeO)_2Salen\}]_2$ (**6**); Atoms Carrying the Suffix "B" Are Related to Their Counterparts by the Symmetry Operator [1 − *x*, −*y*, −*z*]

Bond Distances			
Ti(1)−N(1)	1.737(1)	Ti(1)−O(2)	1.927(1)
Ti(1)−N(2)	2.155(1)	Ti(1)−O(1B)	2.490(1)
Ti(1)−N(3)	2.168(1)	N(1)−C(1)	1.374(2)
Ti(1)−O(1)	1.978(1)	O(3)...H(262B)	2.51(2)
Ti(1)···(N_2O_2 plane)	0.39		

Bond Angles			
N(1)−Ti(1)−N(2)	96.76(6)	O(1)−Ti(1)−O(1B)	74.50(5)
N(1)−Ti(1)−N(3)	98.91(6)	O(2)−Ti(1)−O(1B)	83.16(5)
N(2)−Ti(1)−N(3)	76.17(6)	N(1)−Ti(1)−O(2)	102.89(6)
N(1)−Ti(1)−O(1)	103.45(6)	N(2)−Ti(1)−O(2)	154.25(5)
N(2)−Ti(1)−O(1)	82.56(5)	N(3)−Ti(1)−O(2)	84.42(6)
N(3)−Ti(1)−O(1)	150.70(5)	O(1)−Ti(1)−O(2)	108.40(5)
N(1)−Ti(1)−O(1B)	173.94(5)	Ti(1)−N(1)−C(1)	172.2(1)
N(2)−Ti(1)−O(1B)	77.37(5)	Ti(1)−O(1)−Ti(1B)	105.50(5)
N(3)−Ti(1)−O(1B)	81.30(5)		

Angles between Least-Squares Mean Planes	
[C(9), C(10), C(11), C(12), C(13), C(14)] to [N(2), N(3), O(1), O(2)]	29.0
[C(17), C(18), C(19), C(20), C(21), C(22)] to [N(2), N(3), O(1), O(2)]	13.7
[C(9), C(10), C(11), C(12), C(13), C(14)] to [C(17), C(18), C(19), C(20), C(21), C(22)]	16.4

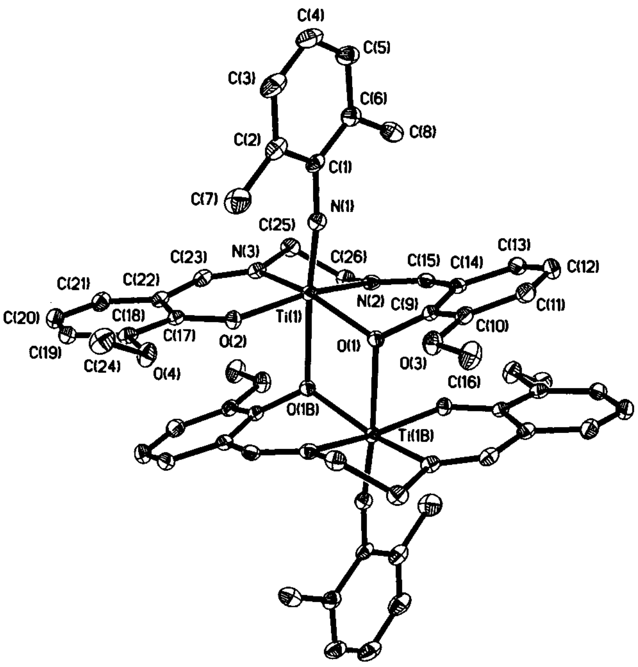

Figure 4. Displacement ellipsoid plot of $[Ti(N\text{-}2,6\text{-}C_6H_3Me_2)\{\mu\text{-}(MeO)_2salen\}]_2$ (**6**). Atoms carrying the suffix "B" are related to their counterparts by the symmetry operator [1 − *x*, −*y*, −*z*]. Hydrogen atoms are omitted and displacement ellipsoids are drawn at the 45% probability level.

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O⋯H−C contact in **6** [O(3)⋯C(26) = 3.298(2) Å] is nevertheless within the accepted range.[63] Furthermore, the Me−O⋯H and C_{aryl}−O⋯H angles of 111.2(4) and 125.1(4) are also reasonable, and the sum of the angles subtended at oxygen O(3) is 352.7(9)°.

The apparent O⋯H−C hydrogen bond interactions in **5** and **6** are not possible in **2** − **4** and may assist in the dimerization of the $(MeO)_2$salen complexes. An additional factor that might also promote the salen ligand bridging mode in **5** and **6** is the electron-withdrawing nature of the *ortho*-methoxy substituent. If the salen phenoxy oxygens were less effective donors, then this would presumably result in a greater Lewis acidity of titanium and increase its tendency to accommodate an additional (axial) donor atom. Either way, the forces holding the binuclear units of **5** and **6** together are apparently quite weak since the NMR spectra of **5** in CD_2Cl_2 show a C_s-symmetrical pattern for $(MeO)_2$salen at −90 °C. This is not consistent with the solid-state structure for which a lower symmetry NMR spectrum (e.g. two different OMe resonances) would be anticipated. Hence **5** and **6** either exist as a monomers in the solution state, or as dimers which undergoes a rapid (on the NMR time scale) dissociative equilibration process even at low temperature.

The bridging mode of $(MeO)_2$salen in **5** and **6** is the first such example for this particular salen ligand; three related examples have been reported for homologous N_2O_2-coordinating Schiff bases.[35,66,67] A complex that is closely related to **5** is $[Ti_4(salen)_2(\mu\text{-salen})_2(\mu\text{-O})_3][BPh_4]_2$. This contains salen ligands that bridge Ti centers in the same way as for **5** and **6**,[35] and comprises dimeric $[Ti(O)(\mu\text{-salen})]_2$ subunits that are then linked through $[(salen)Ti(\mu\text{-O})Ti(salen)]^{2+}$ cations coordinated to the two Ti═O oxygens of the neutral subunits, thus forming an infinite, polymeric chain. The binuclear complexes $[Ti(NR)\{\mu\text{-(MeO)}_2salen\}]_2$ (R = **5**, 2,6-$C_6H_3Me_2$ (**6**)) can thus be thought of isoelectronic "capped" analogues of the $[Ti(O)(\mu\text{-salen})]_2$ subunit, the organic N-substituents preventing further aggregation. Similarly, $[Ti(NR)(Et_2salen)]$ (R = Bu^t (**2**), 2,6-$C_6H_3Me_2$ (**3**)) and $[Ti(NBu^t)(Bu^t_4salen)]$ (**4**) are the imido analogues of the hypothetical mononuclear [Ti(O)(salen)].

Summary and Conclusions

We have described the synthesis, structures and imido exchange reactions of a number of mono- and binuclear Schiff base-supported titanium imido complexes. These are the first examples of their class for the group 4 metals. $[Ti(N\text{-}2,6\text{-}C_6H_3Me_2)(Et_2salen)]$ (**3**) and $[Ti(NR)\{(MeO)_2salen\}]_2$ (R = Bu^t (**5**), or 2,6-$C_6H_3Me_2$ (**6**)), are the first structurally characterized salen-supported terminal imido compounds for any metal. The dimeric nature of **5** and **6** in the solid state may be assisted by weak O⋯H−C hydrogen bonds, while the mononuclear compounds may be viewed as isoelectronic analogues of the as yet unknown titanyl species [Ti(O)(salen)].

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Supporting Information Available: X-ray crystallographic files, in CIF format, for **3**, **5·CH_2Cl_2**, and **6** are available on the Internet only. Ordering and access information is given on any current masthead page.

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