Reactions of Silylated Schiff Bases with Trichloro(cyclopentadienyl)titanium, Dichloro(cyclopentadienyl)methoxotitanium, and Dichlorobis(methoxo)titanium

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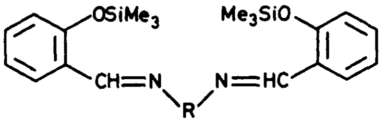
The interactions of silylated quadridentate Schiff bases *OO'*-bis(trimethylsilyl)-*NN'*-ethylenebis(salicylideneimine) and -*NN'*-*o*-phenylenebis(salicylideneimine) with [Ti(η-C_5H_5)Cl_3], [Ti(η-C_5H_5)Cl_2(OMe)], and [$TiCl_2$$(OMe)_2$] are described. Structures for the compounds are proposed on the basis of elemental analyses, i.r. and ^1H n.m.r. spectroscopic data.

ALTHOUGH Schiff-base complexes of most transition metals have been thoroughly studied,[1-10] there are few known organo- and organo-oxo-titanium(IV) Schiff-base complexes.[11,12] In fact, there are no reports of the reactions of silylated Schiff bases with organo- and organo-oxo-titanium(IV) halides, other than a recent study by us.[13] Earlier, Dilworth *et al.*[14] studied the reactions of silylated Schiff bases with [$MoCl_3O(thf)_2$] (thf = tetrahydrofuran) producing [MoCl(O)L] (H_2L = quadridentate Schiff base). In addition, Lappert and co-workers [15,16] have prepared a range of metal ketimides including the organotitanium derivatives, [Ti$(C_5H_5)_2$Cl($N{=}CR_2$)] (R = CMe_3 or Ph), chlorosilane elimination being used to prepare the products in high yield.



R = $(CH_2)_2$, btsalen
R = *o*-C_6H_4, btsalphen

This paper reports the reactions of *OO'*-bis(trimethylsilyl)-*NN'*-ethylenebis(salicylideneimine) (btsalen) and *OO'*-bis(trimethylsilyl)-*NN'*-*o*-phenylenebis(salicylideneimine) (btsalphen) with [Ti(η-C_5H_5)Cl_3], [Ti(η-C_5H_5)Cl_2(OMe)] and [$TiCl_2(OMe)_2$]. The reactivity of [Ti(η-C_5H_5)Cl(salen)] towards MeSH, $SiMe_3(NMe_2)$, Tl(acac) (acac = acetylacetonate), and $SiMe_3(N_3)$ and the reaction of [Ti(η-C_5H_5)(salen)(OMe)] with $SiMe_3(N_3)$ are also described.

EXPERIMENTAL

All solvents were purified and dried before use according to standard procedures. Manipulations were carried out under an atmosphere of nitrogen.

Titanium tetrachloride was a commercial product and used as such while [Ti(η-C_5H_5)Cl_3] (Alfa Inorganic) was recrystallized from toluene. The compounds [Ti(η-C_5H_5)Cl_3], [Ti(η-C_5H_5)Cl_2(OMe)], and [$TiCl_2(OMe)_2$] were prepared by literature methods.[17-20] Schiff bases were prepared by the usual methods and silylation was carried out according to the process described elsewhere.[13] Physical measurements were carried out as described previously.[21,22]

Preparation of Complexes.—Reactions of btsalen or btsalphen with [Ti(η-C_5H_5)Cl_3], [Ti(η-C_5H_5)Cl_2(OMe)], and [$TiCl_2(OMe)_2$] in equimolar proportions in thf–toluene (50 : 50 v/v) yielded coloured solid complexes on evaporation of the solvent under reduced pressure. In some cases hexane or pentane was added and the mixture cooled to −20 °C to produce crystals. The precipitated solids were filtered off, washed with suitable organic solvents, and dried *in vacuo* {[Ti(η-C_5H_5)Cl(salen)] (1) red-brown, yield 60%, m.p. 280—285 °C (decomp.); [Ti(η-C_5H_5)(salen)(OMe)] (2), yellow-brown, yield 55%, m.p. 210—212 °C (decomp.); [Ti(salen)$(OMe)_2$] (3), orange-red, yield 70%, m.p. 198—205 °C (decomp.); [Ti(η-C_5H_5)Cl(salphen)] (4), red-brown, yield 70%, m.p. >300 °C; [Ti(η-C_5H_5)(salphen)(OMe)] (5), brown, yield 65%, m.p. 285 °C (decomp.); [Ti(salphen)$(OMe)_2$] (6), red-orange, yield 70%, m.p. 250 °C}. Analytical data are given in Table 1.

Some Reactions of [Ti(η-C_5H_5)Cl(salen)] (1).—*With* MeSH.

TABLE 1

Analytical data for titanium(IV) complexes

		Analysis (%) [a]				
	Compound	C	H	N	Cl	Ti
(1)	[Ti(η-C_5H_5)Cl(salen)]	61.2 (60.8)	4.00 (4.60)	7.00 (6.75)	9.00 (8.55)	11.8 (11.55)
(2)	[Ti(η-C_5H_5)(salen)(OMe)]	64.8 (64.4)	5.10 (5.35)	7.20 (6.85)		11.55 (11.7)
(3)	[Ti(salen)$(OMe)_2$]	57.7 (57.45)	5.00 (5.30)	7.80 (7.45)		13.0 (12.75)
(4)	[Ti(η-C_5H_5)Cl(salphen)]	65.0 (64.9)	4.00 (4.10)	5.85 (6.05)	7.50 (7.70)	10.7 (10.35)
(5)	[Ti(η-C_5H_5)(salphen)(OMe)]	68.55 (68.1)	5.00 (4.80)	6.55 (6.10)		10.2 (10.45)
(6)	[Ti(salphen)$(OMe)_2$]	62.5 (62.25)	5.00 (4.70)	6.00 (6.60)		11.9 (11.3)
(7)	[Ti(η-C_5H_5)(salen)(SMe)]	62.2 (62.0)	5.85 (5.15)	6.00 (6.55)		11.8 (11.25)
(8)	[Ti(η-C_5H_5)(salen)(NMe_2)]	65.5 (65.25)	6.15 (5.90)	10.25 (9.95)		11.1 (11.35)
(9)	[Ti(η-C_5H_5)(salen)($SnPh_3$)]	64.3 (64.25)	4.90 (4.65)	4.00 (3.85)		11.5 (11.3)
(10)	[Ti(η-C_5H_5)(salen)(acac)] [b]	65.45 (65.3)	5.00 (5.45)	6.00 (5.85)		10.4 (10.0)

[a] Calculated values are given in parentheses. [b] The diketo-form of the acetylacetonato-ligand is co-ordinated to the titanium ion in a unidentate manner through the central (γ) carbon atom.

Complex (1) was added to MeSH (1 : 1) in thf–toluene (50 : 50 v/v) and the mixture stirred at room temperature in the presence of a stoicheiometric amount of NEt_3 for 3 d. After removal of $NEt_3{\cdot}HCl$, the volume of the solution was reduced under vacuum, to yield dark brown crystals of $[Ti(\eta\text{-}C_5H_5)(salen)(SMe)]$ (7) on cooling to −20 °C. These were filtered off, washed with hexane, and dried *in vacuo*. Yield 80%, m.p. >300 °C.

With $SiMe_3(NMe_2)$. Complex (1) was treated with an equimolar quantity of $SiMe_3(NMe_2)$ as above and $[Ti(\eta\text{-}C_5H_5)(salen)(NMe_2)]$ (8) was isolated in 50% yield, m.p. 240—245 °C (decomp.). Complex (8) was then treated with $SnPh_3H$ (1 : 1) in thf and the mixture thoroughly stirred at room temperature for 8 d to yield $[Ti(\eta\text{-}C_5H_5)(salen)(SnPh_3)]$ (9).

TABLE 2

Proton n.m.r. [a] and i.r. (cm^{-1}) [b] spectral data of $[Ti(\eta\text{-}C_5H_5)(salen)(acac)]$ (10)

		C-bonded ' acac '		Other			
		CH_3	Ti–CH	C_5H_5	C_6H_5	CH=N	CH_2N
(*a*)	^1H n.m.r.	7.92 (s)	4.72 (s)	6.58 (s)	6.60—7.70 (m)	8.30 (s)	3.85 (s)
(*b*)	I.r.	ν(C=O) in *C*-bonded ' acac ' 1 695vs, 1 650m					

[a] In $(CD_3)_2SO$ with $SiMe_4$ as internal standard, δ/p.p.m. with right integrations. [b] In Nujol mull.

With Tl(acac). Complex (1) was treated with Tl(acac) (1 : 1) in thf as above to yield (45%) a brown complex with *C*-bonded acetylacetonate, $[Ti(\eta\text{-}C_5H_5)(salen)(acac)]$ (10), m.p. 180—185 °C (decomp.).

RESULTS AND DISCUSSION

Synthesis.—Reactions of $[Ti(\eta\text{-}C_5H_5)Cl_3]$, $[Ti(\eta\text{-}C_5H_5)Cl_2(OMe)]$, and $[TiCl_2(OMe)_2]$ with the silylated quadridentate Schiff bases btsalen and btsalphen gave the coloured Schiff-base complexes (1)—(6). Complex (1) reacted smoothly with MeSH, $SiMe_3(NMe_2)$, and Tl(acac) to yield thiolato-, amido-, and carbon-bonded acetylacetonato-complexes of titanium(IV) respectively, $[Ti(\eta\text{-}C_5H_5)(salen)L]$ [where L = SMe (7), NMe_2 (8), or acac (10)]. Treatment of (8) with $SnPh_3H$ in thf gave a solution from which a brown crystalline solid, $[Ti(\eta\text{-}C_5H_5)(salen)(SnPh_3)]$ (9) [equation (1)] could be isolated. Complex (9) is unstable in air and decomposes

$$[Ti(\eta\text{-}C_5H_5)(salen)(NMe_2)] + SnPh_3H \xrightarrow{thf} [Ti(\eta\text{-}C_5H_5)(salen)(SnPh_3)] + NMe_2H \quad (1)$$

on heating at 220—225 °C.

TABLE 3

Proton n.m.r. spectral data (δ/p.p.m.) of some representative titanium compounds *

	Compound	C_6H_5	C_5H_5	CH=N	N–CH_2	CH_3S	$(CH_3)_2N$	CH_3O
(1)	$[Ti(\eta\text{-}C_5H_5)Cl(salen)]$	6.8—7.6 (m)	6.75 (s)	8.28 (s)	3.88 (s)			
(2)	$[Ti(\eta\text{-}C_5H_5)(salen)(OMe)]$	7.0—7.5 (m)	6.72 (s)	8.31 (s)	3.86 (s)			1.20 (s)
(7)	$[Ti(\eta\text{-}C_5H_5)(salen)(SMe)]$	6.5—7.3 (m)	6.52 (s)	8.15 (s)	3.85 (s)	3.38 (s)		
(8)	$[Ti(\eta\text{-}C_5H_5)(salen)(NMe_2)]$	6.9—7.5 (m)	6.68 (s)	8.30 (s)	3.80 (s)		3.47 (s)	
	H_2salen	6.75—7.60 (m)		8.62 (s)	3.95 (s)			

* Recorded in $(CD_3)_2SO$ with $SiMe_4$ as internal standard; right integrations are obtained; m = multiplet, s = singlet.

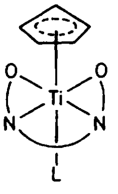
It was observed, in a preliminary reaction, that complex (1) afforded an azido-complex, $[Ti(\eta\text{-}C_5H_5)(salen)(N_3)]$ (11), when it was made to react with $SiMe_3(N_3)$ in thf [equation (2)]. A similar reaction of (2) with

$$[Ti(\eta\text{-}C_5H_5)Cl(salen)] + SiMe_3(N_3) \longrightarrow [Ti(\eta\text{-}C_5H_5)(salen)(N_3)] + SiMe_3Cl \quad (2)$$

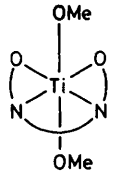
$SiMe_3(N_3)$ also gave compound (11). The azido-complex decomposed in a mild explosion at 235—240 °C. Synthesis of azido-complexes of titanium(IV) by metathetical reaction between metal–chlorine and metal–alkoxo-bonds and $SiMe_3(N_3)$ has recently been demonstrated.[23,24]

Characterization and Spectroscopic Data.—The complexes are soluble in co-ordinating solvents. In the i.r. spectra ν(C=N) appeared in the range 1 620—1 635 cm^{-1}, *ca.* 15 ± 5 cm^{-1} lower than that observed in the free Schiff-base ligands. This demonstrates the co-ordination of azomethine nitrogen. The phenolic C–O stretching vibrations are shifted to higher frequencies by about 10 ± 5 cm^{-1} in relation to the free ligands, suggesting the co-ordination of phenolic C–O to the titanium(IV) ion.[25,26] The O–H stretching frequencies characteristic of the ligands do not appear in the i.r. spectra of the complexes. However, several new bands appear in the 370—680 cm^{-1} region, typical of ν(Ti–O), ν(Ti–N), ν(Ti–S), and ν(Ti–Cl) frequencies.[27,28] In complex (11) i.r. bands were observed at 2 190 (ν_{asym}) and at 1 345 cm^{-1} (ν_{sym}). However, these data do not establish the mode of attachment (terminal or bridging) of the N_3 group, as was stressed in a recent report.[29] Furthermore, the complex $[Ti(\eta\text{-}C_5H_5)(salen)(acac)]$ (10) shows two bands (Table 2) at 1 695 and 1 650 cm^{-1} in the i.r. spectrum which may be assigned to the ν(C=O) vibrations of the carbon-bonded acetylacetonate ligand.[30]

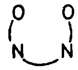
The ^1H n.m.r. spectral data together with assignments are given in Table 3. In the present titanium(IV) complexes both $salen^{2-}$ and $salphen^{2-}$ assume planar configurations as inferred from a singlet for each of the HC=N– and N–CH_2 protons.[31-33] The broad signal due to the hydrogen-bonded phenolic OH group at δ *ca.* 12.5 in the free ligand disappeared in the complex indicating the deprotonation and co-ordination of phenolic oxygen to titanium(IV). In addition, the sharp signals for C_5H_5, CH_3S, $(CH_3)_2N$, and CH_3O in the complexes suggest a *trans* arrangement of these ligands, as shown in I and II. In the ^1H n.m.r. spectrum of complex (10) (Table 2), one methyl proton signal is observed at δ 7.92, which is lower than the methyl proton resonances generally observed for chelating acetylacetonate.[30,34] This indicates that the two methyl groups of the carbon-bonded acetylacetonate ligand are equivalent due to free rotation of the ligand around the Ti–C bond.



I



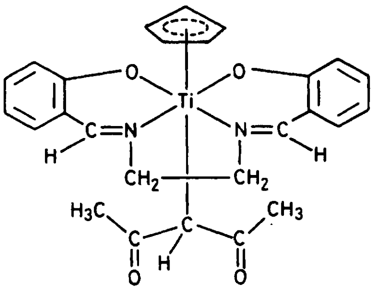
II



= salen^{2-} or salphen^{2-}

L = Cl, OMe, SMe, NMe_2, or $SnPh_3$

It is now well established that for metal–acetylacetonato-complexes,[34,35] the methine proton of carbon-bonded acac absorbs at higher field than that of chelating acac. This assignment also holds for the present complex (10), the methine proton signal appearing as a singlet at δ 4.72. The following structure (III) may therefore be tentatively proposed for the complex.



III

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