Alkylation and Arylation of Dichloro[*N*,*N*′-ethylenebis(salicylideneiminato)]titanium(IV)†

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The alkylation of $[Ti(salen)Cl_2]$ **1** [salen = *N*,*N*′-ethylenebis(salicylideneiminate)] using LiMe in toluene gave the first octahedral *trans*-dimethyltitanium(IV) derivative, $[Ti(salen)Me_2]$ **2**. Complex **2** is thermally labile and a thermally induced methyl migration to the ligand salen was observed in solution. The isolation of a compound derived from an aryl migration to the ligand was achieved in the reaction of MgBr(mes) (mes = $2,4,6-Me_3C_6H_2$) with **1** leading to [Ti(L)(mes)] **3**, containing the mesityl group bonded to the metal, and the second one attached to the carbon of the imino group of salen. The alkylation reaction is greatly affected by the solvent. When alkylation or arylation of **1** is carried out in tetrahydrofuran (thf) with MgXR (R = Ph or mes) reductive arylation of **1** occurs with the isolation of the corresponding titanium(III) derivatives [Ti(salen)R(thf)] (R = Ph **4** or mes **5**). Crystallographic details: complex **2**, orthorhombic, space group $P2_12_12_1$, a = 22.795(2), b = 14.734(1), c = 6.849(1) Å, Z = 4, and R = 0.047 for 882 independent observed reflections; **3**, monoclinic, space group $P2_1/n$, a = 12.804(1), b = 26.566(3), c = 10.014(1) Å, β = 95.27(1)°, Z = 4, and R = 0.057 for 3625 observed reflections; **4**, orthorhombic, space group $P2_12_12_1$, a = 18.455(2), b = 14.633(2), c = 13.172(2) Å, Z = 4, and R = 0.118 for 1524 observed reflections.

The chemistry of an organometallic functionality is affected by the electronic and geometrical influence of the ancillary ligands, but studies of this have been very limited for titanium[1] and, in general, early transition metals. The organometallic chemistry of titanium-(III) and -(IV) is almost exclusively limited to some conventional ancillary ligands, like cyclopentadienyls[1] and alkoxides.[2] Rarely has advantage been taken of the chemical environment provided by a multidentate or macrocyclic ligand for introducing and studying the chemistry of organic functionalities at titanium[3] or other early transition metals.[4] One of the reasons may be the fact that such an environment is not innocent and introduces reactive sites in addition to that of the metal centre. Such a chemical complexity can be, however, informative on the generation and behaviour of an organometallic functionality in the presence of relatively complex ligands having reactive organic groups. In addition, owing to their conformational rigidity, macrocyclic or polydentate ligands provide a special geometrical environment for a metal–carbon functionality.

We report here a detailed study on the alkylation reactions of $[Ti(salen)Cl_2]$,[5] salen being the well known tetradentate Schiff-base dianion *N*,*N*′-ethylenebis(salicylideneiminate), largely used in cobalt organometallic and dioxygen chemistry.[6] A short communication on the alkylation of $[Ti(salen)Cl_2]$ has been published.[7]

Experimental

All the reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. The ^1H NMR spectra were recorded with a Bruker AC200 instrument. The synthesis of $[Ti(salen)Cl_2]$ **1** was carried out as reported.[5a]

Preparations.—$[Ti(salen)Me_2]$ **2**. To a benzene (200 cm^3) suspension of $[Ti(salen)Cl_2]$ (4.35 g, 11.29 mmol) kept at 6–10 °C and with stirring was added dropwise an Et_2O solution of LiMe (21.58 mmol). The complex $[Ti(salen)Cl_2]$ dissolved giving a yellow-red solution, which was warmed to room temperature. Two hours after the addition of LiMe the suspension was filtered to remove LiCl. Then the solution, kept at 6–10 °C for 24 h, gave a brown-red crystalline solid (60%), which can be recrystallized from toluene giving crystals suitable for X-ray analysis {Found: C, 68.75; H, 6.40; N, 6.45. $[Ti(salen)Me_2]\cdot C_7H_8$, $C_{25}H_{28}N_2O_2Ti$ requires C, 68.80; H, 6.45; N, 6.40%}, ν(C=N) 1610 cm^{-1}. ^1H NMR (CD_2Cl_2): δ − 0.25 (s, 6 H, Me), 4.31 (s, 4 H, CH_2CH_2), 7.02 (m, 4 H, Ph), 7.35 (m, 4 H, Ph) and 8.37 (s, 2 H, CH).

[Ti(L)(mes)] **3** [L = *mono*(α-*mesityl*) *derivative of salen, mes = mesityl*]. *Method A*. To a toluene (200 cm^3) suspension of $[Ti(salen)Cl_2]$ (5.37 g, 13.94 mmol) kept stirring at room temperature was added dropwise a solution of MgBr(mes) (27.88 mmol). The complex dissolved giving an orange-yellow solution, to which was added 1,4-dioxane (6.0 cm^3, 70.3 mmol). The mixture was allowed to stand at room temperature for 12 h, then filtered to remove magnesium halides. After standing at −20 °C for 48 h the product was collected as an orange-yellow crystalline solid (70%). The solid is thermally stable under an inert atmosphere at room temperature {Found: C, 75.75; H, 7.10; N, 4.40. $[Ti(L)(mes)]\cdot C_7H_8$, $C_{40}H_{42}N_2O_2Ti$ requires C, 76.40; H, 6.90; N, 4.35%}, ν(C=N) 1600 cm^{-1}. ^1H NMR (C_6D_6): δ 1.60 (s, 3 H, Me), 2.03 (s, 3 H, Me), 2.12 (s, 3 H, Me), 2.43 (s, 3 H, Me), 2.49 (s, 6 H, Me), 2.70 (m, 1 H, CH_2CH_2), 3.17 (m, 1 H, CH_2CH_2), 3.39 (m, 1 H, CH_2CH_2), 4.29 (m, 1 H, CH_2CH_2), 6.30–7.25 (series of multiplets) and 7.28 (s, 1 H, CH).

Method B. To a 1,4-dioxane (200 cm^3) suspension of $[Ti(salen)Cl_2]$ (5.05 g, 13.11 mmol) stirred at room temperature was added dropwise a tetrahydrofuran (thf) solution of MgBr(mes) (26.22 mmol). The complex dissolved giving an emerald-green solution, which was allowed to stand at room temperature for 2 h, then filtered in order to remove magnesium halides. After standing at room temperature for 24 h the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Experimental data for the X-ray diffraction studies on crystalline complexes **2**,[a] **3**[b] and **4**[a]

Complex	**2**	**3**	**4**
Formula	$C_{18}H_{20}N_2O_2Ti{\cdot}C_7H_8$	$C_{34}H_{36}N_2O_2Ti{\cdot}C_4H_8O_2$	$C_{26}H_{27}N_2O_3Ti{\cdot}C_4H_8O$
M	436.4	640.7	535.5
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$	$P2_1/n$	$P2_12_12_1$
Cell parameters at 295 K[c]			
a/Å	22.795(2)	12.804(1)	18.455(2)
b/Å	14.734(1)	26.566(3)	14.633(2)
c/Å	6.849(1)	10.014(1)	13.172(2)
β/°	90	95.27(1)	90
U/Å^3	2300.3(4)	3391.9(6)	3557.1(8)
Z	4	4	4
D_c/g cm^{-3}	1.260	1.255	1.000
Crystal dimensions/mm	0.19 × 0.31 × 0.72	0.21 × 0.21 × 0.65	0.18 × 0.25 × 0.55
μ/cm^{-1}	3.88	24.56	2.64
2θ Range/°	6–46	6–130	6–46
Reflections measured	$h\ k\ l$	$\pm h\ k\ l$	$h\ k\ l$
Unique total data	3221	5755	4944
Unique observed [$I > 2\sigma(I)$] data, N_O	882	3625	1524
Parameters varied, N_V	204	406	143
N_O/N_V	4.3	8.9	10.7
Maximum shift/error on last cycle	0.4	0.5	0.1
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.047	0.057	0.118
$R' = \Sigma w^{\frac{1}{2}}\lvert\Delta F\rvert/\Sigma w^{\frac{1}{2}}\lvert F_o\rvert$	—	0.062	0.120

[a] Experimental details pertaining to complexes **2** and **4**: graphite monochromatized Mo-Kα radiation (λ = 0.7106 Å), Philips PW1100 diffractometer, equatorial diffraction geometry, ω–2θ scan type, scan width 1.20 + 0.35tanθ, scan speed 3–12° min^{-1}. [b] Nickel-filtered Cu-Kα radiation (λ = 1.541 78 Å), Siemens AED diffractometer, equatorial diffraction geometry, θ–2θ scan type, scan width 1.20 + 0.35tanθ and scan speed 3–12° min^{-1}. [c] Unit-cell parameters were obtained by least-squares analysis of the setting angles of several carefully centred reflections chosen from diverse regions of reciprocal space.

Table 2 Fractional atomic coordinates (× 10^4) for complex **2**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ti	3594(1)	2003(2)	−514(4)
O(1)	4270(5)	1598(7)	−1658(14)
O(2)	3174(5)	2746(7)	−2217(13)
N(1)	3857(8)	1245(9)	2007(19)
N(2)	2875(7)	2188(10)	1485(20)
C(1)	4661(6)	926(8)	−1303(33)
C(2)	5064(6)	696(8)	−2754(33)
C(3)	5460(6)	−11(8)	−2445(33)
C(4)	5453(6)	−488(8)	−686(33)
C(5)	5050(6)	−258(8)	764(33)
C(6)	4654(6)	449(8)	456(33)
C(7)	4266(10)	652(13)	2107(27)
C(8)	3490(11)	1430(10)	3795(19)
C(9)	2877(8)	1616(11)	3221(27)
C(10)	2449(10)	2696(13)	1209(25)
C(11)	2326(8)	3280(8)	−500(18)
C(12)	1839(8)	3854(8)	−497(18)
C(13)	1735(8)	4425(8)	−2085(18)
C(14)	2117(8)	4421(8)	−3676(18)
C(15)	2603(8)	3847(8)	−3680(18)
C(16)	2708(8)	3276(8)	−2092(18)
C(17)	3925(7)	3114(11)	1185(22)
C(18)	3148(6)	732(9)	−951(21)
C(21)	553(5)	1978(10)	178(27)
C(22)	932(5)	1369(10)	1093(27)
C(23)	1425(5)	1047(10)	104(27)
C(24)	1538(5)	1334(10)	−1800(27)
C(25)	1159(5)	1943(10)	−2715(27)
C(26)	666(5)	2265(10)	−1726(27)
C(27A)	1078(19)	2509(28)	−4408(64)
C(27B)	493(18)	2808(28)	−3623(51)

The site occupation factors for atoms C(27A) and C(27B) are 0.5.

product was collected as an orange-yellow crystalline solid (75%) {Found: C, 71.80; H, 6.85; N, 4.15. [Ti(L)(mes)]·$C_4H_8O_2$, $C_{38}H_{44}N_2O_4Ti$ requires C, 71.25; H, 6.90; N, 4.35%}, ν(C=N) 1610 cm^{-1}.

[Ti(salen)Ph(thf)]·thf **4**. To a thf (70 cm^3) suspension of [Ti(salen)Cl_2] (3.71 g, 9.63 mmol) at room temperature and with stirring was added dropwise a thf solution of MgBrPh (19.26 mmol). The complex dissolved giving a blue-green solution, to which was added 1,4-dioxane (2.5 cm^3, 30 mmol). The mixture was allowed to stand at room temperature for 5 h, then filtered in order to remove magnesium halides. After 48 h the product was collected as a blue-green crystalline solid (70%) {Found: C, 67.10; H, 5.70; N, 5.90. [Ti(salen)Ph(thf)], $C_{26}H_{27}N_2O_3Ti$ requires C, 67.40; H, 5.85; N, 6.05%} (the thf of crystallization was lost on drying the solid *in vacuo*), ν(C=N) 1610 cm^{-1}.

[Ti(salen)(mes)(thf)] **5**. To a thf (70 cm^3) suspension of [Ti(salen)Cl_2] (4.20 g, 11.0 mmol) at −10 °C and with stirring was added dropwise a thf solution of MgBr(mes) (22.0 mmol). The complex dissolved, while the colour of the solution turned from wine-red to blue-green. 1,4-Dioxane (3.0 cm^3, 35 mmol) was added, and the solution allowed to stand in a freezer for 5 h, then filtered in order to remove magnesium halides. After standing at −30 °C for 24 h the product was collected as a blue-green crystalline solid (2.28 g, 70%) {Found: C, 68.70; H, 6.60; N, 5.20. [Ti(salen)(mes)(thf)], $C_{29}H_{33}N_2O_3Ti$ requires C, 68.90; H, 6.60; N, 5.55%}, ν(C=N) 1600 cm^{-1}, μ_{eff} 1.76 at 294 K.

X-Ray Crystallography.—The crystals selected for study were mounted in glass capillaries and sealed under nitrogen. The reduced cells were obtained with use of TRACER.[8] Crystal data and details associated with data collection are given in Table 1. The structure amplitudes were obtained after the usual Lorentz and polarization corrections[9] and the absolute scale was established by the Wilson method.[10] The crystal quality for complexes **2** and **4** was tested by ψ scans showing that crystal absorption effects could be neglected. The intensity data for complex **3** were corrected for absorption using the program ABSORB.[11] The function minimized during the least-squares refinement was $\Sigma w\lvert\Delta F_o\rvert^2$. A weighting scheme based on counting statistics was applied for **3** and **4**. Unit weights were used for **2**. Scattering factors for neutral atoms were taken from ref. 12 for non-hydrogen atoms and from ref. 13 for H. Among

Table 3 Fractional atomic coordinates (× 10^4) for complex **3**

Atom	*X/a*	*Y/b*	*Z/c*
Ti	62.73(5)	1956.9(3)	2143.3(7)
O(1)	1035(2)	1664(1)	1088(3)
O(2)	−1078(2)	1561(1)	1700(3)
N(1)	1471(2)	2262(1)	3172(3)
N(2)	−167(2)	1892(1)	4010(3)
C(1)	2068(4)	1625(2)	1014(4)
C(2)	2458(4)	1349(2)	−23(5)
C(3)	3514(5)	1300(2)	−114(6)
C(4)	4221(4)	1525(2)	808(6)
C(5)	3872(4)	1811(2)	1840(5)
C(6)	2781(3)	1861(2)	1959(4)
C(7)	2443(3)	2160(2)	3032(4)
C(8)	1189(3)	2529(2)	4378(4)
C(9)	518(4)	2150(2)	5054(4)
C(10)	−926(3)	1567(1)	4668(4)
C(11)	−1719(3)	1283(1)	3731(4)
C(12)	−2458(3)	993(2)	4333(5)
C(13)	−3247(4)	730(2)	3556(6)
C(14)	−3307(3)	765(2)	2196(6)
C(15)	−2590(3)	1047(2)	1564(5)
C(16)	−1800(3)	1302(2)	2337(4)
C(17)	−479(3)	2682(1)	1446(4)
C(18)	−1412(3)	2897(2)	1843(4)
C(19)	−1748(3)	3371(2)	1384(4)
C(20)	−1181(3)	3650(2)	526(4)
C(21)	−280(3)	3444(2)	112(4)
C(22)	79(3)	2972(2)	550(4)
C(23)	−2090(3)	2627(2)	2773(4)
C(24)	−1559(4)	4163(2)	25(6)
C(25)	1071(3)	2784(2)	−2(5)
C(26)	−379(3)	1209(1)	5702(4)
C(27)	278(3)	824(2)	5310(4)
C(28)	729(3)	489(2)	6270(5)
C(29)	562(4)	532(2)	7621(5)
C(30)	−62(4)	912(2)	8009(5)
C(31)	−537(3)	1254(2)	7085(4)
C(32)	525(3)	751(2)	3889(5)
C(33)	1067(5)	158(2)	8632(6)
C(34)	−1208(4)	1666(2)	7615(5)
O(1S)	1945(6)	4261(2)	3029(6)
C(2S)	2275(6)	4769(4)	2809(9)
C(3S)	1699(8)	5120(3)	3367(9)
O(4S)	679(6)	5079(3)	2923(7)
C(5S)	315(7)	4596(4)	3187(11)
C(6S)	897(8)	4230(3)	2699(11)

Table 4 Fractional atomic coordinates (× 10^4) for complex **4**

Atom	*X/a*	*Y/b*	*Z/c*
Ti	2606(2)	1156(3)	−156(2)
O(1)	2835(7)	2059(10)	773(11)
O(2)	1773(7)	467(10)	185(11)
N(1)	3363(10)	1831(12)	−1038(14)
N(2)	2478(13)	425(15)	−1589(12)
O(3)	1761(9)	2239(11)	−792(13)
C(1)	3340(7)	2728(10)	875(14)
C(2)	3362(7)	3214(10)	1785(14)
C(3)	3852(7)	3932(10)	1905(14)
C(4)	4320(7)	4163(10)	1114(14)
C(5)	4299(7)	3676(10)	204(14)
C(6)	3808(7)	2959(10)	85(14)
C(7)	3819(14)	2513(20)	−858(20)
C(8)	3540(20)	1391(28)	−2184(28)
C(9)	3047(21)	706(26)	−2350(30)
C(10)	2066(17)	−190(21)	−1823(22)
C(11)	1470(8)	−517(12)	−1173(13)
C(12)	1027(8)	−1203(12)	−1568(13)
C(13)	467(8)	−1565(12)	−980(13)
C(14)	350(8)	−1240(12)	2(13)
C(15)	793(8)	−554(12)	397(13)
C(16)	1353(8)	−193(12)	−191(13)
C(17)	3410(8)	172(11)	359(12)
C(18)	4068(8)	497(11)	736(12)
C(19)	4571(8)	−111(11)	1147(12)
C(20)	4416(8)	−1043(11)	1180(12)
C(21)	3759(8)	−1368(11)	803(12)
C(22)	3256(8)	−760(11)	392(12)
C(23)	1039(19)	1973(22)	−1052(24)
C(24)	668(22)	2906(32)	−1566(34)
C(25)	1250(24)	3596(32)	−1480(33)
C(26)	1930(20)	3234(29)	−820(31)
C(1S)	7768(25)	539(31)	5440(36)
C(2S)	7278(37)	631(45)	4557(49)
C(3S)	7339(27)	1511(37)	4007(38)
C(4S)	7921(24)	1974(29)	4583(35)
C(5S)	8276(26)	1302(33)	5261(43)

Table 5 Selected bond distances (Å) and angles (°) for complexes **2**–**4** [X = C(18) and O(3) for **2** and **4**, respectively]

	2	**3**	**4**
Ti–C(17)	2.145(16)	2.142(3)	2.176(16)
Ti–X	2.152(14)		2.376(17)
Ti–O(1)	1.829(11)	1.874(3)	1.850(15)
Ti–O(2)	1.864(10)	1.822(3)	1.892(14)
Ti–N(1)	2.142(14)	2.151(3)	2.068(19)
Ti–N(2)	2.153(15)	1.927(3)	2.182(18)
O(1)–C(1)	1.354(17)	1.335(6)	1.358(20)
C(1)–C(6)	1.395(29)	1.401(6)	1.394(23)
C(6)–C(7)	1.466(28)	1.435(6)	1.403(32)
C(7)–N(1)	1.280(27)	1.294(5)	1.327(33)
N(1)–C(8)	1.508(23)	1.474(5)	1.673(42)
C(8)–C(9)	1.477(30)	1.522(7)	1.371(55)
C(9)–N(2)	1.457(23)	1.471(5)	1.509(44)
N(2)–C(10)	1.240(26)	1.497(5)	1.218(38)
C(10)–C(11)	1.480(22)	1.518(5)	1.474(34)
C(11)–C(16)	1.395(21)	1.391(6)	1.395(24)
C(16)–O(2)	1.321(20)	1.358(5)	1.334(22)
O(1)–Ti–O(2)	110.9(4)	100.5(1)	114.2(6)
O(1)–Ti–N(1)	86.5(5)	81.7(1)	82.9(7)
O(1)–Ti–N(2)	162.8(5)	132.7(1)	161.3(7)
O(2)–Ti–N(2)	86.1(5)	89.7(1)	81.7(7)
N(1)–Ti–N(2)	76.5(6)	76.4(1)	79.7(7)
O(2)–Ti–N(1)	162.6(5)	162.2(1)	159.5(7)
C(17)–Ti–X	154.9(6)		177.2(6)

the low-angle reflections no corrections for secondary extinction were deemed necessary. Solution and refinement were based on the observed reflections. The structures were solved by the heavy-atom method starting from a three-dimensional Patterson map.

Complex **2**. Refinement was first isotropic, then anisotropic for all the non-hydrogen atoms, except for the carbon atoms of the toluene of crystallization down to $R = 0.047$ ($R_G = 0.050$). The toluene methyl carbon was found to be statistically distributed over two positions (site occupation factors 0.5). Since the space group is polar, all the coordinates were inverted and refined to convergence once again. The result ($R = 0.050$, $R_G = 0.053$) indicated the original choice should be considered the correct one. During the refinement all the aromatic rings were constrained to be regular hexagons (C–C 1.395 Å). All the H atoms except those of toluene were placed in geometrically calculated positions and introduced in calculations prior to the last stage of refinement as fixed contributors (isotropic $U = 0.08$ Å^2). The final difference maps showed no unusual feature, the maximum residual peak being 0.3 e Å^{-3}.

Complex **3**. Refinement was first isotropic, then anisotropic for all the non-hydrogen atoms. All the H atoms except those of dioxane of crystallization were located from difference maps and introduced in calculations prior to the last stage of refinement as fixed contributors (isotropic $U = 0.12$ Å ^{2}). The final difference maps showed no unusual feature, the maximum residual peak being 0.4 e Å^{-3}.

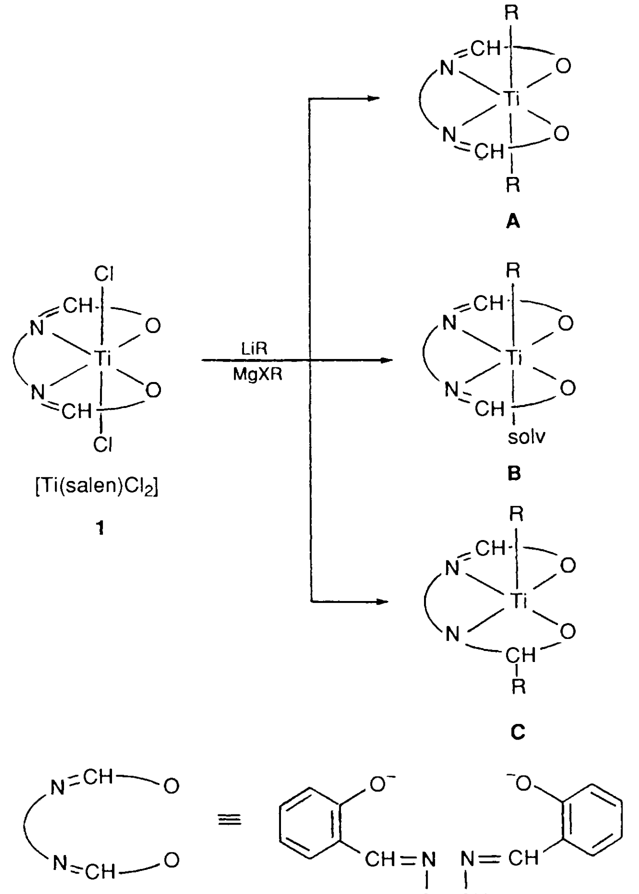
Complex **4**. Refinement was first isotropic, then anisotropic only for titanium and co-ordinated atoms. During the refinement the aromatic rings were constrained to be regular hexagons (C–C 1.395 Å). Only H atoms of salen and phenyl were placed in geometrically calculated positions and introduced in calculations prior to the last stage of refinement as fixed contributors (isotropic $U = 0.08$ Å^2). Owing to the high thermal motion it was not possible to distinguish between oxygen and carbon for the thf of crystallization. The final difference maps showed no unusual feature, with no significant peak above the general background (maximum residual peak 0.6 e Å^{-3}).

Final atomic coordinates are given in Tables 2–4, selected bond distances and angles in Table 5.

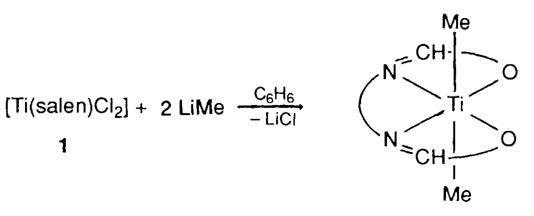
Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The alkylation of [Ti(salen)Cl$_2$] **1** is highly affected by the reaction conditions, namely the solvent and the temperature. Under the conditions specified in the Experimental section we identified three different alkylation pathways leading to complexes **A**–**C** (Scheme 1).



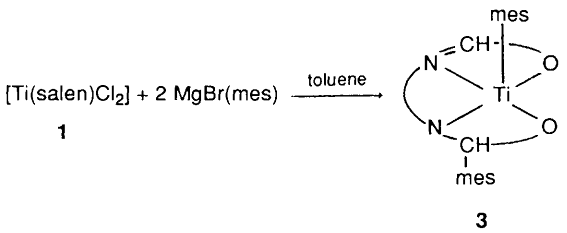
Scheme 1 solv = solvent



(1)

Methyllithium in benzene gave the *trans*-dimethyl derivative **2** under the conditions specified in the Experimental section [equation (1)]. Although the reaction was carried out partially at room temperature, complex **2** was not thermally stable in solution, while it is reasonably stable in the solid state, but only under an inert atmosphere. Complex **2** is a unique six-co-ordinate octahedral *trans*-dialkyl derivative of titanium(IV). The thermal lability of the Ti–C bond may be associated with the autolabilization effect of the two alkyl groups *trans* to each other. The structure of **2** is shown in Fig. 1 and will be discussed jointly with that of **3** and **4**. Gentle heating in benzene did not reveal any paramagnetic titanium(III), but rather a mixture of titanium(IV) compounds, as can be inferred by the appearance of different methyl groups. At the same time we observed that the methine (=CH–) proton disappears from its usual position. This is in agreement with the migration of one or both methyl groups from the metal to the imino group (see below). The same ^{1}H NMR spectrum was observed for the residue left by the mother solution when **2** was filtered off. The thermal decomposition mentioned above is solely temperature dependent and was also observed in other solvents, such as toluene and CH$_2$Cl$_2$.

The migration of an alkyl or aryl group to the ligand was clarified and the product identified by carrying out the alkylation of complex **1** with MgBr(mes) in toluene and dioxane. The reaction in toluene afforded a good yield of **3** as a yellow-orange crystalline solid [equation (2)]. We did not observe any reduction in toluene. Complex **3** is derived formally from the alkylation of the metal and the monoalkylation of the salen ligand. The ^{1}H NMR spectrum showed the disappearance of the methine (=CH–) proton from its usual position and the presence of two different mesityl groups. One of them has the *o*-methyls non-equivalent due to the absence of free rotation of the mesityl group. A close examination of the solid-state structure (see Fig. 2) showed an important steric hindrance for the mesityl group bonded to the salen ligand. Such a mesityl group along



(2)

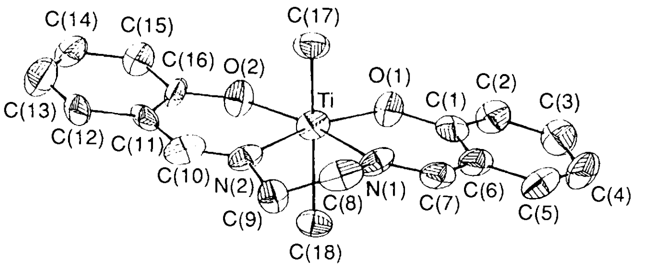
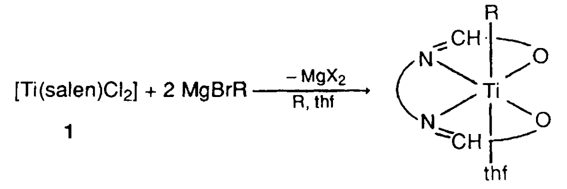


Fig. 1 An ORTEP[14] drawing for complex **2** (30% probability ellipsoids)

with the loss of planarity of the salen ligand, as a consequence of the alkylation, is responsible for the inaccessibility of the sixth co-ordination position of titanium in **3**. Alkylation of the tetradentate ligand has never been observed in cobalt(III),[6] vanadium(III)[3] or titanium(III)[3]–Schiff base organometallic derivatives. Such an event is the consequence of the electrophilic activation of the imino groups induced by high-oxidation-state metals like titanium(IV) and zirconium(IV). The alkylation of the Schiff base may proceed either by direct attack of the alkylating agent on the electrophilic carbon of the imino groups of the salen or by migration of the aryl carbanion from the metal to the same carbon. Based on our qualitative observation on the thermal lability of complex **1**, we prefer the later hypothesis, admitting double arylation of the metal followed by migration of one of the mesityl groups. This migration should be regarded as an intramolecular insertion of an imino group into a metal–carbon bond, a quite common reaction in early transition-metal chemistry.[15] Reaction (2) carried out in dioxane instead of in toluene gave mainly complex **3**, with some traces of the titanium(III) derivatives, as revealed by the blue-green colour of the solution. Complex **3** crystallizes either with a molecule of toluene or dioxane, the latter derivative being used for the X-ray analysis.

When the alkylation of complex **1** was attempted in thf solutions we observed reduction of titanium(IV) to titanium(III), as seen from the appearance of blue-green solutions. The results obtained on treating **1** with MgBrR (R = Ph or mes) in thf solution are shown in equation (3). Reaction (3) led to the isolation of blue-green crystals of **4** and **5**, which are organotitanium(III) derivatives. They are thermally stable in the solid state and in solution as specified in the Experimental section, but are quickly oxidized in the air. The X-ray structure of **4** is shown in Fig. 3 and we can propose from analytical and spectroscopic data the same structure for **5**. Reduction of Ti^{IV} to Ti^{III} should not involve the preliminary formation of the corresponding dialkyl or aryl derivative. The dimethyl derivative **2** does not form any titanium(III) when dissolved in thf or other oxygenated solvents. Therefore titanium(III) forms from the reduction by the alkylating agent in oxygenated solvents, rather than from a decomposition of a dialkyltitanium(IV) intermediate. The role of the solvent in the alkylation reaction consists, probably, in changing the reducing properties of the alkylating agent.



(3)

4 R = Ph
5 R = mes

Selected bond distances and angles for complexes **2**–**4** are listed in Table 5. In Table 6 their most significant con-

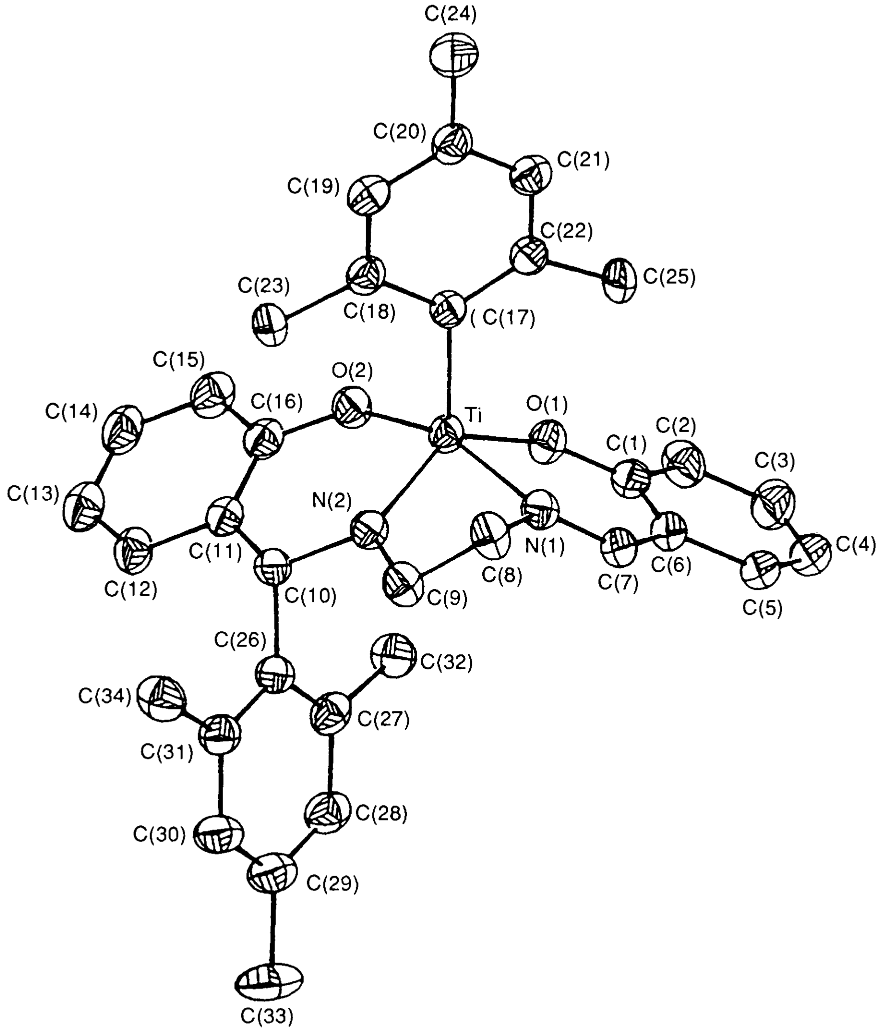


Fig. 2 An ORTEP[14] drawing for complex **3** (30% probability ellipsoids)

formational parameters are compared. The structures of the three complexes are shown in Figs. 1–3.

Complex **2** consists of discrete complex [Ti(salen)Me$_2$] molecules and toluene solvent molecules of crystallization in a complex/solvent molar ratio of 1 : 1. The co-ordination around titanium is pseudo-octahedral, two methyl groups being σ bonded to a Ti(salen) moiety in a *trans* arrangement [C(17)–Ti–C(18) 154.9(6)°]. The Ti–C (Table 5), Ti–O and Ti–N distances[5b] are in good agreement with those previously observed in titanium organometallic[1b,2d] and Schiff-base derivatives.[3,5b,16] The titanium atom lies on the plane of the N$_2$O$_2$ core, which is planar within experimental error. The two six-membered chelation rings are slightly folded along the respective N ··· O lines, titanium being displaced by 0.303(3) and 0.161(3) Å from the planes through N(1),C(7),C(6), C(1),O(1) and N(2),C(10),C(11),C(16),O(2) respectively. The five-membered chelation ring is in a *gauche* conformation (Table 6). There are no significant differences between the corresponding distances in the two symmetric parts of the Ti(salen) unit.

Complex **3** crystallizes with a dioxane molecule. The geometry of the ligand is strongly affected by the mesityl bonded to the imino carbon. The co-ordination polyhedron can be described as a distorted square pyramid (Fig. 2). Titanium is out of the N$_2$O$_2$ core toward the apical aromatic carbon by 0.487(1) Å (Table 6). The N$_2$O$_2$ core shows significant tetrahedral distortions as reported[3] in five-co-ordinate titanium(III) and vanadium(III) organometallic derivatives. The alkylation leads to the trianionic ligand L and would account for the large shortening of the Ti–N(2) distance, the Ti–O and Ti–N(1) distances falling in the usual range (Table 5). The conformation of the two six-membered chelation rings is only slightly affected by alkylation (Table 6). They are pushed down to produce an umbrella conformation as a consequence of steric hindrance between the *o*-methyl groups and the Ti(salen) moiety. This conformation, owing to its steric hindrance, prevents the approach of a sixth ligand, as previously observed[3] in other five-co-ordinated complexes. The mesityl ligand is perpendicular to the mean plane through the N$_2$O$_2$ core [dihedral angle 90.4(1)°] giving rise to almost symmetrical interactions as can be seen from the interatomic contacts reported in Table 7. The metal atom is only 0.019(1) Å out of the plane through the aromatic ring. Rotation of the group bonded to the mesityl around the Ti–C(17) bond is forbidden by steric interaction with the ethylene bridge, as is rotation of the other mesityl group around the C(10)–C(26) bond. In the latter case the rotation is also prevented by the umbrella conformation of the Ti(salen) molecule.

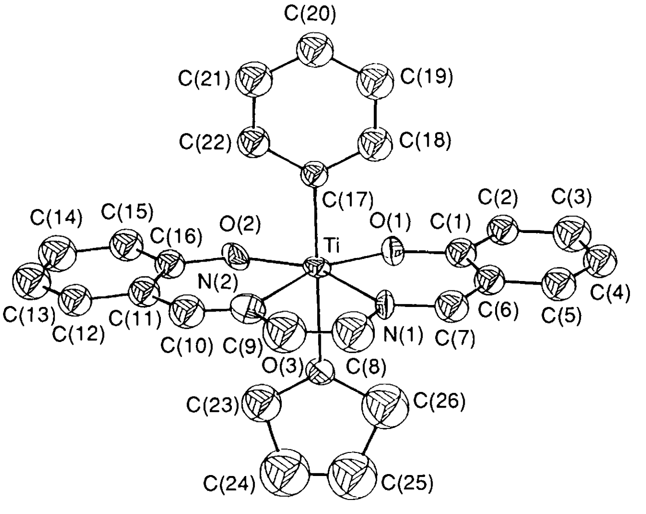


Fig. 3 An ORTEP[14] drawing for complex **4** (30% probability ellipsoids)

Complex **4** crystallizes with a thf molecule. The structure is affected by high thermal motion and strong disorder involving the solvent molecule. This accounts for the rather low accuracy of the X-ray analysis. The co-ordination polyhedron can be described as a distorted octahedron, the two *trans* positions being occupied by a phenyl ligand and a thf molecule. Bond distances and angles in the titanium co-ordination sphere are in good agreement with those found in complex **2** and in the analogous acacen [4,4′-ethylenedinitrilobis(pentan-2-onate)] derivative.[3] The N$_2$O$_2$ core is planar with titanium protruding

Table 7 Interatomic contacts (distances in Å, angles in °) in complexes **4** and **5**

Complex 4			
C(25) ··· O(1)	3.171(6)	C(23) ··· O(2)	3.333(6)
C(25)–H(253)	1.07	C(23)–H(233)	1.06
H(253) ··· O(1)	2.49	H(233) ··· O(2)	2.48
C(25)–H(253) ··· O(1)	121	C(23)–H(233) ··· O(2)	136
C(25) ··· N(1)	3.463(6)	C(32) ··· N(2)	3.163(6)
C(25) ··· H(252)	1.06	C(32) ··· H(323)	1.05
H(252) ··· N(1)	2.64	H(323) ··· N(2)	2.73
C(25)–H(252) ··· N(1)	133	C(32)–H(323) ··· N(2)	105
Complex 5			
C(18) ··· O(1)	3.226(21)	C(22) ··· O(2)	3.285(20)
C(18)–H(18)	1.04	C(22)–H(22)	1.05
H(18) ··· O(1)	2.77	C(22) ··· O(2)	2.84
C(18)–H(18) ··· O(1)	106	C(22)–H(22) ··· O(2)	106
C(18) ··· N(21)	3.311(24)	C(22) ··· N(2)	3.446(26)
H(18) ··· N(21)	2.89	H(22) ··· N(2)	3.12
C(18)–H(18) ··· N(1)	103	C(22)–H(22) ··· N(2)	99

Table 6 Comparison of structural parameters within the Ti(salen) units of complexes **2**–**4**

	2	**3**	**4**
Folding* along the N(1)···O(1) line/°	12.1(5)	4.2(1)	5.8(5)
N(2) ··· O(2) line/°	6.3(4)	4.4(1)	3.6(6)
Angle between Ti–N(1)–O(1) and Ti–N(2)–O(2) planes/°	177.2(5)	134.1(1)	167.8(5)
Angle between OC$_3$N planes/°	7.5(5)	53.7(1)	3.1(5)
Torsion angle N(1)–C(8)–C(9)–N(2)/°	−41.8(19)	−40.0(4)	−1.4(46)
Distances/Å C(8) from the Ti–N(1)–N(2) plane	−0.304(17)	−0.817(5)	−0.222(39)
C(9) from the Ti–N(1)–N(2) plane	0.242(17)	−0.274(5)	−0.181(39)
Ti from the N$_2$O$_2$ core	−0.018(3)	0.487(1)	−0.159(4)
O(1) from the N$_2$O$_2$ core	0.017(10)	−0.207(3)	−0.007(14)
O(2) from the N$_2$O$_2$ core	−0.017(10)	0.210(3)	0.007(14)
N(1) from the N$_2$O$_2$ core	−0.037(15)	0.235(3)	0.014(18)
N(2) from the N$_2$O$_2$ core	−0.039(15)	−0.238(3)	−0.021(22)

* The folding is defined as the dihedral angle between the TiNO and OC$_3$N planes of a six-membered chelation ring.

from it by 0.159(4) Å towards the σ-bonded phenyl carbon. This causes a slight distortion of the Ti(salen) moiety towards an umbrella conformation, although to a much lesser extent than that observed in complex **3** (Table 6). The phenyl ligand is nearly perpendicular to the N_2O_2 core [dihedral angle 90.9(5)°] giving rise to symmetrical interactions with the N_2O_2 core as can be seen from the interatomic contacts reported in Table 7. These contacts could be considered as hydrogen-bonding interactions which may play an important role in stabilizing the metal–carbon bond.

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