Monocyclopentadienylchlorooxotitanium(IV) Dimers, Trimers and Tetramers†

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High-yield syntheses ($\geqslant$90%) of the monocyclopentadienyloxochloro complexes [$(TiLCl_2)_2(\mu$-O)] **2**, [$(TiLCl)_4(\mu$-O$)_4$] **3**, [$(TiL)_4(\mu$-O$)_6$] **4** and [$(TiLCl)_3(\mu$-O$)_3$] **5** have been achieved by hydrolysis of the precursors [$TiLCl_3$] **1** [L = η^5-C_5H_5, C_5H_4Me, $C_5H_4(SiMe_3)$ or C_5Me_5]. In addition [Ti{η^5-$C_5H_4(SiMe_3)$}Br_3] **7**, [Ti_4{η^5-$C_5H_4(SiMe_3)$}$_4Br_4(\mu$-O$)_4$] **8** and [Ti_4{η^5-$C_5H_4(SiMe_3)$}$_4(NCS)_4(\mu$-O$)_4$] **9** have been prepared. The structures of the cyclic trimer **5** (L = η^5-C_5Me_5) and tetramer **9** have been determined by X-ray analysis: **5**, monoclinic, space group $P2_1/c$, a = 16.724(2), b = 8.958(1), c = 22.871(2) Å, β = 91.73(1)°, Z = 4 and R = 0.065 for 3159 independent observed reflections; **9**, monoclinic, space group Cc, a = 24.527(2), b = 12.520(2), c = 18.931(2) Å, β = 115.46(2)°, Z = 4 and R = 0.060 for 3088 independent observed reflections. The electronic configurations of complexes **2**–**5** have been calculated by extended-Hückel molecular orbital calculations.

Transition-metal complexes of general formula $(RMX_nO_m)_q$, X being a halogen and R an organic fragment assuring solubility in organic solvents, are considered among the most attractive starting materials in organometallic chemistry for a number of unconventional transformations: (*i*) reductive coupling leading to the aggregation of reactive unsaturated fragments[1] (such aggregates, which are electron rich and can be functionalized, may be regarded as homogeneous models of some heterogeneous oxides[2]); (*ii*) controlled hydrolysis or oxidation of the R residue analogous to the formation of high-oxidation-state polyoxo derivatives, as for metal oxo deposition on surfaces; and (*iii*) bonding of M–C and M–O functionalities to the same or neighbouring metals.

The major problem encountered in such chemistry is the availability of the starting materials. Convenient and high-yield syntheses of many of the oxochloro organometallic derivatives, which can be considered as secondary products, have not yet been established. However, some syntheses have been in the literature for several years. Our attention was focused, in particular, on the generation, high-yield synthesis, substitution at the cyclopentadienyl ligand, structural characterization, and the electronic configuration of compounds belonging to the following classes [{Ti(η^5-$C_5H_4R)X_2$}$_2(\mu$-O)], [{Ti(η^5-C_5H_4R)X(μ-O)}$_4$], [$Ti_4(\eta^5$-$C_5H_4R)_4(\mu$-O$)_6$] and [{Ti(η^5-C_5H_4R)X(μ-O)}$_3$].

Experimental

General Procedures.—All non-hydrolytic procedures were carried out under nitrogen using modified Schlenk-type methods. All reagents and solvents were reagent grade and were dried and degassed by standard procedures before use. Infrared spectra were taken as Nujol mulls between KBr plates on a Perkin-Elmer model 883 spectrometer, ^{1}H and ^{13}C-{^{1}H} NMR spectra on a Bruker AC 200 spectrometer, using the solvent as reference. Elemental analyses were performed on a CHNS-O EA1108 Carlo Erba instrument. The compounds $C_5H_5(SiMe_3)$,[3] $C_5H_4(SiMe_3)_2$,[4] C_5Me_5H,[5] [Ti(η^5-$C_5H_5)_2Cl_2$],[6a] [Ti{η^5-$C_5H_4(SiMe_3)$}X_3][7] (X = Cl or Br), [Ti(η^5-$C_5Me_5)Cl_3$],[8] [Ti(η^5-$C_5H_5)Cl_3$][6b] and [Ti(η^5-$C_5H_4Me)Cl_3$][6b] were prepared by literature methods. The hydrolysis reactions were carried out in the air using non-purified commercial solvents.

Syntheses.—[Ti(η^5-$C_5H_4Me)_2Cl_2$]. This compound was prepared by a modified version of the published method for [Ti(η^5-$C_5H_5)_2Cl_2$].[6a] To a chilled toluene (−70 °C, 300 cm^3) solution of $TiCl_4$ (54 cm^3, 93.4 g, 0.492 mol), anhydrous tetrahydrofuran (thf) (90 cm^3) was added. After the precipitation of the yellow $TiCl_4$·2thf adduct, the temperature was allowed to rise to −10 °C and a thf solution of Na(η^5-C_5H_4Me) (330 cm^3, 3.1 mol dm^{-3}, 1.023 mol) was added dropwise over 1 h. A black suspension was obtained, which was stirred for 1 d, then treated with gaseous HCl to obtain a red suspension of [Ti(η^5-$C_5H_4Me)_2Cl_2$]. This suspension was evaporated to dryness and the solid extracted in air with CH_2Cl_2 using a Soxhlet extractor. Crystalline [Ti(η^5-$C_5H_4Me)_2Cl_2$] was obtained, which was filtered off, washed with Et_2O (3 × 100 cm^3) and dried *in vacuo* (95 g, 94%) (Found: C, 52.35; H, 5.10. $C_{12}H_{14}Cl_2Ti$ requires C, 52.00; H, 5.10%). Proton NMR ($CDCl_3$): δ 6.40 (m, 4 H), 6.30 (m, 4 H) and 2.34 (s, 6 H).

[{Ti(η^5-C_5H_5)Cl(μ-O)}$_4$]. To a refluxing acetone (150 cm^3) solution of [Ti(η^5-$C_5H_5)Cl_3$] (6.2 g, 24.4 mmol) distilled water (≈20 cm^3) was added through the condenser until a yellow crystalline solid was formed. The resulting mixture was refluxed for 30 min, then allowed to cool to room temperature. The solid was filtered off, washed with acetone–water (4:1) and dried *in vacuo* for 12 h (4.5 g, 96%) (Found: C, 35.35; H, 2.95. $C_{20}H_{20}Cl_4O_4Ti_4$ requires C, 36.50; H, 3.05%). NMR ($CDCl_3$): ^{1}H, δ 6.63; ^{13}C, δ 119.9. ν(Ti–O) 808 cm^{-1}.

[{Ti(η^5-C_5H_4Me)Cl(μ-O)}$_4$]. To a refluxing acetone (600 cm^3) solution of [Ti(η^5-$C_5H_4Me)Cl_3$] (80.0 g, 0.343 mol)

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† *Supplementary data available* (No. SUP 56868, 8 pp.): molecular orbital data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI unit employed: eV ≈ 1.60 × 10^{-19} J.

distilled water was added through the condenser until a yellow crystalline solid formed. The mixture was allowed to cool to room temperature, and the resultant solid filtered off, washed with hexane (5 × 100 cm^3) and dried *in vacuo* overnight (56 g, 92%) (Found: C, 40.45; H, 4.00. $C_{24}H_{28}Cl_4O_4Ti_4$ requires C, 40.40; H, 3.95%). Proton NMR ($CDCl_3$): δ 6.46 (m, 4 H) and 2.40 (s, 3 H). ν(Ti–O) 798 cm^{-1}.

$[\{Ti[\eta^5\text{-}C_5H_4(SiMe_3)]Cl(\mu\text{-}O)\}_4]$. To a refluxing acetone (50 cm^3) solution of $[Ti\{\eta^5\text{-}C_5H_4(SiMe_3)\}Cl_3]$ (5.16 g, 17.7 mmol) distilled water was added through the condenser until a lemon-yellow crystalline solid formed. The mixture was refluxed for 30 min, and the resultant solid was filtered off at room temperature and dried *in vacuo* for 12 h (4.0 g, 95%) (Found: C, 40.85; H, 5.70. $C_{36}H_{52}Cl_4O_4Si_4Ti_4$ requires C, 40.60; H, 5.55%). Proton NMR (CD_2Cl_2): δ 6.82 (m, 2 H), 6.71 (m, 2 H) and 0.36 (s, 9 H). ν(Ti–O) 808 cm^{-1}.

$[\{Ti[\eta^5\text{-}C_5H_4(SiMe_3)]Br(\mu\text{-}O)\}_4]$. To a refluxing acetone (130 cm^3) solution of $[Ti\{\eta^5\text{-}C_5H_4(SiMe_3)\}Br_3]$ (5.82 g, 13.7 mmol) distilled water was added through the condenser until a yellow crystalline solid formed. The mixture was refluxed for 30 min, then the solid was filtered off at room temperature, washed with a cold mixture of acetone–water and dried for 12 h (3.3 g, 84%) (Found: C, 35.90; H, 4.90. $C_{32}H_{52}Br_4O_4Si_4Ti_4$ requires C, 34.20; H, 4.65%). Proton NMR (CD_2Cl_2): δ 6.94 (m, 2 H), 6.75 (m, 2 H), and 0.36 (s, 9 H). ν(Ti–O) 820 cm^{-1}. Chemical ionization (CI) mass spectrum (NH_3): *m/z* 1122 (M^+) (calc. 1124).

$[\{Ti[\eta^5\text{-}C_5H_4(SiMe_3)](NCS)(\mu\text{-}O)\}_4]$. To a thf (100 cm^3) solution of $[\{Ti[\eta^5\text{-}C_5H_4(SiMe_3)]Cl(\mu\text{-}O)\}_4]$ (2.17 g, 2.3 mmol) NH_4NCS (0.85 g, 11.2 mmol) was added dropwise. A red solution was obtained together with some white solid (NH_4Cl), which was eliminated by filtration. The solution was evaporated to dryness to yield a yellow solid which was recrystallized from hot hexane (1.55 g, 65%) (Found: C, 41.30; H, 5.30; N, 5.60. $C_{36}H_{52}N_4O_4S_4Si_4Ti_4$ requires C, 41.70; H, 5.05; N, 5.40%). Proton NMR (CD_2Cl_2): δ 6.79 (m, 2 H), 6.75 (m, 2 H), and 0.39 (s, 9 H). ν(Ti–NCS) 2005 cm^{-1}. CI mass spectrum (NH_3): *m/z* 1058 (M^+) (calc. 1054).

$[\{Ti(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}O)\}_3]$. To a refluxing acetone (40 cm^3 solution of $[Ti(\eta^5\text{-}C_5Me_5)Cl_3]$ (1.08 g, 3.7 mmol) an excess of distilled water (70 cm^3) was added until a yellow suspension was obtained. The suspension was filtered and the resultant solid dried *in vacuo* (0.8 g, 90%). Recrystallization from hot octane gave crystals suitable for X-ray analysis (Found: C, 51.55; H, 6.55. $C_{30}H_{45}Cl_3O_3Ti_3$ requires C, 51.20; H, 6.45%). Proton NMR ($CDCl_3$): δ 2.12 (s, 30 H) and 2.10 (s, 15 H). ν(Ti–O) 782 cm^{-1}. Mass spectrum: *m/z* 703 (M^+).

$[Ti_4(\eta^5\text{-}C_5H_4Me)_4(\mu\text{-}O)_6]$. To a thf (50 cm^3) solution of $[\{Ti(\eta^5\text{-}C_5H_4Me)Cl(\mu\text{-}O)\}_4]$ (3.0 g, 4.2 mmol) was added NH_4OH (30 cm^3, 25% solution). A milky white suspension formed which was stirred for 15 min, then filtered. The resultant solid was washed thoroughly with water, acetone and diethyl ether and then dried for 12 h (2.37 g, 95%) (Found: C, 47.20; H, 4.65. $C_{24}H_{28}O_6Ti_4$ requires C, 47.70; H, 4.65%). ν(Ti–O) 785 cm^{-1}.

$[Ti_4\{\eta^5\text{-}C_5H_4(SiMe_3)\}_4(\mu\text{-}O)_6]$. To a thf (50 cm^3) solution of $[\{Ti[\eta^5\text{-}C_5H_4(SiMe_3)]Cl(\mu\text{-}O)\}_4]$ (2.0 g, 2.11 mmol) was added NH_4OH (1 cm^3, 25%). The yellow mixture obtained was refluxed, then distilled water was added through the condenser until the yellow colour disappeared and a milky white solid formed. After 30 min of refluxing the volatiles were removed *in vacuo* and the resultant solid washed with water and dried for 12 h (1.55 g, 88%). This solid can be recrystallized by extraction with hexane (Found: C, 44.80; H, 6.60. $C_{32}H_{52}O_6Si_4Ti_4$ requires C, 45.95; H, 6.25%). Proton NMR (CD_2Cl_2): δ 6.49 (m, 2 H), 6.33 (m, 2 H) and 0.31 (s, 9 H). ν(Ti–O) 840 cm^{-1}.

X-Ray Crystallography.*—Intensity data were collected at room temperature on a Siemens AED single-crystal four-circle diffractometer. Crystal data and details of the parameters associated with data collection and structure refinement are given in Table 1. The reduced cells cited were obtained with use of TRACER.[10] For intensities and background, individual reflection profiles were analysed.[11] The structure amplitudes were obtained after the usual Lorentz and polarization corrections. For both complexes data were corrected for absorption using ABSORB.[12] The function minimized during the full-matrix least-squares refinement was $\Sigma w(\Delta F)^2$. Unit weights were used for complex **5**, while a weighting scheme based on counting statistics[9] was applied for **9**. Anomalous scattering corrections were included in all structure-factor calculations.[12] Scattering factors for neutral atoms were taken from ref. 13*a* for non-H atoms and from ref. 14 for hydrogen atoms. Among the low-angle reflections no correction for secondary extinction was deemed necessary.

The structures were solved using SHELXS 86.[15] For **5** refinement was first isotropic, then anisotropic for all the non-H atoms; all the hydrogen atoms were put in geometrically calculated positions and introduced in the refinement as fixed contributors (U_{iso} = 0.08 Å^2). The methyl carbons are affected by a very high thermal motion as often happens in situations like these. Attempts to interpret the thermal motion of disordered atoms were unsuccessful. The final difference map showed no unusual features, with no significant peaks above the general background.

The isotropic refinement of complex **9** showed the structure to be affected by severe disorder, involving all the sulfur atoms of the four isothiocyanato ligands and some methyl carbons. The best fit was found considering each sulfur atom statistically distributed over three positions (A, B, C) and the methyl carbons associated with Si(2) [C(29), C(30)] and Si(3) [C(31), C(32), C(33)] statistically distributed over two positions (A and B). Refinement was then carried out anisotropically for all the atoms, except C(28) and the disordered ones, which were refined isotropically with the site occupation factors in Table 3. A constraint [Si–C 1.90(1) Å] was applied to the Si(3), C(31), C(32), C(33) (A and B) group. The cyclopentadienyl hydrogens were put in geometrically calculated positions and introduced in the refinement as fixed contributors (U_{iso} = 0.08 Å^2). All the methylic hydrogens were ignored. The final difference map showed no unusual features, with no significant peaks above the general background. During the refinement of both compounds the cyclopentadienyl rings were constrained to be regular pentagons (C–C 1.42 Å).

Final atomic coordinates are given in Tables 2 and 3, selected bond distances and angles in Tables 4 and 5.

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

Computational Details.—All the calculations were performed by using the extended-Hückel approximation.[16] The following orbitals were used: 3d, 4s and 4p for titanium; 3s and 3p for chlorine; 2s and 2p for carbon and oxygen; and 1s for hydrogen. The parameters, taken from ref. 17, have been deposited as SUP 56868. The geometries of $[\{Ti(\eta^5\text{-}C_5H_5)Cl_2\}_2(\mu\text{-}O)]$ and $[\{Ti(\eta^5\text{-}C_5H_4R)Cl(\mu\text{-}O)\}_4]$ were taken from the published structures.[18,19] The structures of $[Ti_4(\eta^5\text{-}C_5Me_5)_4(\mu\text{-}O)_6]$[20] and $[\{Ti(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}O)\}_3]$ (this work) were used for describing the geometries of $[Ti_4(\eta^5\text{-}C_5H_5)_4(\mu\text{-}O)_6]$ and $[\{Ti(\eta^5\text{-}C_5H_5)Cl(\mu\text{-}O)\}_3]$ respectively. Minor deviations in equivalent distances and angles were averaged in order to obtain a structure with the highest symmetry possible. A standard geometry was used for the cyclopentadienyl rings, with C–C–C 108° and C–C–H 120°. The C–H bond length was taken to be 1.014 Å. The effective symmetries are C_{2h} for $[\{Ti(\eta^5\text{-}C_5H_5)Cl_2\}_2(\mu\text{-}O)]$, C_s for $[\{Ti(\eta^5\text{-}C_5H_5)Cl(\mu\text{-}O)\}_3]$, C_{2v} for $[\{Ti(\eta^5\text{-}C_5H_5)Cl(\mu\text{-}O)\}_4]$ and T_d for $[Ti_4(\eta^5\text{-}C_5H_5)_4(\mu\text{-}O)_6]$.

Energy levels of their valence orbitals, the net atomic charges

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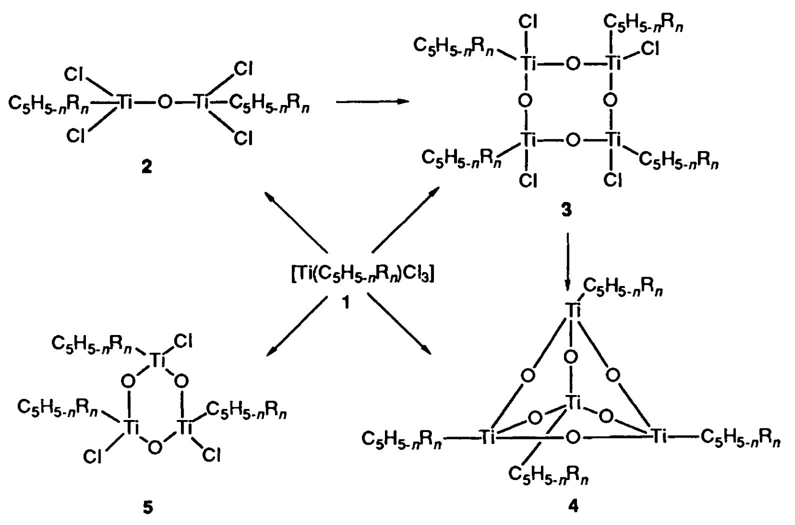
* Data reduction, structure solution and refinement were carried out on a GOULD 6040 computer using SHELX 76.[9]



Scheme 1 R = H (**1**, **2** or **3**), Me (**1**, **3** or **4**), SiMe$_3$ (**1** or **4**), n = 1; R = Me (**1**, **4** or **5**), n = 5

for the neutral, oxidized (2+) and reduced (2−) forms, extended-Hückel parameters, and atomic populations (%) of the valence orbitals are listed in SUP 56868.

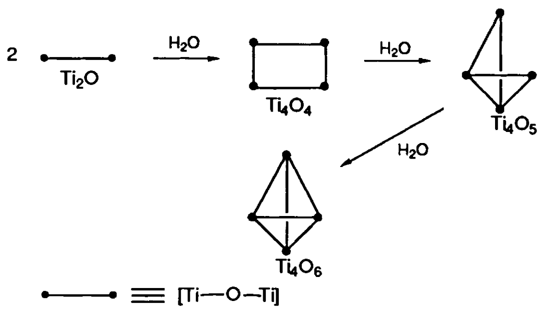
Results and Discussion

Controlled hydrolysis of [Ti(C$_5$H$_{5-n}$R$_n$)Cl$_3$] is the best route to oxo dimers, trimers and tetramers in the monocyclopentadienyltitanium series. The detailed procedures are reported in the Experimental section, while the correlation between the various species is summarized in Scheme 1. The two major controlling factors of this hydrolysis are the substituent at the cyclopentadienyl ligand and the reaction conditions, as summarized below.

Under very controlled conditions[18] complex **1** was hydrolysed to **2**, for the unsubstituted cyclopentadienyl (R = H) exclusively. Its further hydrolysis to **3** has been reported.[19] Hydrolysis of **1** with a large excess of water in refluxing acetone produces either **3** or **5** depending on the degree of substitution and the acidity of the solution. A fully substituted cyclopentadienyl like C$_5$Me$_5$ leads to the trimer, while less-substituted cyclopentadienyls lead to the tetramer. This happens very probably because of the acidity of the medium. It was shown that, under acidic conditions like those of the hydrolysis in acetone, **5** is the only compound formed. An aqueous solution of cyclopentadienyl derivatives of titanium(IV), such as [Ti(η^5-C$_5$H$_5$)$_2$Cl$_2$], is very acidic.[21,22] Where hydrolysis is carried out under slightly basic conditions, as in the presence of tertiary amines, the formation of the tetramer **3** is also observed in the case of [Ti(η^5-C$_5$Me$_5$)Br$_3$].[23] Hydrolysis of **1** or **3**, carried out under very basic conditions (in the presence of ammonia), led to the fully hydrolysed tetramer **4**. The formation of **4** should be considered as a stepwise process in which the intermediacy of **2** and **3** has been shown through their isolation under different reaction conditions. There is, however, a missing intermediate from **3** to **4**, [Ti$_4$(C$_5$H$_{5-n}$R$_n$)$_4$Cl$_2$(μ-O)$_5$] **6**, for which indirect proof has been obtained from the elegant 'retrohydrolysis' carried out on **4** by Babcock and Klemperer[24] using TiCl$_4$ [equation (1)].

$$\underset{\mathbf{4}}{[Ti_4(C_5Me_5)_4O_6]} \xrightarrow[-TiO_2]{TiCl_4} \underset{\mathbf{6}}{[Ti_4(C_5Me_5)_4O_5Cl_2]} \xrightarrow[-TiO_2]{TiCl_4} \underset{\mathbf{3}}{[Ti_4(C_5Me_5)_4O_4Cl_4]} \quad (1)$$

The entire hydrolysis leading from complex **1** to **4** may be exemplified as in Scheme 2 where Ti–O–Ti is the building block for trimers and tetramers. The influence on the entire hydrolysis process of the cyclopentadienyl substituents could be rather complex because they affect (*i*) the solubility of the compound (a major factor in a hydrolysis reaction), (*ii*) the acidity of the metal centre; and (*iii*) the steric hindrance.



Scheme 2

Scheme 1 reports our own reactions along with some known in the literature, for which an improved procedure is given in the Experimental section. The use of complexes **2**–**5** in the reactions outlined in the Introduction sometimes requires a halide other than chloride. This can be achieved by starting from the corresponding trihalide or by replacing Cl in some of the oxo compounds. Some attempted preparations of this type can be found in the literature.[25] The hydrolysis of [Ti{η^5-C$_5$H$_4$(SiMe$_3$)}Br$_3$] **7** and substitution of Cl in **3** (R = SiMe$_3$, n = 1) are further examples of this reaction type. The hydrolysis of **7** in acetone produces exclusively the tetramer [{Ti[η^5-C$_5$H$_4$(SiMe$_3$)]Br(μ-O)}$_4$] **8**, details of which are in the Experimental section. Replacement of Cl has been attempted on complexes **3** because they are the key compounds in reductive coupling reactions. Reaction of **3** (R = SiMe$_3$, n = 1) with NH$_4$SCN led to the corresponding tetraisothiocyanate [{Ti[η^5-C$_5$H$_4$(SiMe$_3$)](NCS)(μ-O)}$_4$] **9**. X-Ray analyses have been carried out on **5** and **9**, the structures of which have not been previously determined. Reduction of complexes **2**–**5**, **8** and **9** is a major goal in the use of such starting materials. A careful study of their electronic configurations should help in understanding their chemical behaviour.

The molecular structure of complex **5** is shown in Fig. 1. The structure of the analogous bromo derivative [{Ti(η^5-C$_5$Me$_5$)Br(μ-O)}$_3$] has recently been reported.[23] Selected bond distances and angles are given in Table 4. Titanium and oxygen atoms give rise to a six-membered ring having an almost flattened half-boat conformation, Ti(2) and O(3) being 0.137(2) and 0.397(6) Å out of the plane defined by Ti(1),Ti(3),O(1),O(2). The displacements of these atoms from the plane are not

Table 1 Experimental data for the X-ray diffraction studies for complexes **5** and **9**[a]

	5	**9**
Formula	$C_{30}H_{45}Cl_3O_3Ti_3$	$C_{36}H_{52}N_4O_4S_4Si_4Ti_4$
M	703.7	989.0
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	*Cc*
Cell parameters at 295 K[b]		
a/Å	16.724(2)	24.527(2)
b/Å	8.958(1)	12.520(2)
c/Å	22.871(2)	18.931(2)
α,γ/°	90	90
β/°	91.73(1)	115.46(2)
U/Å^3	3424.8(6)	5248.7(14)
Z	4	4
D_c/g cm^{-3}	1.365	1.252
F(000)	1464	2048
μ/cm^{-1}	82.95	76.86
Crystal dimensions/mm	0.16 × 0.28 × 0.45	0.21 × 0.30 × 0.52
2θ range/°	6–130	6–120
Unique total data	5108	3909
Unique observed data, N_o	3159	3088
Parameters varied, N_v	325	469
N_o/N_v	9.7	6.6
$R = \Sigma\|\Delta F\|/\Sigma\|F_o\|$	0.065	0.060
$R' = \Sigma w^{\frac{1}{2}}\|\Delta F\|/\Sigma w^{\frac{1}{2}}\|F_o\|$	Unit weights	0.064
Goodness of fit $= [\Sigma w\|\Delta F\|^2/(N_o - N_v)]^{\frac{1}{2}}$	—	0.78

[a] Details pertaining to both complexes: scan type θ–2θ; nickel-filtered Cu-Kα radiation (λ = 1.541 78 Å); criterion for observation, $I > 2\sigma(I)$. [b] Unit-cell parameters were obtained by least-squares analysis of the setting angles of 25 carefully centred reflections chosen from diverse regions of reciprocal space.

Table 2 Atomic coordinates (× 10^4) for complex **5**

Atom	*X/a*	*Y/b*	*Z/c*
Ti(1)	3724.0(8)	2887.8(18)	1225.7(6)
Ti(2)	1742.5(8)	2880.6(18)	920.0(6)
Ti(3)	2450.6(8)	3774.5(18)	2265.7(6)
Cl(1)	4132(1)	5279(2)	1074(1)
Cl(2)	1339(1)	442(3)	992(1)
Cl(3)	2667(1)	6284(2)	2245(1)
O(1)	2801(3)	2756(7)	780(2)
O(2)	1714(2)	3531(6)	1672(2)
O(3)	3360(2)	2970(6)	1973(2)
C(1)	4834(3)	1401(8)	1506(2)
C(2)	5078(3)	2252(8)	1019(2)
C(3)	4600(3)	1815(8)	525(2)
C(4)	4061(3)	694(8)	706(2)
C(5)	4206(3)	439(8)	1313(2)
C(6)	5176(8)	1508(22)	2102(5)
C(7)	5741(7)	3336(16)	1011(10)
C(8)	4617(9)	2389(19)	−83(5)
C(9)	3500(8)	−139(18)	324(6)
C(10)	3789(9)	−717(14)	1662(6)
C(11)	1522(4)	5190(6)	454(3)
C(12)	1666(4)	4132(6)	7(3)
C(13)	1035(4)	3072(6)	2(3)
C(14)	500(4)	3475(6)	446(3)
C(15)	801(4)	4784(6)	725(3)
C(16)	2054(11)	6489(15)	564(7)
C(17)	2326(8)	4196(21)	−393(6)
C(18)	985(12)	1815(17)	−411(6)
C(19)	−241(7)	2625(24)	549(8)
C(20)	432(13)	5628(27)	1199(5)
C(21)	2151(6)	1787(6)	2895(3)
C(22)	1446(6)	2666(6)	2838(3)
C(23)	1609(6)	4083(6)	3092(3)
C(24)	2415(6)	4080(6)	3308(3)
C(25)	2750(6)	2661(6)	3186(3)
C(26)	2241(15)	198(16)	2726(7)
C(27)	670(9)	2210(26)	2578(5)
C(28)	1048(9)	5330(20)	3129(6)
C(29)	2801(9)	5317(19)	3637(5)
C(30)	3586(8)	2236(25)	3344(6)

significant, being 0.000(2), −0.000(2), −0.007(6), 0.006(6) respectively. The Ti–O bond distances range from 1.812(5) to 1.833(5) Å, averaging 1.823(5) Å. They are in good agreement with those found in the bromide analogue.[23] The Ti–O bond distances and Ti–O–Ti angles, and the approximate planarity of the ring, are in accord with a significant Ti–O double-bond character. The co-ordination geometry around the Ti atoms is best described as a three-legged piano stool (distorted tetrahedral). Displacements from the basal plane of titanium are 0.842(2), 0.817(2) and 0.829 Å for T(1), Ti(2) and Ti(3) respectively. The titanium–centroid directions are nearly perpendicular to the basal planes, the dihedral angles formed with the normals to the planes being 175.7(2), 176.8(2) and 176.9(1)° for Ti(1), Ti(2) and Ti(3) respectively. The dihedral angles between the basal planes and the cyclopentadienyl rings are 175.6(2), 175.0(2) and 176.5(2)° for Ti(1), Ti(2) and Ti(3) respectively.

The molecular structure of complex **9** is shown in Fig. 2. Selected bond distances and angles are given in Table 5. Titanium and oxygen atoms give rise to an eight-membered ring which is roughly planar.[19,23] The best mean plane passes through all the atoms except Ti(3), the displacements from it being as follows: Ti(1), 0.000(1); Ti(2), −0.027(3); Ti(4), −0.017(3); O(1), 0.172(9); O(2), 0.150(9); O(3), 0.069(8); O(4), 0.029(10); and Ti(3), 0.565(3) Å. The ring is nearly rectangular, the Ti(2)–O(2)–Ti(3) and Ti(1)–O(4)–Ti(4) angles being close to 180°, while Ti(1)–O(1)–Ti(2) and Ti(3)–O(3)–Ti(4) are much narrower (Table 5). The Ti–O bond distances [mean 1.811(9) Å] are not significantly different and are in a very good agreement with those observed in complex **5**. The co-ordination geometry around the titanium atoms is similar to that found in complex **5** and can be described as a trigonal pyramid having the basal plane defined by the N and O heteroatoms and the apex by the centroid of the cyclopentadienyl ligand. Displacements from the basal plane of titanium are 0.799(1),

Table 3 Atomic coordinates (× 10^4) for complex **9**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ti(1)	3954.1(–)	3646.6(16)	2233.2(–)
Ti(2)	2952.4(12)	1585.9(15)	2055.3(16)
Ti(3)	4236.1(13)	−94.8(14)	3137.4(17)
Ti(4)	5192.9(13)	2097.9(15)	3597.5(17)
Si(1)	2830(2)	5331(3)	632(3)
Si(2)	1868(2)	−486(3)	2220(3)
Si(3)	5445(3)	−2196(4)	3861(4)
Si(4)	4950(2)	2054(3)	5404(3)
S(1A)	3568(8)	6001(12)	3916(9)
S(1B)	3914(12)	5708(20)	4259(15)
S(1C)	3273(10)	6020(15)	3658(12)
S(2A)	2485(8)	−707(14)	−87(10)
S(2B)	2199(7)	−822(12)	−61(9)
S(2C)	2255(8)	−363(13)	−306(10)
S(3A)	3715(7)	−1235(8)	5140(7)
S(3B)	4040(10)	−1396(15)	5349(11)
S(3C)	3442(10)	−1079(14)	4908(11)
S(4A)	6444(5)	1018(9)	2415(8)
S(4B)	6208(8)	1366(14)	2036(11)
S(4C)	6576(10)	652(19)	2755(14)
O(1)	3309(4)	2751(6)	1892(5)
O(2)	3569(4)	735(7)	2649(5)
O(3)	4850(4)	829(6)	3635(4)
O(4)	4579(4)	2864(8)	2900(6)
N(1)	3792(6)	4567(9)	2958(7)
N(2)	2646(6)	845(10)	1043(7)
N(3)	4088(6)	−688(9)	4003(7)
N(4)	5617(6)	1701(11)	2963(8)
C(1)	3619(3)	4788(7)	1142(5)
C(2)	3826(3)	3821(7)	949(5)
C(3)	4457(3)	3744(7)	1423(5)
C(4)	4640(3)	4663(7)	1909(5)
C(5)	4122(3)	5308(7)	1736(5)
C(6)	2157(4)	929(6)	2338(5)
C(7)	2601(4)	1388(6)	3033(5)
C(8)	2632(4)	2497(6)	2898(5)
C(9)	2207(4)	2724(6)	2120(5)
C(10)	1913(4)	1754(6)	1774(5)
C(11)	4779(4)	−1593(7)	3022(5)
C(12)	4816(4)	−778(7)	2523(5)
C(13)	4226(4)	−597(7)	1926(5)
C(14)	3824(4)	−1300(7)	2057(5)
C(15)	4166(4)	−1916(7)	2734(5)
C(16)	5411(4)	2554(6)	4890(5)
C(17)	5930(4)	2040(6)	4899(5)
C(18)	6171(4)	2700(6)	4492(5)
C(19)	5800(4)	3622(6)	4231(5)
C(20)	5331(4)	3532(6)	4477(5)
C(21)	3689(9)	5110(14)	3370(11)
C(22)	2509(8)	220(15)	546(10)
C(23)	3934(9)	−910(11)	4486(10)
C(24)	5960(8)	1405(15)	2711(12)
C(25)	2349(8)	4182(18)	64(13)
C(26)	2837(10)	6422(20)	−54(18)
C(27)	2578(10)	5850(20)	1347(14)
C(28)	1411(10)	−509(19)	2774(14)
C(29A)	2415(18)	−1341(33)	2273(26)
C(29B)	1634(22)	−987(38)	1213(27)
C(30A)	1230(15)	−514(27)	1145(19)
C(30B)	2516(19)	−1380(33)	2780(27)
C(31A)	5788(20)	−1346(30)	4773(16)
C(31B)	6009(17)	−1170(28)	4497(24)
C(32A)	6062(30)	−2137(74)	3502(49)
C(32B)	5571(17)	−3633(13)	3680(23)
C(33A)	5320(26)	−3630(18)	4069(34)
C(33B)	5132(35)	−2893(61)	4502(41)
C(34)	4119(8)	2091(15)	4681(12)
C(35)	5189(9)	645(14)	5727(11)
C(36)	5163(12)	2914(18)	6299(12)

The site occupation factors are 0.5 for atoms S(1A), S(3A), S(4A), C(29A), C(29B), C(30A), C(30B), C(31A), C(31B), C(32A), C(32B) and C(33B), 0.25 for S(1B), S(1C), S(3B), S(3C), S(4B) and S(4C) and 0.3333 for S(2A), S(2B) and S(2C).

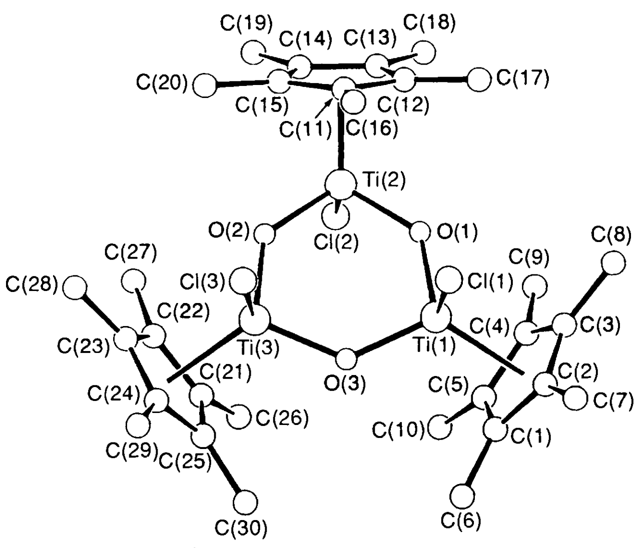


Fig. 3 A SCHAKAL[26] view of complex **5**

0.792(3), 0.797(3) and 0.826(3) Å for Ti(1), Ti(2), Ti(3) and Ti(4) respectively. The titanium–centroid directions are nearly perpendicular to these basal planes, the dihedral angles formed with the normals to the planes being 177.1(2), 179.1(3), 178.8(3) and 176.2(2)° for Ti(1), Ti(2), Ti(3) and Ti(4) respectively. The dihedral angles between the basal planes and the cyclopentadienyl rings are 178.1(3), 179.0(4), 179.7(3) and 177.9(3)° for Ti(1), Ti(2), Ti(3) and Ti(4) respectively.

Table 4 Selected bond distances (Å) and angles (°) for complex **5**

Ti(1)–O(1)	1.828(5)	Ti(3)–O(2)	1.819(5)
Ti(1)–O(3)	1.833(5)	Ti(3)–O(3)	1.828(5)
Ti(1)–Cl(1)	2.278(3)	Ti(3)–Cl(3)	2.278(3)
Ti(1)–Cp1	2.045(7)	Ti(3)–Cp3	2.053(7)
Ti(2)–O(1)	1.812(5)		
Ti(2)–O(2)	1.818(5)		
Ti(2)–Cl(2)	2.294(3)		
Ti(2)–Cp2	2.036(7)		
Cl(1)–Ti(1)–Cp1	113.6(2)	Cl(3)–Ti(3)–Cp3	112.4(1)
O(3)–Ti(1)–Cp1	119.7(2)	O(3)–Ti(3)–Cp3	118.9(2)
O(1)–Ti(1)–Cp1	113.1(2)	O(2)–Ti(3)–Cp3	114.0(2)
Cl(1)–Ti(1)–O(3)	102.3(2)	Cl(3)–Ti(3)–O(3)	104.3(2)
Cl(1)–Ti(1)–O(1)	103.2(2)	Cl(3)–Ti(3)–O(2)	102.0(2)
O(1)–Ti(1)–O(3)	102.9(2)	O(2)–Ti(3)–O(3)	103.4(2)
O(2)–Ti(2)–Cp2	115.2(3)	Ti(1)–O(1)–Ti(2)	135.3(3)
O(1)–Ti(2)–Cp2	114.3(3)	Ti(2)–O(2)–Ti(3)	135.1(3)
Cl(2)–Ti(2)–Cp2	115.0(2)	Ti(1)–O(3)–Ti(3)	131.4(3)
Cl(2)–Ti(2)–O(2)	102.8(2)		
Cl(2)–Ti(2)–O(1)	104.2(2)		
O(1)–Ti(2)–O(2)	103.9(2)		

Cp1, Cp2 and Cp3 refer to the centroids defined by the cyclopentadienyl rings C(1)–C(5), C(11)–C(15) and C(21)–C(25) respectively.

The electronic structures of the parent compounds **2**–**5** have been determined by performing extended-Hückel molecular orbital calculations. Only the unsubstituted cyclopentadienyl rings have been considered as organic ligands and the valence electrons have been included in the calculations (see SUP

56868). Only the energy levels of the most relevant molecular orbitals, *i.e.* the highest occupied (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) are shown, owing to the fact that the compounds are mainly used in redox reactions which involve the character and the occupation of these two sets of orbitals. The analysis of the HOMOs and LUMOs, in terms of the contribution of the starting atomic orbitals, suggests that the first set of orbitals centred at around −13.0 eV are mainly localized on the cyclopentadienyl ligands with little contribution from the metal d components, while the second set of orbitals centred at around −8.0 eV are mainly non-bonding metal d orbitals (Fig. 3) (see also SUP 56868). This point has been confirmed by the results of calculations performed on the oxidized and reduced species **2**–**5** (see SUP 56868). The removal of two electrons affects mainly the charge of the cyclopentadienyls, while all the other atoms are not significantly affected. On the contrary, a reduction process implies mainly a variation in the oxidation state of the metal, while the charge does not change significantly for the other atoms.

Although reduction by normal reducing agents led to the reductive aggregation of type **2** and **3** complexes,[1a] the introduction of electrons did not affect M–O and M–Cl bonds. The M–O and M–Cl bonding orbitals are indeed very low in energy, so that the corresponding antibonding orbitals are not

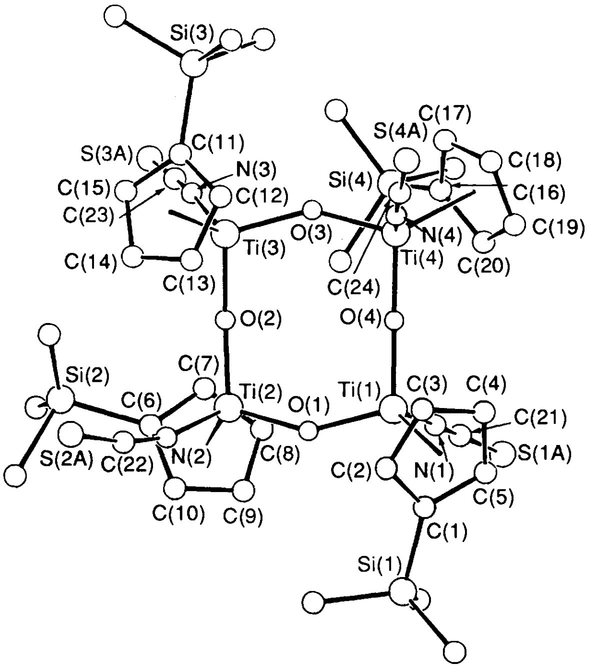


Fig. 2 A SCHAKAL[26] view of complex **9**. For clarity the disordered atoms labelled B and C are omitted

Table 5 Selected bond distances (Å) and angles (°) for complex **9**

Ti(1)–O(1)	1.816(8)	Ti(3)–O(2)	1.819(9)
Ti(1)–O(4)	1.800(9)	Ti(3)–O(3)	1.809(8)
Ti(1)–N(1)	1.959(14)	Ti(3)–N(3)	1.970(16)
Ti(1)–Cp1	2.029(1)	Ti(3)–Cp3	2.042(3)
Ti(2)–O(1)	1.795(9)	Ti(4)–O(3)	1.813(9)
Ti(2)–O(2)	1.796(8)	Ti(4)–O(4)	1.795(9)
Ti(2)–N(2)	1.965(13)	Ti(4)–N(4)	1.961(18)
Ti(2)–Cp2	2.038(4)	Ti(4)–Cp4	2.040(3)
N(1)–Ti(1)–Cp1	113.6(4)	N(3)–Ti(3)–Cp3	113.4(4)
O(4)–Ti(1)–Cp1	114.0(3)	O(3)–Ti(3)–Cp3	117.3(3)
O(1)–Ti(1)–Cp1	118.8(3)	O(2)–Ti(3)–Cp3	115.2(3)
O(4)–Ti(1)–N(1)	101.4(5)	O(3)–Ti(3)–N(3)	102.6(4)
O(1)–Ti(1)–N(1)	101.8(5)	O(2)–Ti(3)–N(3)	101.0(6)
O(1)–Ti(1)–O(4)	105.2(4)	O(2)–Ti(3)–O(3)	105.4(4)
N(2)–Ti(2)–Cp2	113.1(5)	N(4)–Ti(4)–Cp4	113.1(5)
O(1)–Ti(2)–Cp2	116.0(3)	O(4)–Ti(4)–Cp4	115.2(3)
O(2)–Ti(2)–Cp2	117.1(3)	O(3)–Ti(4)–Cp4	121.0(3)
O(2)–Ti(2)–N(2)	101.3(5)	O(4)–Ti(4)–N(4)	100.5(5)
O(1)–Ti(2)–N(2)	103.1(5)	O(3)–Ti(4)–N(4)	100.3(5)
O(1)–Ti(2)–O(2)	104.4(5)	O(3)–Ti(4)–O(4)	103.9(4)
Ti(1)–O(1)–Ti(2)	148.8(6)	Ti(3)–O(3)–Ti(4)	146.7(4)
Ti(2)–O(2)–Ti(3)	171.2(6)	Ti(1)–O(4)–Ti(4)	177.6(7)

Cp1, Cp2, Cp3 and Cp4 refer to the centroids defined by the cyclopentadienyl rings C(1)–C(5), C(6)–C(10), C(11)–C(15) and C(16)–C(20) respectively.

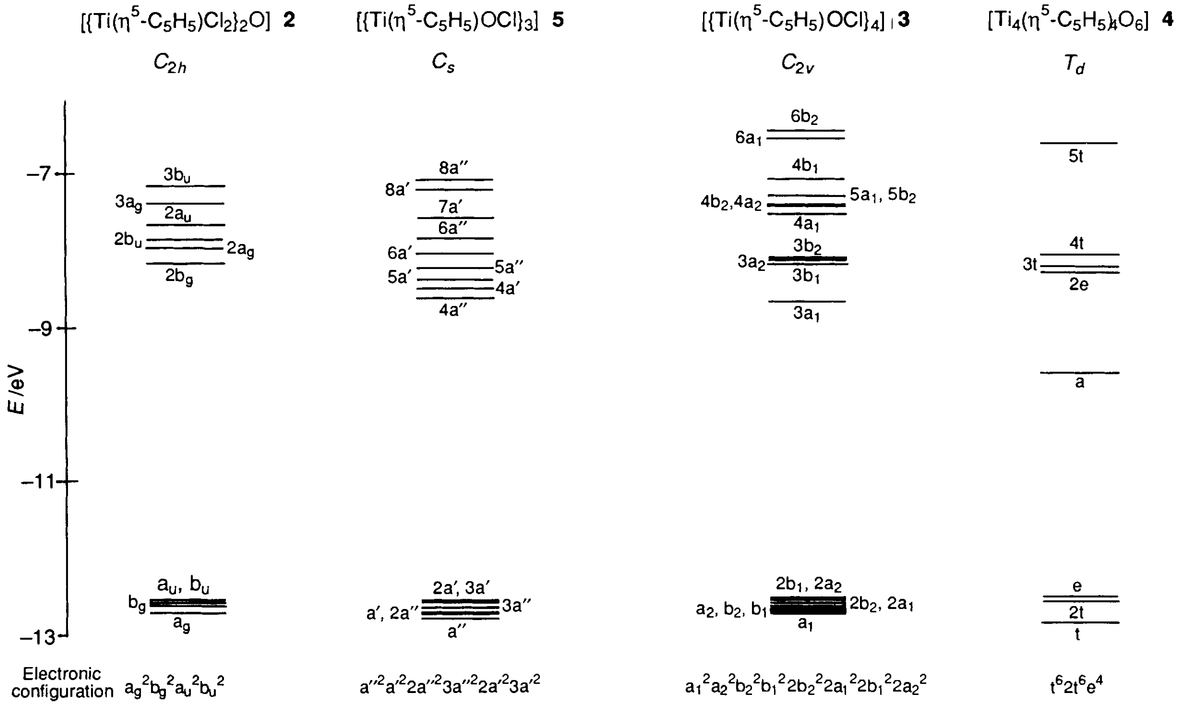


Fig. 3 Energy level diagram for the electronic configurations of complex types **2**–**5**

expected to be suitable electron acceptors. Reduction will place electrons in titanium d orbitals. A chemical reducing agent can only interact with these orbitals *via* the oxygen and chloride bridges. Therefore the preliminary stage of the reductive coupling should not be envisaged as any weakening of the M–O and M–Cl bond, but rather in some Cl and O interaction with a component of the reducing agent. A schematic representation of the energy levels is shown in Fig. 3. A significant feature is the consistent spreading of the LUMO orbitals, which have mainly metal d character as previously noted, over a wide range of energy depending on the symmetry and the complexity of the aggregate. Provided that the topology allows close 'contacts' of several metal atoms, the mixing of the d orbitals of the different metal atoms becomes more efficient and generates a sort of metallic band (see compound **4** *vs.* **2**). In the latter case these orbitals may be considered as the 'aggregate orbitals', rather than orbitals localized on the separate metal atoms. There is a relationship between the existence of a metallic band and the metal–metal distance in an aggregate.[1b] Therefore, the definition of an aggregate should be based more on such electronic properties than on empirical molecular complexity.

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