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FULL PAPER

Stepwise substitution of *N*,*N*-di-isopropylcarbamato groups of $Ti(O_2CN^iPr_2)_4$ by triphenylsilanol leading from eight- to six- and four-co-ordinated titanium(IV)

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Carbamato displacement from the hydrocarbon soluble *N*,*N*-diisopropylcarbamato derivative $Ti(O_2CN^iPr_2)_4$, **1**, by triphenylsilanol led to the bis(silanolato)bis(carbamato) complex $Ti(O_2CN^iPr_2)_2(OSiPh_3)_2$, **2**. X-Ray diffraction showed the mononuclear compound **1** to contain eight-co-ordinated titanium with slightly asymmetric bidentate carbamato groups in a distorted dodecahedral geometry. Titanium is six-co-ordinated in **2** to six oxygen atoms belonging to two bidentate carbamato groups and to two *cis*-arranged silanolato ligands in a distorted octahedral geometry. Exhaustive carbamato displacement from titanium, carried out with a silanol : titanium molar ratio > 4 : 1, afforded the mononuclear tetrasilanolato complex $Ti(OSiPh_3)_4$, **3**, containing a tetrahedral titanium centre.

Introduction

Transition metal catalytic precursors can be used to prepare heterogeneous catalysts by impregnation of a suitable support, or by chemically anchoring the metal to the surface. Surface hydroxyl groups on partially dehydroxylated silica are acidic enough to react with alkyls,[1] allyls,[2] or amido complexes.[3] *N*,*N*-Dialkylcarbamates of main group and transition metals,[4] characterized by a prompt reactivity with protic reagents under mild conditions,[5] have been implanted on silica (M = Sn,[6] Pt[7] or Pd[8]) by exploiting the Brønsted acidity of the surface silanols, and the co-ordination environment of the supported cation has been verified by ^{13}C CP MAS NMR, DRIFT (diffuse reflectance infrared Fourier transform) and XPS spectra and by Wide Angle X-ray Spectroscopy (WAXS) measurements. In order to collect structural information to be compared with the outcome from a metal containing silica, molecular models are currently extensively used.[9] By using the reactions of triphenylsilanol on tetrakis(*N*,*N*-diisopropylcarbamato)-titanium(IV), **1**, we now report the synthesis and structural characterization of bis(*N*,*N*-diisopropylcarbamato)bis(triphenylsilanolato)titanium(IV), **2**, and of the homoleptic silanolato complex of titanium(IV), $Ti(OSiPh_3)_4$, **3**. A recent paper has appeared reporting the preparation and the molecular structure of **3**, obtained by a different route.[10] We were therefore urged to publish our own data, which are complementary to those by Johnson *et al.*

Results and discussion

Compounds of formula $Ti(O_2CNR_2)_4$ have been prepared starting from the titanium amido complexes, $Ti(NR_2)_4$ and CO_2,[11] or by reaction of $TiCl_4$ with the system NHR_2/CO_2.[12] The latter is an example of a general synthetic method for carbamato complexes[13] involving metal halides as reagents. The colourless compounds $Ti(O_2CNR_2)_4$ (R = Et or ^iPr) have been suggested to be mononuclear.[12] In fact they have a good solubility in hydrocarbons and their IR spectra are very similar to those of the isomorphous $Sn(O_2CN^iPr_2)_4$ and $Hf(O_2CN^iPr_2)_4$, whose molecular and crystal structures have previously been reported.[6,12] In the course of this work fine crystals, suitable for an X-ray study, were obtained by recrystallization of $Ti(O_2CN^iPr_2)_4$ from heptane and the compound has been found to be isomorphous with the hafnium and tin derivatives. Also in this case the co-ordination geometry is slightly distorted dodecahedral and involves the eight oxygen atoms of the four bidentate carbamato ligands, whose short bite is mainly responsible for the departure from ideal $\bar{4}2m$ (D_{2d}) symmetry.

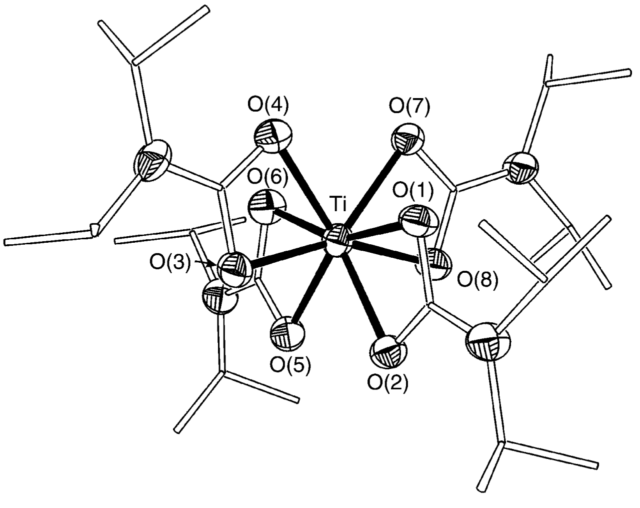

Fig. 1 The molecular structure of $Ti(O_2CN^iPr_2)_4$. Only oxygen and nitrogen atoms are shown as 30% probability ellipsoids.

Fig. 1 shows a view of the molecule, whose bond lengths and angles are listed in Table 1. A comparison between the

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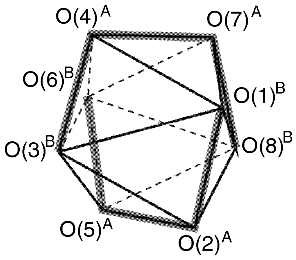
Table 1 Bond lengths (Å) and angles (°) around metal in $Ti(O_2CN^iPr_2)_4$

Ti–O(8)	2.035(4)	Ti–O(4)	2.084(4)
Ti–O(6)	2.034(4)	Ti–O(5)	2.090(4)
Ti–O(3)	2.033(4)	Ti–O(7)	2.106(4)
Ti–O(1)	2.051(4)	Ti–O(2)	2.110(4)
O(8)–Ti–O(6)	92.4(2)	O(4)–Ti–O(5)	127.7(2)
O(8)–Ti–O(3)	156.3(2)	O(8)–Ti–O(7)	62.7(2)
O(6)–Ti–O(3)	94.3(2)	O(6)–Ti–O(7)	81.7(2)
O(8)–Ti–O(1)	92.7(2)	O(3)–Ti–O(7)	140.9(2)
O(6)–Ti–O(1)	155.9(2)	O(1)–Ti–O(7)	79.8(2)
O(3)–Ti–O(1)	90.5(2)	O(4)–Ti–O(7)	77.9(2)
O(8)–Ti–O(4)	140.6(2)	O(5)–Ti–O(7)	127.8(2)
O(6)–Ti–O(4)	80.6(2)	O(8)–Ti–O(2)	80.2(2)
O(3)–Ti–O(4)	63.1(2)	O(6)–Ti–O(2)	141.6(2)
O(1)–Ti–O(4)	80.7(2)	O(3)–Ti–O(2)	80.5(2)
O(8)–Ti–O(5)	80.5(2)	O(1)–Ti–O(2)	62.5(2)
O(6)–Ti–O(5)	63.4(2)	O(4)–Ti–O(2)	127.7(2)
O(3)–Ti–O(5)	82.2(4)	O(5)–Ti–O(2)	78.2(2)
O(1)–Ti–O(5)	140.7(2)	O(7)–Ti–O(2)	125.4(2)

Table 2 Comparison between titanium co-ordination polyhedron in compound **1** and the ideal dodecahedron. The superscripts A and B distinguish the two distorted tetrahedra inscribed in the dodecahedron



Torsion angle/°	1	D_{2d} Dodecahedron
O(4)–O(3)–O(1)–O(2)	31.5	29.5
O(7)–O(8)–O(1)–O(2)	27.3	29.5
O(7)–O(8)–O(6)–O(5)	29.7	29.5
O(4)–O(3)–O(6)–O(5)	28.5	29.5
O(3)–O(4)–O(7)–O(8)	3.6	0
O(1)–O(2)–O(5)–O(6)	0.9	0

geometry of the co-ordination polyhedron and the ideal dodecahedron is reported in Table 2.[14] Moreover, the angles θ^A and θ^B formed by the Ti–O^A and Ti–O^B bonds with the $\bar{4}$ axis (for superscripts A and B, see Table 2) range from 38.7 to 39.3° and from 77.4 to 78.8°, respectively, in fairly good agreement with the corresponding values in a number of $M(L–L)_4$ complexes.[15] The four carbamato ligands chelate the titanium atom in a somewhat asymmetric bidentate way, the differences between the Ti–O distances ranging from 0.05 to 0.07 Å, giving rise to planar four-membered OCOTi rings.

As shown by a literature survey, eight-co-ordination for titanium with oxygen donor ligands is rather uncommon. Only tetrakis(nitrato)titanium(IV)[16] has a titanium atom bonded to eight oxygens. As far as other donor atoms are concerned, the crystal structures of a few eight-co-ordinated compounds are worth mentioning, namely tetrakis(*N*,*N*-diethyldithiocarbamato)titanium(IV),[17] tetrakis(3,5-diphenylpyrazolato)titanium(IV),[18] tetrakis(*N*,*N*-diethylmonothiocarbamato)titanium(IV),[19] tetrakis(*N*,*N*-diethylhydroxylamido-*O*,*N*)titanium(IV),[20] and the ion [bis(oxyiminodiacetato)titanium(IV)]$^{2-}$,[21] the donor atoms being, respectively, eight sulfurs, eight nitrogens, four sulfurs/four oxygens, four oxygens/four nitrogens, six oxygens/two nitrogens. Finally, the only structurally established dialkylcarbamato complex of titanium(IV) is bis(dimethylamido)bis(*N*,*N*-dimethylcarbamato)titanium(IV),[11c] in a severely distorted octahedral geometry, with Ti–O bond lengths in the 2.030–2.197 Å range.

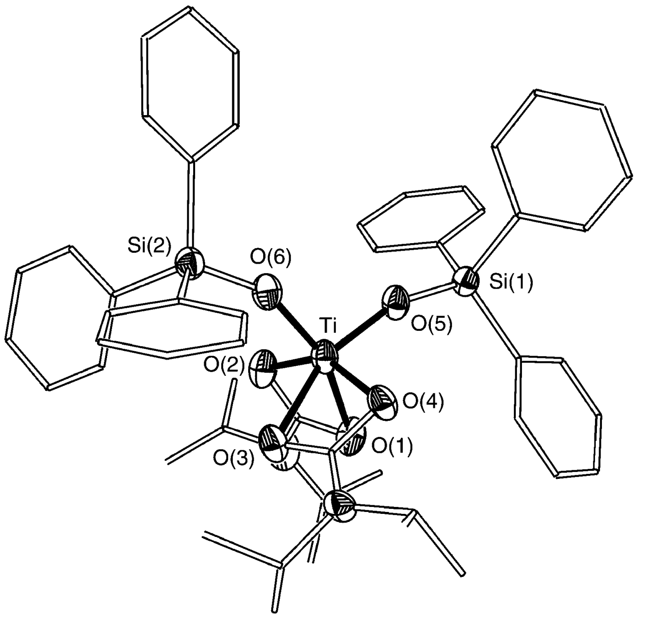


Fig. 2 The molecular structure of $Ti(O_2CN^iPr_2)_2(OSiPh_3)_2$. Only oxygen, nitrogen and silicon atoms are shown as 30% probability ellipsoids.

Table 3 Bond lengths (Å) and angles (°) around titanium in $Ti(O_2CN^iPr_2)_2(OSiPh_3)_2$

Ti–O(6)	1.788(4)	Ti–O(1)	2.114(4)
Ti–O(5)	1.804(4)	Ti–O(3)	2.115(4)
Ti–O(2)	1.988(4)	Si(1)–O(5)	1.634(4)
Ti–O(4)	2.006(4)	Si(2)–O(6)	1.638(4)
O(6)–Ti–O(5)	101.6(2)	O(4)–Ti–O(1)	92.2(2)
O(6)–Ti–O(2)	93.8(2)	O(6)–Ti–O(3)	91.7(2)
O(5)–Ti–O(2)	105.9(2)	O(5)–Ti–O(3)	57.2(2)
O(6)–Ti–O(4)	105.4(2)	O(2)–Ti–O(3)	91.5(2)
O(5)–Ti–O(4)	94.6(2)	O(4)–Ti–O(3)	63.7(2)
O(2)–Ti–O(4)	148.5(2)	O(1)–Ti–O(3)	82.3(2)
O(6)–Ti–O(1)	156.6(2)	Si(1)–O(5)–Ti	159.6(3)
O(5)–Ti–O(1)	92.0(2)	Si(2)–O(6)–Ti	154.2(3)
O(2)–Ti–O(1)	63.9(2)		

Earlier work from these Laboratories had shown the carbamato ligand to be a good leaving group, releasing carbon dioxide in the presence of proton active substances of even moderate acidity.[5] Consistent with this well established reactivity, $Ti(O_2CN^iPr_2)_4$ reacts promptly with triphenylsilanol (pK_a in THF 10.8[22]) in toluene at room temperature according to eqn. (1). The disubstituted product **2** is soluble in toluene, and

$$Ti(O_2CN^iPr_2)_4 + 2\,Ph_3SiOH \longrightarrow Ti(O_2CN^iPr_2)_2(OSiPh_3)_2 + 2\,HN^iPr_2 + 2\,CO_2 \quad (1)$$

therefore easily purified from the products of further substitution which are much less soluble: high purity and good yields of the product can be secured by using a $Ph_3SiOH : Ti(O_2CN^iPr_2)_4$ molar ratio as close as possible to 2 : 1.

The molecular structure of compound **2** is shown in Fig. 2 and the bonding parameters around the metal are in Table 3. Titanium is surrounded by six oxygen atoms whose disposition cannot be traced to any regular polyhedron. The small bite of the carboxyl groups reduces the O(1)–Ti–O(2) and O(3)–Ti–O(4) angles to 64°, thus allowing the more bulky silanol ligands to occupy a larger section of the co-ordination sphere around the metal. According to this, a large O(5)–Ti–O(6) angle of 102° is observed. The Ti–O distances involving the carbamato oxygen atoms are similar to those observed in compound **1**, while those pertaining to the silanolato groups are significantly shorter by about 0.2 Å. The values reported in Table 3 compare well with the Ti–O distances for terminal carboxy- and terminal alkoxy- ligands generally found in titanium compounds.[23] For compound **2** the short Ti–O distances observed in silanolato bonds with respect to carbamato is possibly due to less crowding in the area occupied by the former ligands, or to some degree of π bonding to Ti^{IV}. The Ti–O–Si angles are substantially lower than 180° and rather different from each other, packing requirements being probably also important in this connection. As it can be seen from Fig. 2, the molecule shows an approximate 2 (C_2) symmetry around an axis bisecting the O(5)–Ti–O(6) angle.

The use of an excess of silanol leads to complete displacement of the carbamato ligands affording the tetrasilanolato, $Ti(OSiPh_3)_4$, **3**, see eqn. (2). The reactivity of TiX_4 compounds

$$Ti(O_2CN^iPr_2)_4 + 4\,Ph_3SiOH \longrightarrow Ti(OSiPh_3)_4 + 4\,HN^iPr_2 + 4\,CO_2 \qquad (2)$$

(X = OR or Cl) with alkylsilanols for the preparation of siloxytitanium derivatives has been exploited from the beginning of this type of chemistry,[10,24,25] the first preparation of a titanium silanolato complex, $Ti(OSiMe_3)_4$, dating back to 1955.[24a]

Recently, the high interest in reactions catalysed by TS-1[26] or by Ti/MCM-4[27] led several groups to study molecular models of the heterogeneous catalysts believed to contain tetrahedral titanium centres.[28]

The molecular structure of compound **3**, determined independently by us by X-ray diffraction at room temperature, corresponds to that measured on the same compound at 100 K with a Synchrotron Radiation Source.[10]

Experimental

All preparations were carried out using standard Schlenk techniques. All solvents were freshly distilled over standard drying agents under dinitrogen and all reactions carried out under a dinitrogen atmosphere. $Ti(O_2CN^iPr_2)_4$ was synthesized as previously described.[12] Commercially available (Aldrich) Ph_3SiOH was dried for 12 h over P_4O_{10} *in vacuo*. Elemental analyses (C, H, N) were performed by Laboratorio di Microanalisi della Facoltà di Farmacia, Università di Pisa, with a C. Erba model 1106 analyser. IR spectra were measured with a FT-IR Perkin-Elmer model 1725X spectrophotometer, NMR spectra using a Varian Gemini 200 MHz spectrometer.

Syntheses

$Ti(O_2CN^iPr_2)_2(OSiPh_3)_2$ 2. To a toluene solution (250 mL) of $Ti(O_2CN^iPr_2)_4$ (1.83 g, 2.93 mmol), Ph_3SiOH (1.61 g, 5.82 mmol) dissolved in 100 mL toluene was added dropwise in 3 h. During the addition, repeated vacuum/dinitrogen cycles were carried out. After 12 h stirring a small amount of a colourless solid was discarded by filtration, and all the volatiles were removed *in vacuo.* To the residue, 100 mL of heptane were added and the suspension was filtered. The colourless solid was dried for 6 h *in vacuo* (1.68 g, 64.9% yield) (Found: C, 67.2; H, 5.8; N, 2.1. Calc. for $C_{50}H_{58}N_2O_6Si_2Ti$: C, 67.5; H, 6.8; N, 3.2%). IR (range 1700–1300 cm^{-1}, Nujol): 1558vs, 1505s, 1430s and 1359s. NMR (C_6D_6, ppm from TMS): ^1H, δ 0.96 (CH_3, d, 24 H), 3.60 (CH, sept, 4 H), 7.23 (*m*- and *p*-CH, m, 18 H) and 8.00 (*o*-CH, m, 12 H); ^{13}C, δ 20.69 (CH_3), 45.68 (CH), 129.71 ($C_{ar}H$), 136.03 ($C_{ar}H$), 137.18 ($C_{ar}H$) and 168.60 (CO_2). The product was recrystallized from heptane.

$Ti(OSiPh_3)_4$ 3. A toluene solution (120 mL) of Ph_3SiOH (2.47 g, 8.94 mmol) was added dropwise (3 h) to a toluene solution (250 mL) of $Ti(O_2CN^iPr_2)_4$ (1.28 g, 2.05 mmol). During the addition several vacuum/dinitrogen cycles were carried out. After the addition of the second equivalent of silanol a colourless solid began to precipitate. When the addition was complete, toluene was partially evaporated *in vacuo*. After 12 h stirring the suspension was filtered and the solid (2.06 g, 87.4% yield) dried *in vacuo* (Found: C, 74.6; H, 3.9. Calc. for **3**, $C_{72}H_{60}O_4Si_4Ti$: C, 75.2; H, 5.3%). IR (range 1700–1300 cm^{-1}, Nujol): 1662w, 1588m, 1567w, 1485s, 1428vs, 1333m and 1304m. The solid is stable in air for several minutes and has a low solubility in many organic solvents. It was recrystallized from hot THF giving colourless crystals.

Table 4 Crystal data and structure refinement for compounds **1** and **2**

	1	**2**
Chemical formula	$C_{28}H_{56}N_4O_8Ti$	$C_{50}H_{58}N_2O_6Si_2Ti$
Formula weight	624.67	887.06
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	12.589(2)	11.003(1)
b/Å	21.768(4)	13.298(2)
c/Å	14.617(3)	18.403(3)
α/°		83.63(1)
β/°	112.67(2)	84.05(1)
γ/°		66.80(1)
V/Å^3	3696(1)	2454.4(6)
T/K	293(2)	203(2)
Z	4	2
μ/mm^{-1}	0.277	0.271
Data/restraints/parameters	1999/0/386	6398/0/5502
$R(F_o)$ $[I > 2\sigma(I)]$	0.0457	0.0625
$R_w(F_o^2)$ $[I > 2\sigma(I)]$	0.1052	0.1439

X-Ray crystallographic studies

The diffractometric measurements were carried out by using an Enraf-Nonius CAD-4 diffractometer for compound **1** and a Siemens P4 diffractometer for **2** and **3**, equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). All data were collected in the ω–2θ scan mode, and three standard reflections were monitored every 97 for checking crystal decay and equipment stability. Data reduction was done by the SDP package for **1**[29a] and by the XSCANS program for **1** and **2**.[29b]

Crystals of compound **1** from heptane are colourless prisms. One was sealed in a glass capillary under a dinitrogen atmosphere and 6934 intensity data were collected and corrected in a standard way. The space group determined from systematic absences, the chemical composition and the cell parameters indicated that the crystal was isotypical with the corresponding hafnium[12] and tin[6] compounds. The atomic positions were taken from the structure of the hafnium derivative $Hf(O_2CN^iPr_2)_4$ and refined by the SHELX 97 program.[30] In the final refinement cycles, based on *F*, anisotropic thermal parameters were used for all non-hydrogen atoms. Lattice parameters and the final reliability factors are listed in Table 4.

Crystals of compound **2** are colourless plates. One, sealed in a glass capillary under an N_2 atmosphere, showed the cell parameters listed in Table 4. 6801 Intensities were collected and corrected for Lorentz and polarization effects and for absorption by the ψ-scan method. After merging of equivalent reflections ($R_{int} = 0.0391$), 6398 independent reflections were obtained. The structure was solved by direct methods and refined by least squares based on F^2 (SHELXTL).[31] The final reliability factors listed in Table 4 refer to the last refinement cycle with anisotropic thermal factors for all non-hydrogen atoms. Some thermal factors of the carbon atoms within the external parts of the ligands were abnormally high (disorder and thermal motion), the *R* factors being therefore affected.

The crystals of compound **3** were analysed at room temperature and found to have cell parameters consistent with those reported.[10]

CCDC reference number 186/2202.

See http://www.rsc.org/suppdata/dt/b0/b005114o/ for crystallographic files in .cif format.

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