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Routes to titanium tetrazole complexes ☆

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Abstract

The titanium tetrazole coordination complex $[TiCl_4 \cdot (PhCN_4H)_2]$ has been prepared by treatment of $TiCl_4$ with two equivalents of 5-phenyltetrazole in dichloromethane and spectroscopically and crystallographically characterised. The solid-state structure of this compound consists of six-coordinate titanium centres with *cis* ligated tetrazoles. The individual $[TiCl_4 \cdot (PhCN_4H)_2]$ dimerise via intermolecular N···H–N hydrogen bonding interactions and are further organised into 2D supramolecular arrays. Mass spectral evidence indicates that the individual tetrazole ligands are only weakly bound, limiting the potential of this complex as a titanium nitride precursor. 3 + 2 cycloaddition of tributyltin azide with 2-toluinitrile at 200 °C has afforded the tributylstannyl tetrazole $[SnBu_3\{5\text{-}(2\text{-}MeC_6H_4)CN_4\}]_n$. Crystallographic analysis shows that this compound exists as a supramolecular coordination polymer propagated via trigonal bipyramidal tin centres linked by N^1–Sn–N^3 interactions. Preliminary reactivity studies of this tin complex with titanium tetrachloride in an effort to synthesise a covalently bound titanium tetrazolyl complex have thus far yielded incomplete elimination of the expected Bu_3SnCl by-product and intractable titanium-containing products.

Keywords: Titanium; Tin; Tetrazole; Nitride precursor; Cycloaddition

1. Introduction

The combination of a better conductivity (4698 kS cm^{-1}) than titanium metal (2381 kS cm^{-1}), extreme hardness (9–10 Moh) and a refractory nature dictate that titanium nitride (TiN) is perhaps the most extensively applied transition metal nitride in both microelectronic (metal/semiconductor interconnects) and architectural applications (protective coatings) [1,2]. High quality thin films of cubic TiN may be produced by atmospheric pressure chemical vapour deposition (APCVD) in a process which conventionally employs ammonia gas and gaseous titanium tetrachloride transported in an inert carrier [3]. Although efficient, this process suffers problems of pre-reaction and requires removal of the corrosive HCl by-product. These qualities, coupled to inconveniently high substrate temperatures of 600–900 °C required by this process, have prompted a search for alternative 'designed' or 'single source' molecular precursors with more amenable reaction/decomposition characteristics. Although successfully attenuating undesirable prereactions, alternative dual source systems which apply volatile tetrakis(dialkyl)amido titanium precursors such as $Ti(NMe_2)_4$ and $Ti(NEt_2)_4$ and ammonia and mixed $TiCl_4$/alkyl amine feedstocks have provided their own additional problems of carbon contamination and poor step coverage [4–7]. Initial efforts to address these difficulties by design of suitable single source precursors containing a preprogrammed combination of titanium and nitrogen were prompted by speculation about the nature of intermediate products formed by these systems prior to film growth. Accordingly, a number of titanium amido and imido species, such as $[CpTiCl_2\{N(SiMe_3)_2\}]$ and $[\{Ti(\mu\text{-}N^tBu)(NMe_2)_2\}_2]$, have been prepared and examined in this context [8–12]. Neither these nor more recent studies of mono- or bis-azido complexes [for example $[\{Ti(N^tBu)Cl(N_3)(py)_2\}_2]$ and $[\{Ti(NCy)(N_3)_2(py)_2\}_2]$ (py = pyridine)] have, however, yielded effective TiN precursors. Film growth in these latter cases is hampered either by a lack of volatility or unacceptably

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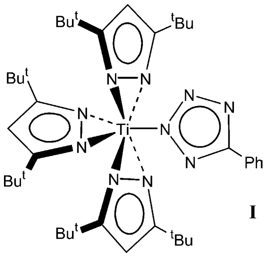
high levels of carbon contamination approaching 35% [13,14].

Pyrazolate anions derived by deprotonation of parent pyrazole heterocycles have been shown to provide a flexible N-donor ligand set in titanium chemistry [15–17]. The use of titanium pyrazolyl derivatives as molecular precursors to TiN is likely to be hampered, however, by similar problems of carbon contamination to those outlined above due to the presence of direct carbon to nitrogen bonds in the delocalised heterocycle. We have turned our attention therefore to the synthesis of titanium tetrazolato derivatives in the hope that the high nitrogen content of this latter ligand type will encourage clean elimination of thermodynamically stable small molecule (N_2 and nitrile) side products and retention of Ti–N linkages at relatively low temperatures.

Although a number of inorganic and organometallic tetrazolyl derivatives have been cystallographically characterised in recent years [18–34], structurally authenticated titanium derivatives are restricted to the seven coordinate tris(3,5-di-*tert*-butylpyrazolato)(5-phenyltetrazolato)titanium (**I**) [31]. Although the subject of a low precision X-ray structural determination and not reported in detail, η_1-N^2 coordination of the tetrazolyl anion to titanium was confirmed. Due to the multiplicity of potential nitrogen donors, many metal-coordinated tetrazoles are prone to coordination polymerisation. The monodenticity of the tetrazolyl ligand of **I** is, most likely, therefore enforced by the η^2-coordination of the three bulky pyrazolato co-ligands. As such co-ligands were reasoned to be of likely detriment to clean precursor decomposition, our initial studies have targeted titanium tetrazole complexes with simple chloride ligands sets. We now report our studies which have resulted in the high yield synthesis of a simple Ti(IV) tetrazole coordination complex along with our initial exploration of an organotin-based strategy that attempts to effect both clean formation of titanium tetrazolyl derivatives and a means by which the steric demands at the C^5 position of the tetrazole ring may be readily modulated.



I

2. Experimental

2.1. General

All reactions were conducted under an atmosphere of dry argon and manipulated either on a double manifold vacuum line or in a dinitrogen-filled drybox operating at less than 1 ppm of O_2. Solvents were purified by distillation from an appropriate drying agent (THF from potassium, CH_2Cl_2 from CaH_2 and hexane from Na/K alloy). NMR spectra were recorded at 300.13 (^{1}H), 125.8 (^{13}C) and 186.4 MHz (^{119}Sn) from samples in $CDCl_3$ or d_8-THF; Chemical shifts are relative to $SiMe_4$ for ^{1}H and ^{13}C NMR. ^{119}Sn NMR were referenced externally to Me_4Sn. Mass spectra were obtained at 70 eV. Tributyltin azide was synthesised by a literature procedure [35].

Caution! All reactions of azides and tetrazole compounds must be treated as potentially explosive and conducted behind a rigid safety screen.

2.2. $[TiCl_4 \cdot (PhCN_4H)_2]$ (**1**)

A solution of titanium tetrachloride (1.97 g, 10.4 mmol) in dichloromethane (30 cm^3) was added at room temperature to a stirred slurry of $PhCN_4H$ (3.04 g, 20.8 mmol) in dichloromethane (40 cm^3). This resulted in the formation of a dense pale yellow precipitate and a yellow solution. The yellow solid, **1** (4.70 g, 94%), was isolated by filtration and dried under vacuum. Cooling of the filtrate to −30 °C resulted in the formation of a small number of yellow crystals suitable for X-ray diffraction after 3 days. Elemental and spectroscopic analysis of the bulk powder was consistent with an unsolvated form. *Anal.* Calc. for $C_{14}H_{12}Cl_4N_8Ti$: C, 34.87; H, 2.51; N, 23.25. Found: C, 34.71; H, 2.36; N, 23.00%. ^{1}H NMR [d^8-THF, 298 K] δ: 7.49 (m, 6H, m, *p*-C_6H_5), 8.01 (m, 4H, *o*-C_6H_5), 15.1 (br.s, 2H, N–H). ^{13}C{^{1}H} NMR [d^8-THF, 298 K] δ: 126.3 (*i*-C_6H_5), 127.4 (*o*-C_6H_5), 129.3 (*m*-C_6H_5), 131.2 (*p*-C_6H_5). MS (EI$^+$, 70 eV), 190 (55%, $TiCl_4$), 153 (100, $TiCl_3$), 118 (70, $TiCl_2$), 103 (25, PhCN), 83 (45, TiCl).

2.3. $[SnBu_3\{5\text{-}(2\text{-}MeC_6H_4)CN_4\}]_n$ (**2**)

Bu_3SnN_3 (3.17 g, 9.75 mmol) and 2-toluinitrile (1.25 g, 9.75 mmol) were heated at 200 °C for 2 h under nitrogen to yield a pale amber glass. This was washed with hexane (30 cm^3) and dried in vacuo. Storage of the resultant colourless glass at room temperature for 3 days induced crystallisation to produce compound **2** in effectively stoichiometric yield. *Anal.* Calc. for $C_{20}H_{34}N_4Sn$: C, 53.47; H, 7.64; N, 12.48. Found: C, 53.56; H, 7.64; N, 12.48%. ^{1}H NMR [$CDCl_3$, 298 K] δ: 0.71 (t, 9H, $(CH_2)_3C\mathit{H}_3$), 1.05–1.34 (m, 18H, $(C\mathit{H}_2)_3CH_3$), 2.17 (s, 3H, Ar–Me), 7.15–7.29 (m, 4H, Ar–H). ^{13}C{^{1}H} NMR [$CDCl_3$, 298 K] δ: 13.6 $(CH_2)_3\mathit{C}H_3$, 18.2 ($\mathit{C}H_2(CH_2)_2CH_3$, $^1J_{117,119\ \mathrm{Sn/C}} = 457$ Hz), 20.2 (Ar–Me), 27.0 ($(CH_2)_2\mathit{C}H_2CH_3$, $^3J_{117,119\ \mathrm{Sn/C}} = 70.9$ Hz), 28.0 ($CH_2\mathit{C}H_2CH_2CH_3$ $^2J_{117,119\ \mathrm{Sn/C}} = 27.9$ Hz), 125.6, 128.6, 129.8, 130.5, 137.7 (Ar–C), 161.5 (CN_4). ^{119}Sn{^{1}H} NMR [$CDCl_3$, 298 K] δ: −17.9 ($\Delta\nu_{1/2}$ −2 kHz).

2.4. Attempted reaction of **2** and $TiCl_4$

To a solution of compound **2** (2.37 g, 5.26 mmol) in dichloromethane (120 cm^3) was added a solution of titanium tetrachloride (1.0 g, 5.26 mmol) in dichloromethane (20 cm^3). This resulted in the immediate formation of an orange solution which darkened to a vivid red over the subsequent 48 h. In vacuo removal of the solvent produced a dark red sticky solid, which was washed with hexane (2 × 30 cm^3) to produce a yellow solid. The ^1H NMR spectrum of this material in d^8-THF displayed resonances corresponding to both Bu_3Sn and the tetrazole ligand. Crystals which formed in the NMR tube were suitable for X-ray analysis and proved to be a hydrolysis product, the oxo-bridged species $(THF)_2Cl_3Ti–O–TiCl_3(THF)_2$.

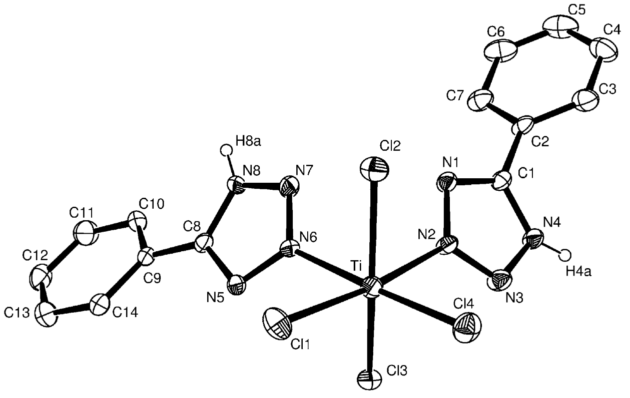


Fig. 1. The asymmetric unit of **1** with thermal ellipsoids drawn at the 30% probability level. All hydrogen atoms apart from H4a, H4b removed for clarity.

3. Results and discussion

Winter [36] has studied the treatment of titanium tetrachloride with two equivalents of a variety of substituted pyrazoles. Reaction with 3,5-di-*tert*-butylpyrazole resulted in HCl elimination and the formation of a mixture of molecular L_2TiCl_4 and ionic $[LH^+]_2[TiCl_6^{2-}]$ (where L = 3,5-di-*tert*-butylpyrazole) products. Conversely, reaction with less sterically demanding heterocycles produced a series of six-coordinate $TiCl_4 \cdot L'_2$ adducts (where L' = 3,5-dimethylpyrazole, 3-methylpyrazole, 4-iodopyrazole), where the adoption of either a *cis* or *trans* coordination geometry was reasoned to be largely dependent upon the steric profile of the pyrazole ligand. Prompted by these observations, and intrigued by the possible divergent reactivity that may be induced by the increased acidity of the tetrazole heterocycle [37], we carried out the analogous reaction between two equivalents of commercially available 5-phenyltetrazole and $TiCl_4$ in dichloromethane. This resulted in the immediate precipitation of compound **1** as a pale yellow powder, which was isolated by filtration. Elemental analysis indicated that a 2:1 adduct had been formed, while the presence of a tetrazole N–H functionality was confirmed by the observation of weak absorptions at 3340 and 3390 cm^{-1} in the infra-red spectrum. Although **1** was not soluble in non-donor solvents, ^1H NMR data collected in THF-d_8 displayed resonances similar to those of the free neutral tetrazole. Although these data do not preclude the presence of compound **1** in solution, we tentatively conclude that the tetrazole ligands are displaced from the titanium coordination sphere by the donor solvent. Despite this problematic insolubility, storage of the pale yellow, dilute but saturated supernatant dichloromethane solution from the original reaction at −30 °C for one week produced a small number of yellow single crystals of **1** as a bis-dichloromethane solvate suitable for an X-ray diffraction analysis. The asymmetric unit resulting from this analysis is illustrated in Fig. 1. Selected bond lengths and angles are provided in Table 1, while details of the X-ray analysis are listed in Table 2.

Complex **1** is revealed to exist as a six-coordinate adduct with *cis* tetrazole ligands. The coordination sphere exhibits significant deviations from ideal octahedral geometry, with *cis* angles ranging from 81.94(14)° [N(6)–TiCl(3)] to 99.30(8)° [Cl(4)–Ti–Cl(1)] and the *trans* angles between 160.92(8)° [Cl(3)–TiCl(2)] and 174.06(14)° [Cl(4)–Ti–N(6)]. The Ti–Cl(1) [2.231(2) Å] and Ti–Cl(4) [2.216(2) Å] bonds that are *trans* to the tetrazole N-donor atoms are significantly shorter than the mutually *trans* Ti–Cl(2) [2.275(2) Å] and Ti–Cl(3)

Table 1
Selected bond lengths (Å) and angles (°) for compound **1**

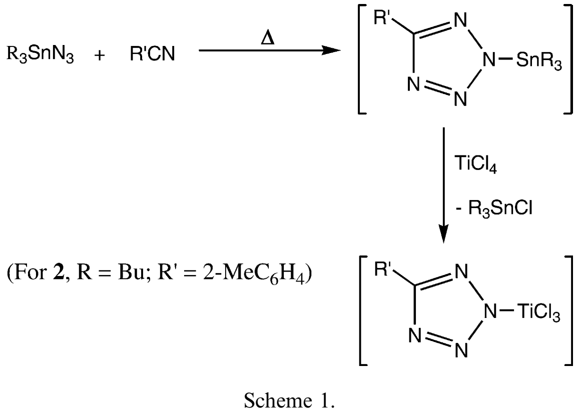
Bond lengths			
Ti–Cl(4)	2.216(2)	Ti–Cl(1)	2.231(2)
Ti–N(6)	2.265(5)	Ti–Cl(3)	2.271(2)
Ti–Cl(2)	2.275(2)	Ti–N(2)	2.279(5)
N(1)–C(1)	1.326(7)	N(1)–N(2)	1.357(6)
N(2)–N(3)	1.294(6)	N(3)–N(4)	1.344(7)
N(4)–C(1)	1.340(7)	N(5)–C(8)	1.324(7)
N(5)–N(6)	1.365(7)	N(6)–N(7)	1.290(6)
N(7)–N(8)	1.329(7)	N(8)–C(8)	1.336(8)
Bond angles			
Cl(4)–Ti–Cl(1)	99.30(8)	Cl(4)–Ti–N(6)	174.06(14)
Cl(1)–Ti–N(6)	86.43(14)	Cl(4)–Ti–Cl(3)	95.71(8)
Cl(1)–Ti–Cl(3)	96.86(8)	N(6)–Ti–Cl(3)	81.94(14)
Cl(4)–Ti–Cl(2)	96.32(8)	Cl(1)–Ti–Cl(2)	95.72(8)
N(6)–Ti–Cl(2)	84.62(14)	Cl(3)–Ti–Cl(2)	160.93(8)
Cl(4)–Ti–N(2)	89.82(14)	Cl(1)–Ti–N(2)	170.84(15)
N(6)–Ti–N(2)	84.48(18)	Cl(3)–Ti–N(2)	82.93(14)
Cl(2)–Ti–N(2)	82.37(14)	C(1)–N(1)–N(2)	105.4(5)
N(3)–N(2)–N(1)	112.0(5)	N(3)–N(2)–Ti	120.5(4)
N(1)–N(2)–Ti	127.0(4)	N(2)–N(3)–N(4)	105.1(5)
C(1)–N(4)–N(3)	109.9(5)	C(8)–N(5)–N(6)	105.8(5)
N(7)–N(6)–N(5)	111.1(5)	N(7)–N(6)–Ti	123.0(4)
N(5)–N(6)–Ti	125.9(4)	N(6)–N(7)–N(8)	105.5(5)
N(7)–N(8)–C(8)	110.6(5)	N(1)–C(1)–N(4)	107.6(5)

Table 2
Selected crystallographic and data collection parameters for compounds **1** and **2**

	1	**2**
Chemical formula	$C_{14}H_{12}Cl_4N_8Ti \cdot 2(CH_2Cl_2)$	$C_{20}H_{34}N_4Sn$
Formula weight	651.87	449.20
T (K)	173(2)	173(2)
Crystal size (mm)	$0.2 \times 0.2 \times 0.1$	$0.4 \times 0.2 \times 0.4$
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$ (No. 14)	$Fdd2$ (No. 43)
a (Å)	12.4934(14)	21.2292(10)
b (Å)	14.1217(19)	33.379(3)
c (Å)	16.0886(17)	12.8979(11)
α (°)	90	90
β (°)	105.519(5)	90
γ (°)	90	90
Z	4	16
V (Å^3)	2735.0(6)	9140(1)
D_{calc} (Mg m^{-3})	1.58	1.31
μ (mm^{-1})	1.12	1.13
θ range (°)	3.76–21.96	3.76–25.04
R_1; $wR_2[I > 2\sigma(I)]$	0.059; 0.108	0.050, 0.101
R_1; wR_2 all data	0.100; 0.122	0.073; 0.110
Measured/independent reflections/R_{int}	10 987/3310/0.092	10 141/3559/0.068
Reflections with $I > 2\sigma(I)$	2277	2755

[2.271(2) Å] bonds. These observations and bond lengths are similar to those in other $TiCl_4 \cdot L_2$ *cis* adducted structures including the bis-pyrazole adduct $[TiCl_4(4\text{-}IC_3H_2N_2)_2]$ [36]. The Ti–N bond distances [2.279(5), 2.265(5) Å] of **1** are, however, significantly longer than those reported for this analogous pyrazole adduct [2.235(7) Å] and possibly result from the reduced basicity of the tetrazole moiety [37].

Mass spectral analysis of compound **1** displayed a highest mass fragment at 190 corresponding to the molecular ion $[TiCl_4]^+$. This is an indication that the tetrazole ligands are only weakly bound and most likely inhibits the practical potential of **1** as a nitride precursor. For this reason, we turned our attention to the synthesis of titanium tetrazolyl derivatives containing more robust covalent Ti–N bonds. Winter [31] has reported previously that reactions of the 5-phenyltetrazolyl anion with titanium tetrahalides resulted in intractable mixtures of products, an observation that was confirmed by the present study. Ab initio calculations undertaken as part of the same study highlighted the small energy difference (ca. 5 kcal/mol) that exists between η^1- and η^2-ligated titanium tetrazolyl derivatives while older quantum mechanical calculations have shown that N^1 and N^2 binding are energetically equivalent [38]. The mixture of species that likely results from such facile isomer interconversion, as well as the potential for the formation of complex extended network structures, mitigates therefore against the isolation of simple homo- and heteroleptic titanium tetrazolyl complexes unless the reaction conditions are very carefully controlled. In an attempt to address this issue, we reasoned that enhanced product solubility may result by variation of the tetrazole C^5 substituent steric demands. A very wide range of tetrazole derivatives may be accessed by the straightforward $3+2$ cycloaddition reaction of organotin azides and RCN dipolarophiles (Scheme 1) [22–27,39]. The ready availability of a great number of substituted nitriles allows facile variation of the resultant tetrazole substituent and provides the heterocycle in a synthetically convenient deprotonated form for subsequent metathesis with $TiCl_4$ (Scheme 1). A similar strategy involving Me_3SiCl elimination has previously been successfully applied to the synthesis of sterically encumbered pyrazolatotrichlotitanium derivatives [16], while R_3SnX elimination from reaction between triorganostannyltetrazoles and alkyl halides has been demonstrated as a straightforward means to tetrazole N-alkylation [40]. Although a great number of potential nitrile precursors are available, our initial



Scheme 1.

efforts identified 2-toluinitrile as a suitable candidate due to the small incremental increase in steric demands over 5-phenyltetrazole and the spectroscopic simplicity of the *ortho*-substituted aryl tetrazolyl product.

Tributyltin azide was synthesised by literature methods [35] while $[SnBu_3\{5\text{-}(2\text{-}MeC_6H_4)CN_4\}]$ (**2**) was synthesised using the well established methodology in which the neat triorganotin azide is heated with a slight excess of the chosen nitrile [39]. The reaction was monitored by the disappearance of the IR bands due to $\nu(CN)$ at ca. 2250 cm^{-1} and $\nu_{asym}(N_3)$ at ca. 2060 cm^{-1}. The glassy, crude solid product that was produced upon cooling was washed with hexane to remove excess nitrile and crystallised upon standing at room temperature for three days to produce analytically pure compound **2**.

Compound **2** was sufficiently soluble in $CDCl_3$ to enable the collection of good quality NMR data. The ^1H and ^{13}C NMR spectra were consistent with the proposed structure. The $^1J(^{13}C–^{119}Sn)$ coupling constant of 457 Hz implied a coordination number of >4 about tin, while use of the semiempirical relationship derived by Holecek and Lycka for correlating ^1J data and coordination geometry yielded a value of 123.2° for the C–Sn–C bond angles, consistent with a *trans*-trigonal bipyramidal N_2SnC_3 geometry about tin [41]. These observations are similar to those of previous solution NMR studies of triorganostannyl tetrazoles that have deduced the formation of concentration- and temperature-dependent *N*,*N*′-bridged oligomeric species in solution [22,23,42]. The fluxionality of these systems and similar dynamic behaviour deduced for certain platinum and cobalt tetrazoles [43,44] may also be used to rationalise the broad $^{119}Sn\{^1H\}$ NMR signal ($\Delta\nu_{1/2}$, ca. 2 kHz) observed at −17.9 ppm.

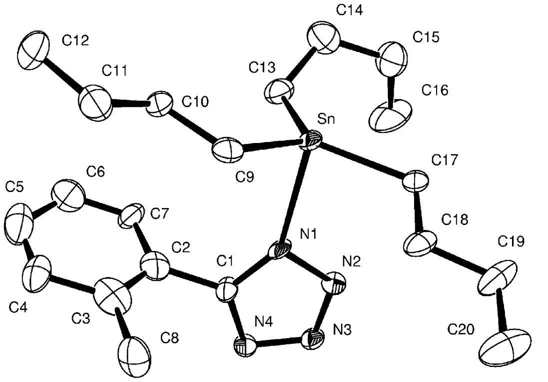


Fig. 2. The asymmetric unit of **2** with thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms removed for clarity.

The solid-state structure of **2** has been crystallographically confirmed. Details of the analysis are listed in Table 2, while selected bond lengths and angles are produced in Table 3. Although the asymmetric unit (Fig. 2) contains only one nitrogen donor, the geometry at tin is best described as trigonal bipyramidal and is defined by *trans*-N_2SnC_3 coordination. The additional tetrazole coordination is provided by a nitrogen atom of an adjacent tetrazole unit. This structural feature is similar to that found in all previously characterised organotin tetrazoles, while both inter- and intramolecular bonding parameters are typical of molecules of this type [22–24]. Within the accuracy of the data, the two Sn–N bonds are identical and serve to propagate a 1D, helical polymeric array along 2_1 screw axes parallel to *c*. This occurs via the $N^1 + N^3$ (N(1)/N(3)) bridging mode, which has previously been observed in a number of related triorganostannyl tetrazole derivatives (Fig. 3)

Table 3
Selected bond lengths (Å) and angles (°) for compound **2**

Bond lengths			
Sn–C(13)	2.131(9)	Sn–C(17)	2.134(8)
Sn–C(9)	2.138(9)	Sn–N(3)′	2.368(7)
Sn–N(1)	2.406(7)	N(1)–C(1)	1.336(9)
N(1)–N(2)	1.354(16)	N(2)–N(3)	1.294(19)
N(3)–N(4)	1.365(8)	N(4)–C(1)	1.315(9)
C(1)–C(2)	1.492(12)		
Bond angles			
C(13)–Sn–C(17)	125.8(4)	C(13)–Sn–C(9)	115.9(3)
C(17)–Sn–C(9)	118.3(3)	C(13)–Sn–N(3)′	89.0(3)
C(17)–Sn–N(3)′	89.9(3)	C(9)–Sn–N(3)′	89.6(3)
C(13)–Sn–N(1)	89.5(3)	C(17)–Sn–N(1)	89.4(3)
C(9)–Sn–N(1)	92.9(3)	N(3)′–Sn–N(1)	177.5(3)
C(1)–N(1)–N(2)	104.6(8)	C(1)–N(1)–Sn	141.5(5)
N(2)–N(1)–Sn	113.7(7)	N(3)–N(2)–N(1)	108.5(7)
N(2)–N(3)–N(4)	110.7(8)	N(2)–N(3)–Sn″	125.1(6)
N(4)–N(3)–Sn″	123.7(5)	C(1)–N(4)–N(3)	103.4(6)
N(4)–C(1)–N(1)	112.8(6)	N(4)–C(1)–C(2)	124.9(7)
N(1)–C(1)–C(2)	121.8(7)		

Symmetry elements: ′, $-x$, $0.5-y$, $-0.5+z$; ″, $-x$, $0.5-y$, $0.5+z$.

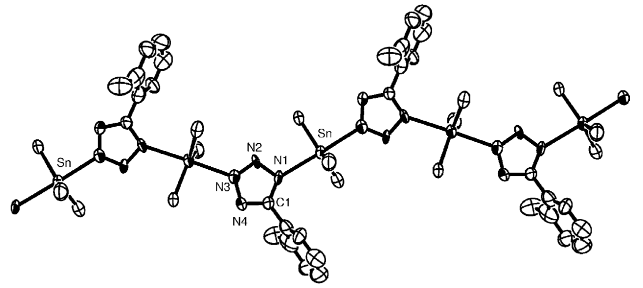


Fig. 3. The 1D polymeric structure of **2**. All hydrogen atoms and butyl carbon atoms except Sn-αC removed for clarity.

[22–24]. Although the thermal parameters of for several of the carbon atoms after refinement were large relative to the rest of the structure, this in no way negates our analysis of the overall lattice structure. The thermal parameters of the C_4H_9 units are ascribed to disorder inherent in the packing of the flexible butyl chains. This feature is common to many structures containing the Bu_3Sn fragment and has been commented upon previously with specific reference to organotin tetrazole compounds [22a].

Although attempts to apply **2** to the synthesis of titanium tetrazolyl derivatives have, thus far, met with only limited success, our initial observations are sufficiently encouraging to prompt further study and also serve to illustrate the difficulties inherent in the application of this class of ligand. Reaction of equimolar quantities of **2** and $TiCl_4$ in dichloromethane at room temperature produced a deep red solution which, upon removal of solvent, yielded a sticky red solid. This material was washed with dry hexane to remove eliminated Bu_3SnCl (confirmed by NMR analysis of the hexane filtrate) and the yellow solid produced by this procedure was analysed by ^1H NMR and 70 eV mass spectrometry. This analysis revealed the presence of both the tetrazole ligand and residual Bu_3Sn-, which persisted even upon repeated hexane washing. This observation is suggestive of either incomplete reaction or inclusion of Bu_3SnCl by adduct formation with the Lewis basic tetrazole nitrogen atoms. Indirect evidence for the formation of a titanium tetrazolyl linkage were provided by an X-ray study of a small quantity of yellow crystals obtained from the NMR tube prepared for the analysis of these reaction products in d_8-THF. These were identified as the known μ-oxo complex $(THF)_2Cl_3Ti–O–TiCl_3(THF)_2$ (**II**) [45], and are tentatively suggested as a result of preferential hydrolysis of the Ti–N bond of the target trichloroamido species.

We are continuing to study related reactivity of more sterically encumbered triorganostannyl-substituted tetrazoles in the hope of obtaining more tractable titanium-containing products. These studies and related work on the synthesis of group 5 and 6 metal complexes will be reported in due course.

4. Crystallography

Crystals of **1** and **2** were covered in oil and suitable single crystals were selected under a microscope and mounted on a KappaCCD diffractometer. Data were collected at 173 K; $\lambda(\text{Mo K}\alpha) = 0.71073$ Å; details are given in Table 2. The structures were solved by direct methods (SHELXS 97) [46] and refined by full matrix least squares (SHELXL 97) [47] with non-H atoms anisotropic and H atoms included in riding mode. No absorption correction was applied.

5. Crystal structure data

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 221843 and 221844 for compounds **1** and **2**, respectively. Copies may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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