

Preliminary communication

**A BIS(TRIMETHYLSTANNYL)AMIDO COMPLEX OF TITANIUM.
 THE SYNTHESIS AND STRUCTURES OF $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2]$
 AND $[\text{TiCl}\{\text{N}(\text{SnMe}_3)_2\}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2]$**

JONATHAN R. DILWORTH, JÜRGEN HANICH,

Chemistry Department, University of Essex, Colchester, Essex, CO4 3SQ (Great Britain)

MAGDA KRESTEL,

Geology Department, Phillips Universität, Lahnberge, Marburg (F.R.G.)

JOHANNES BECK and JOACHIM STRÄHLE

Institut für Anorganische Chemie, Universität Tübingen, Tübingen (F.R.G.)

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Summary

Reaction of TiCl_4 with 2,6-diphenylphenol in toluene gives $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2]$, and this reacts with $(\text{Me}_3\text{Sn})_3\text{N}$ to give $[\text{TiCl}\{\text{N}(\text{SnMe}_3)_2\}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2]$. The crystal structures of both complexes have been determined.

The use of sterically demanding ligands is now well established as a means of obtaining reactive coordinatively unsaturated complexes which frequently exhibit unusual metal coordination geometries. In the field of metal alkoxide and thiolate chemistry this steric hindrance has commonly been introduced through 2,6-dialkyl substitution of aromatic alcohols or thiols [1–3]. In previous studies [4] we have shown that 2,6-diphenylthiophenol exerts considerable steric hindrance and one of the phenyl substituents binds as a labile η^6 -phenyl group to molybdenum and tungsten. We report here a reaction of 2,6-diphenylphenol (DPPH) with TiCl_4 , and the synthesis of the first reported bis(trimethylstannyl)amido-transition metal complex.

Titanium tetrachloride reacts with DPPH in refluxing toluene to give $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2]$ (1) in 90% yield. As for other highly hindered alkoxides such as 2,6-Bu^tC₆H₃OH [5], use of an excess of the phenol or its lithium salt does not cause further substitution of chloride. Complex 1 is isolated as a red crystalline solid which is only moderately sensitive to air and water in solution and the solid

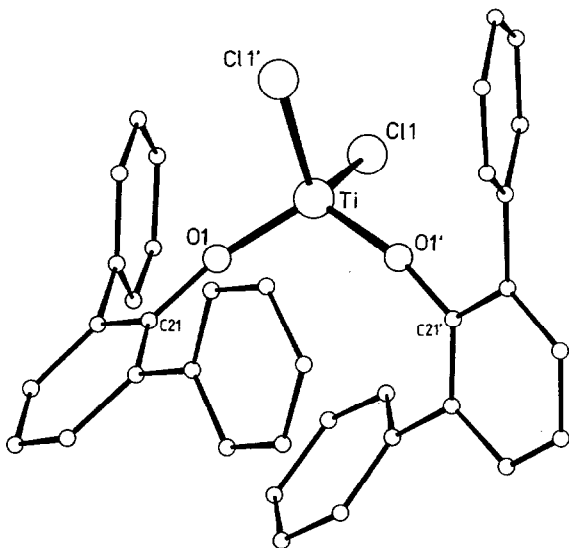


Fig. 1. An ORTEP view of the structure of $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{Ph}_{2-2,6})_2]$ with a partial atom-labelling scheme. Selected bond lengths (pm) and bond angles ($^\circ$): Ti–O 172.6(2); Ti–Cl 220.61(1); O–C(21) 136.7(4); Cl–Ti–O 111.2(1); Ti–O–C(21) 168.5(2).

state. Crystals of **1** suitable for an X-ray structure determination were obtained from toluene/hexane*.

An ORTEP representation of the structure of **1** is shown in Fig. 1 together with a partial atom-labelling scheme and selected bond lengths and angles. The overall geometry about the titanium is tetrahedral, and the considerable bulk of the phenoxide ligands creates only minor distortions in the tetrahedral angles. The nearly linear Ti–O–C systems ($168.5(2)^\circ$) and the Ti–O distance of 172.6(2) pm are very similar to those found in mononuclear alkoxide complexes [2]. These values reflect the considerable p_π – d_π bonding component of the Ti–O bonds. In contrast to the behaviour of the previously reported Mo–thiolato system, the linearity of the Ti–O bond prevents any intramolecular coordination of an aryl substituent. Thus reduction of complex **1** with magnesium in the presence of pyridine gives a Ti^{III} species without any evidence for η^6 -aryl coordination.

The chloride ligands of complex **1** undergo a variety of metathetical reactions. Thus **1** reacts with $(\text{Me}_3\text{Sn})_3\text{N}$ in refluxing toluene to give the bis(trimethylstannyl)amido complex $[\text{TiCl}\{\text{N}(\text{SnMe}_3)_2\}(\text{OC}_6\text{H}_3\text{Ph}_{2-2,6})_2]$ (**2**) in high yield. Even use of prolonged reflux times produced no evidence for further elimination of trimethylstannyl chloride. This behaviour is in contrast with the reaction of other titanium(IV) halido complexes with $(\text{Me}_3\text{Sn})_3\text{N}$. In the latter cases vigorous reactions occur, with complete elimination of Me_3SnCl , to give intractable mixtures of tin-free nitrogen-

* Crystal data for **1**: Space group $P2_12_12_1$; a 15.419(4), b 10.425(2), c 9.369(5) Å; V 1505.95 Å³; Z = 2. 1543 symmetry independent reflections collected and 1543 reflections used in structure solution to give final R value 0.0418. Data collected on Stoe 4-circle diffractometer with Mo-K_α radiation with graphite monochromator over scan range 1 to 25° .

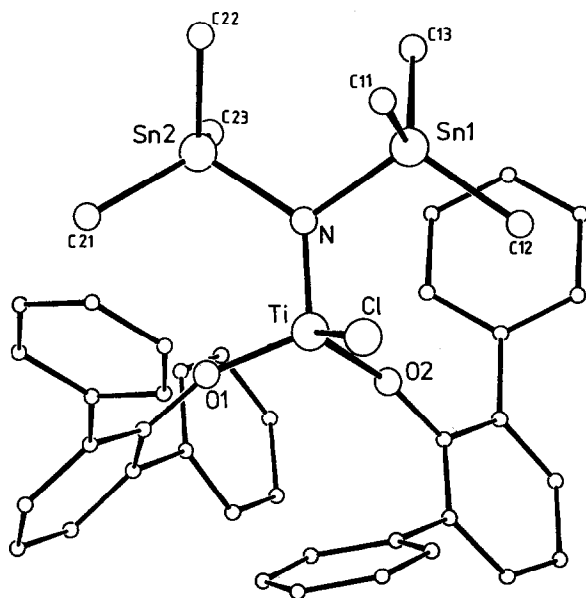


Fig. 2. An ORTEP view of the structure of $[\text{TiCl}\{\text{N}(\text{SnMe}_3)_2\}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2]$ with a partial atom-labelling scheme. Selected bond lengths (pm) and bond angles ($^\circ$): Ti–O(1) 180.5(1); Ti–O(2) 180.8(1); Ti–N 180.0(1); Sn(1)–N 210.7(1); Sn(2)–N 212.0(2). O(1)–Ti–O(2) 114.98(4); Ti–O–C(111) 161.50(8), Ti–O(2)–C(211) 160.15(8); Sn(1)–N–Sn(2) 149.96(4).

containing complexes. The bulky phenoxide ligands in complex **1** evidently exert significant steric control on the reaction, permitting the isolation of **2** in high yield. Complex **2** was isolated as yellow solid sparingly sensitive towards oxygen and water. Crystals suitable for an X-ray crystal structure determination were obtained from toluene/hexane*.

An ORTEP representation of the structure is shown in Fig. 2 together with a partial atom-labelling scheme and selected bond lengths and angles. The geometry about the titanium is again essentially tetrahedral. The average Ti–O distance of 180.7(1) pm is noticeably longer than in complex **1**. There is a comparable reduction in the average Ti–O–C angle from 168.5(2) in **1** to 160.88(4) $^\circ$, both being consistent with decreased π -donation from oxygen to titanium. The nitrogen atom of the $\text{N}(\text{SnMe}_3)_2$ moiety is rigorously planar, and the comparatively short Ti–N distance of 180.0 pm indicates considerable π -interaction between nitrogen and titanium. This Ti–N distance is similar to that of 185.2 pm found for the polymeric pseudo-octahedral Ti^{IV} complex $[\{\text{TiCl}_3(\text{NEt}_2)\}_n]$ [6].

The average Sn–N bond distance of 209.6(1) pm is close to the values found for other Sn^{IV} amido complexes such as $\text{Sn}(\text{NMe}_2)_4$ [7] (Sn–N 203.3(5) pm). The Sn–N bonds are reactive towards both insertion and metathesis reactions, and details of such reactions will be published elsewhere.

* *Crystal data for 2*: Space group $P1$, a 11.241(2), b 18.575(8), c 11.036(2) Å, α 106.95(3), β 113.65(1), γ 75.20(3) $^\circ$. V 1993.9 Å³, $Z = 2$. 6603 reflections collected and 5418 used in structure solution to give final R value of 0.031. Data collected on Enraf–Nonius CAD4 4-circle diffractometer over scan range 3 to 26 $^\circ$ at -40°C using Mo- K_α radiation with graphite monochromator.

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