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Thiolate derivatives of titanium(IV) and tantalum(V) as precursors to metal sulfides

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Reaction of $\mathrm{Ta(NMe_2)_5}$ with 10 equivalents of $\mathrm{2,6\text{-}Me_2C_6H_3SH}$ in toluene resulted in the formation of bright red crystals of $[\mathrm{Ta(SC_6H_3Me_2\text{-}2,6)_4(NMe_2)}]$ (**1**). The related reaction between $\mathrm{Ti(NEt_2)_4}$ and 10 equivalents of $\mathrm{Bu^tSH}$ in toluene afforded a mixture of two complexes, $[\mathrm{Ti(SBu^t)_4}]$ (**3**) and $[\mathrm{Ti(SBu^t)_3(NEt_2)}]$ (**4**). X-Ray crystal structures of **1** and **4** have been determined. Vapour phase thin-film studies of compounds **1** and **3**/**4** revealed that **1** is not an effective tantalum sulfide precursor whereas **3**/**4** produced $\mathrm{TiS_2}$.

Introduction

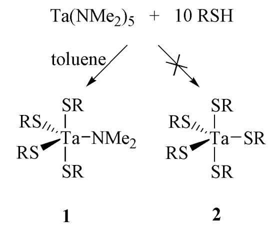
Heightened interest in thiolate derivatives of the early transition metals derives from their use as precursors to the technologically important transition metal disulfides. Materials such as titanium disulfide ($\mathrm{TiS_2}$) are of interest as high-temperature lubricants, as hydrogenation catalysts and in high-energy density batteries.[1,2] In addition, transition metal disulfides display a wide range of electronic properties from semiconductors ($\mathrm{TiS_2}$, $\mathrm{MoS_2}$) to superconductors ($\mathrm{TaS_2}$).[3]

We were interested in developing transition metal thiolate derivatives for use as single-source precursors to metal sulfides. Single-source precursors to $\mathrm{TiS_2}$ include $[\mathrm{TiCl_4(HSR)_2}]$ (R = cyclohexyl or cyclopentyl)[4] and $[\mathrm{Ti(SBu^t)_4}]$.[5,6] The homoleptic thiolate $[\mathrm{Ti(SBu^t)_4}]$ was initially reported to deposit thin films of TiS *via* LPCVD (low pressure chemical vapour deposition).[5] However, a more detailed study showed that LPCVD of $[\mathrm{Ti(SBu^t)_4}]$ produced thin films of $\mathrm{TiS_2}$ at 110–350 °C.[6] We have previously reported the synthesis and characterisation of ionic titanium thiolates including $[\mathrm{Et_2NH_2}][\mathrm{Ti(SC_6F_5)_4(NEt_2)}]$,[7] $[\mathrm{Et_2NH_2}]_3[\mathrm{Ti(SC_6F_5)_5}][\mathrm{SC_6F_5}]_2$,[7] and $[\mathrm{Et_2NH_2}][\mathrm{Ti_2(SCH_2Ph)_9}]$.[8] Unfortunately, their low volatility precluded thin film growth by CVD, although $\mathrm{TiS_2}$ could be produced *via* a thio 'sol–gel' process.[9] Other structurally characterised homoleptic titanium(IV) complexes containing unidentate thiolate ligands include $[\mathrm{Li(thf)_4}][\mathrm{Ti_2(SPh)_9}]$,[10] $[\mathrm{Me_2NH_2}][\mathrm{Ti_2(SMe)_9}]$,[11] $[\mathrm{Ti_3(SMe)_{12}}]$,[11] $[\mathrm{Ti(SC_6HMe_4\text{-}2,3,5,6)_4}]$[12] and $[\mathrm{Et_4N}]_2[\mathrm{Ti(SPh)_6}]$.[13] The only example of a structurally characterised neutral homoleptic tantalum(V) thiolate is $[\mathrm{Ta(SC_6HMe_4\text{-}2,3,5,6)_5}]$.[11] In general, homoleptic thiolate derivatives of the early transition metals represent a class of compound that has only been studied to a limited extent.[14]

In this contribution, we present the synthesis and X-ray structural characterisation of two neutral thiolates $[\mathrm{Ta(SC_6H_3Me_2\text{-}2,6)_4(NMe_2)}]$ and $[\mathrm{Ti(SBu^t)_3(NEt_2)}]$. Vapour phase thin-film experiments on the complexes are also described, enabling assessments to be made of the potential of the compounds to act as precursors to $\mathrm{TaS_2}$ and $\mathrm{TiS_2}$ thin films. Both $[\mathrm{Ta(SC_6H_3Me_2\text{-}2,6)_4(NMe_2)}]$ and $[\mathrm{Ti(SBu^t)_3(NEt_2)}]$ were prepared *via* the reaction of $\mathrm{M(NR_2)}_n$ (M = Ta, $n = 5$, R = Me; M = Ti, $n = 4$, R = Et) with excess thiol ($\mathrm{2,6\text{-}Me_2C_6H_3SH}$ or $\mathrm{Bu^tSH}$). Metal dialkylamido complexes have been shown previously to act as precursors to metal nitrides (*e.g.* TiN) and oxides.[15,16] Thus, the complexes reported herein extend the range of potential CVD applications of these amido precursors.

Results and discussion

The reaction between $\mathrm{Ta(NMe_2)_5}$ and 10 equivalents of $\mathrm{2,6\text{-}Me_2C_6H_3SH}$ in toluene at room temperature resulted, after work up, in a 50% yield of bright red crystalline **1**. Analytical and spectroscopic data for **1** were consistent with the formation of the neutral species $[\mathrm{Ta(SC_6H_3Me_2\text{-}2,6)_4(NMe_2)}]$ rather than that of the anticipated product $[\mathrm{Ta(SC_6H_3Me_2\text{-}2,6)_5}]$ **2** (Scheme 1).



R = $\mathrm{2,6\text{-}Me_2C_6H_3}$

Scheme 1

A single crystal structure determination showed **1** to be the incompletely thiolate-substituted complex illustrated in Fig. 1. The complex has molecular C_2 symmetry about the N–Ta bond direction. The geometry at tantalum is distorted trigonal bipyramidal, the equatorial plane [comprising Ta, N, S(3) and S(4)] being co-planar to within 0.007 Å; the angles within the equatorial plane are in the narrow range 119.04(6)–121.6(2)° whereas that between the axial substituents is noticeably bent at 164.37(5)° (Table 1). As expected, the Ta–S distances to the axial ligands [Ta–S(1) 2.427(2) Å, Ta–S(2) 2.428(2) Å] are longer than those to their equatorial counterparts [Ta–S(3) 2.398(2) Å, Ta–S(4) 2.389(2) Å], a differentiation that is not observed in the homoleptic complex $[\mathrm{Ta(SC_6HMe_4\text{-}2,3,5,6)_5}]$,[12] where the geometry is distorted slightly more towards square pyramidal and the "axial" S–Ta–S angle is 156.7°. In this latter complex the Ta–S distances range between 2.330 and 2.402 Å. In $[\mathrm{Ta(CHBu^t)(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(SEt_2)}]$,[17] which has a distorted

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

Ta–N	1.921(5)	Ta–S(1)	2.427(2)
Ta–S(2)	2.428(2)	Ta–S(3)	2.398(2)
Ta–S(4)	2.389(2)		
N–Ta–S(4)	119.4(2)	N–Ta–S(3)	121.6(2)
S(4)–Ta–S(3)	119.04(6)	N–Ta–S(1)	98.5(2)
S(4)–Ta–S(1)	81.40(6)	S(3)–Ta–S(1)	89.17(6)
N–Ta–S(2)	96.9(2)	S(4)–Ta–S(2)	93.49(6)
S(3)–Ta–S(2)	80.37(6)	S(1)–Ta–S(2)	164.37(5)
C(3)–S(1)–Ta	106.9(2)	C(11)–S(2)–Ta	109.2(2)
C(19)–S(3)–Ta	115.7(2)	C(27)–S(4)–Ta	116.1(2)
C(2)–N–C(1)	111.9(6)	C(2)–N–Ta	125.9(5)
C(1)–N–Ta	122.1(5)		

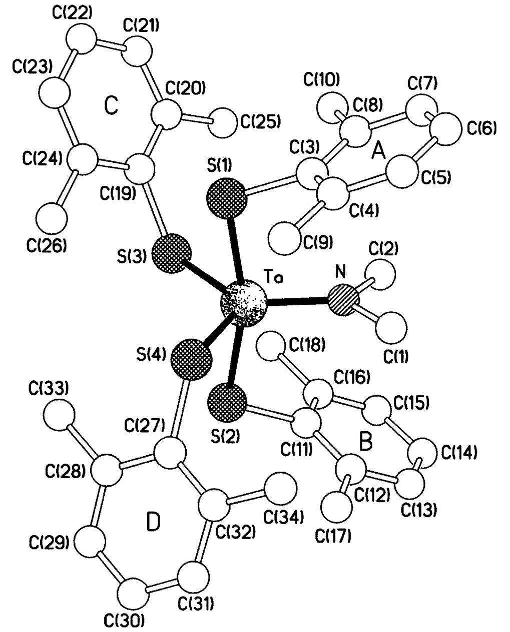


Fig. 1 The molecular structure of **1**.

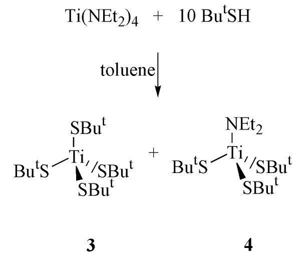
Table 2 Selected bond lengths (Å) and angles (°) for compound **4**

Ti–N	1.856(5)	Ti–S(1)	2.295(2)
Ti–S(2)	2.302(2)	Ti–S(3)	2.283(2)
N–Ti–S(3)	115.5(2)	N–Ti–S(1)	105.2(2)
S(3)–Ti–S(1)	112.52(7)	N–Ti–S(2)	110.06(14)
S(3)–Ti–S(2)	101.16(7)	S(1)–Ti–S(2)	112.62(7)
C(1)–S(1)–Ti	112.7(2)	C(5)–S(2)–Ti	114.6(2)
C(9)–S(3)–Ti	121.2(2)	C(15)–N–C(13)	113.5(4)
C(15)–N–Ti	127.0(4)	C(13)–N–Ti	119.2(3)

trigonal bipyramidal geometry similar to that of **1** (the axial ligands subtended an angle of 162.2° at tantalum), the three equatorial Ta–S distances only range between 2.390 and 2.394 Å, values comparable to those observed in **1**. Although the axial ligands in **1** are bent away from the amide ligand [N–Ta–S(1) 98.5(2)°, N–Ta–S(2) 96.9(2)°] the angles at these two sulfur centres are noticeably contracted [106.9(2)° at S(1) and 109.2(2)° at S(2)] *vis-a-vis* those at their equatorial counterparts [115.7(2)° at S(3) and 116.1(2)° at S(4)]. These deformations, coupled with a positioning of ring **A** "over" C(1) and ring **B** "under" C(2), permit the formation of a pair of weak intramolecular C–H···π interactions between a hydrogen atom on the C(1) and C(2) methyl groups and rings **A** and **B** respectively [C(1)–H···**A**, H···π 3.06 Å, C–H···π 124°; C(2)–H···**B**, H···π 2.94 Å, C–H···π 130°]. These interactions are accompanied by a small torsional twist (*ca.* 4°) about the Ta–N bond such that C(1) and C(2) lie 0.06 and 0.12 Å "above" and "below" the equatorial coordination plane in the directions of rings **A** and **B** respectively. The Ta–N bond length of 1.921(5) Å indicates a degree of multiple bond character, and this is reflected in the near planar geometry at the nitrogen centre (the nitrogen being only 0.026 Å out of the plane of its substituents). This bond distance compares with a Ta=N double bond length of 1.894 Å in $[\{Ta(SC_6H_3Pr^i{}_2\text{-}2,6)_3(thf)\}_2(\mu\text{-}N_2)]$,[18] and Ta–N single bonds of, for example, 1.949 Å in $[TaCl(NSiMe_3)\{N(SiMe_3)_2\}(\mu\text{-}Cl)]_2$[19] and 2.024 Å in $[Ta(OMe)(NSiMe_3)\{N(SiMe_3)_2\}(\mu\text{-}OMe)]_2$.[19] The generally hydrophobic exterior of the complex precludes any significant packing interactions, though there is evidence for a weak intermolecular C–H···π contact between the C(13) hydrogen atom in one molecule and ring **D** in a symmetry related counterpart (H···π 2.90 Å, C–H···π 135°) to create loosely linked chains that extend in the *c* direction.

Commenting more generally on compound **1**, it is interesting that even in the presence of excess thiol incomplete substitution of all the dimethylamide ligands has occurred. We and others have previously reported the results of reacting titanium tetradialkylamides with excess thiols. Ionic compounds, such as $[R_2NH_2][Ti_2(SR')_9]$ (R = R′ = Me;[11] R = Et, R′ = CH_2Ph[8]) and $[Et_2NH_2]_3[Ti(SC_6F_5)_5][SC_6F_5]$,[7] have been isolated from the aforementioned reactions and the compounds were structurally characterised. In contrast, the complex $[Ti(SBu^t)_4]$ **3**, has been reported to result from the reaction of $Ti(NR_2)_4$ (R = Me or Et) with excess Bu^tSH.[5,6] Earlier work indicated that the reaction of excess thiol R′SH (R′ = Me, Et, Pr^i) with $Ti(NR_2)_4$ (R = Me or Et) resulted in the formation of complexes of the type $[Ti(SR')_4(R'SH)_x(R_2NH)_y]$ (where *x* and *y* varied from 0.8 to 1.33).[20] However, controlled addition of R′SH to $Ti(NMe_2)_4$ afforded the partially substituted compounds $[Ti(NMe_2)_{4-x}(SR')_x]$ (where x = 1 or 2; R′ = Et or Pr^i).[20]

We decided to investigate the reaction of $Ti(NR_2)_4$ with Bu^tSH in more detail for two reasons; (a) to attempt to isolate X-ray quality crystals and (b) the importance of **3** as a single-source precursor to TiS_2. Accordingly, $Ti(NEt_2)_4$ was treated with 10 equivalents of Bu^tSH in toluene at room temperature. An immediate colour change from orange to dark red was observed and work-up of the reaction mixture yielded a dark red oil. Crystallisation from hexanes solution resulted in the isolation of a dark red crystalline material. Analytical and spectroscopic data for these crystals are consistent with the formation of a mixture of two complexes, namely $[Ti(SBu^t)_4]$ **3** and $[Ti(SBu^t)_3(NEt_2)]$ **4** (Scheme 2). This is in contrast to the earlier reports that suggest only **3** is isolated from the reaction of $Ti(NEt_2)_4$ with excess Bu^tSH. An X-ray analysis of the red crystalline material determined the structure of compound **4**. Unfortunately, X-ray quality crystals of **3** could not be isolated from the mixture.



Scheme 2

A single crystal structure determination revealed **4** also to be an only partially thiolate substituted species (Fig. 2). The geometry at titanium is distorted tetrahedral with angles in the range 101.16(7)–115.5(2)° (Table 2). The Ti–S distances range between 2.283(2) and 2.302(2) Å, values very similar to those observed in, for example, $[Ti(\eta^5\text{-}NC_4Me_4)(SPh)_3]$,[21] where the Ti–S distances range between 2.285 and 2.314 Å. The angles at sulfur are 112.7(2), 114.6(2) and 121.2(2)° at S(1), S(2) and S(3) respectively, the enlargement of the angle at S(3) reflecting a possible steric conflict between its *tert*-butyl group and the

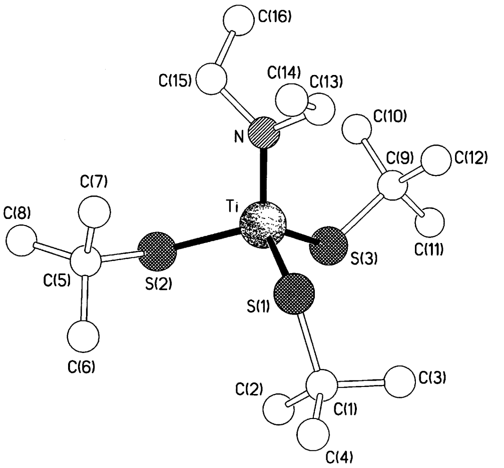


Fig. 2 The molecular structure of **4**.

diethylamino ligand. The geometry at nitrogen is trigonal planar (the nitrogen lies only 0.052 Å out of the plane of its substituents), and the Ti–N bond [1.856(5) Å] is fairly short, but similar in length to those between titanium and the dimethylamido ligands in $[Ti(NMe_2)_2(OC_6H_2Bu^t_3\text{-}2,4,6)_2]$[22] [1.865 and 1.897 Å]. Interestingly, in this latter structure the distortions from tetrahedral geometry are equally large *cf.* those in **4**, with the angles at titanium ranging between 98.6 and 116.7°. The outer surface of the complex is dominated by *tert*-butyl and ethyl groups, and there are no intermolecular packing interactions of note.

The structure of **4** is similar to that of **1** in the sense that one amide ligand remains coordinated to the transition metal centre. The formation of **4** is obviously a result of incomplete substitution of all the amide ligands by the thiol. This is surprising since an excess of thiol is present in the reaction mixture. However, the reaction between $Ti(NEt_2)_4$ and excess Bu^tSH has been repeated a number of times. Analytical data on a number of samples of the red crystalline material isolated, reveals that the %N varies from 0.71 to 2.78. Thus, even after repeated recrystallisation a small amount of nitrogen is still present in the material. The ^1H NMR data shows the presence of $Ti–NEt_2$ ligands in the mixture and so supports the formation of **4**. Overall, these results suggest that the major product is compound **3**, although no X-ray quality crystals were obtained.

In order to study the decomposition pathways of **1** and **3/4** thermal gravimetric analyses (TGA) were carried out. The TGA results of **1** and **3/4** at 10 °C min^{-1} from 20 to 500 °C, under N_2, are shown in Figs. 3 and 4, respectively. The decomposition of **1** has an onset temperature of 230 °C and is completed at 310 °C. The TGA of **1** shows a total weight loss of 67%, in good agreement with the calculated value of 68% for the formation of TaS_2. The decomposition of **3/4** is clean and shows a weight loss of 67%. This behaviour indicates an incomplete decomposition to TiS_2 up to 500 °C (calculated weight loss 72% from **3**). However, since **3/4** is a mixture of ill-defined proportions, an accurate interpretation of the TGA results is not possible.

Vapour phase thin-film studies of **1** and **3/4** were investigated, the details of which are described in the Experimental section. In both instances a film was deposited on the inside of the hot wall glass tube. Compound **1** produced a black film, whereas **3/4** deposited a dark purple film. The films were analysed by EDAX/SEM and Raman spectroscopy. The EDAX data for the film deposited from **1** showed a 2.5 : 1 ratio of Ta : S over a number of spots. These data suggest that TaS_2 has not been isolated, which is in contrast to the TGA results. It is possible that hydrolysis or oxidation of the films has occurred either during or after deposition. However, significant breakthrough of the excitation volume through the coating to the underlying glass meant that accurate quantitative analysis was difficult. The EDAX data for the film deposited from **3/4** showed a 1 : 2 ratio of Ti : S, over a number of spots, which is in good agreement with the formation of TiS_2. We have previously reported the Raman pattern of bulk TiS_2 prepared from a thio 'sol–gel' route.[9] The Raman spectrum of the TiS_2 film prepared here was very similar to that obtained for bulk TiS_2 with bands at 338 and 372 cm^{-1}. A UV-Vis spectrum of the TiS_2 film showed a direct band gap of 1.9 eV. By Scanning Electron Microscopy (SEM) the TiS_2 film shows a 'crazy paving' island-growth mechanism with an island size of 0.2 µm (Fig. 5). The tantalum sulfide film grown from compound **1** shows a finer gain microstructure, by SEM, with a 0.1 µm island growth. Two reports on the decomposition of **3** have been previously published, as described in the introduction.[5,6] Our results support the formation of TiS_2 from **3** (rather than TiS) and suggests that the presence of compound **4** has little effect on the end material obtained.

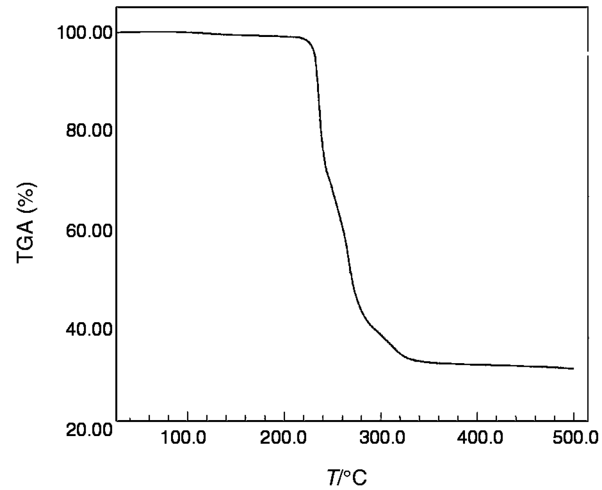


Fig. 3 TGA of **1** under N_2.

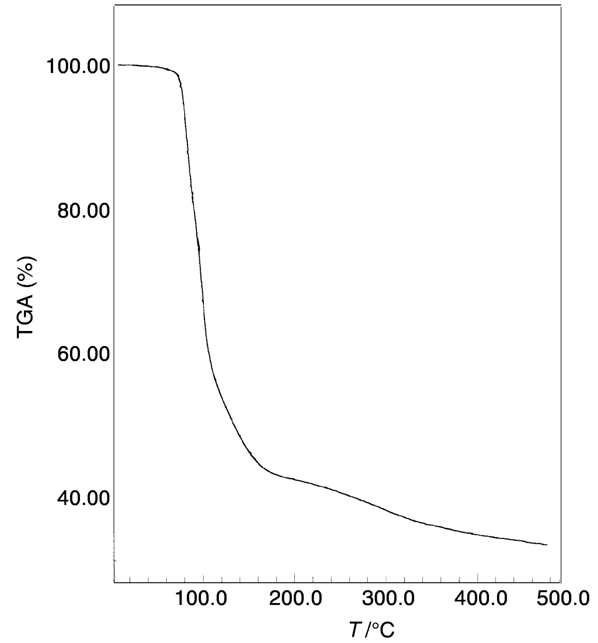


Fig. 4 TGA of **4** under N_2.

In summary, two novel thiolate complexes of tantalum(V) and titanium(IV), namely $[Ta(SC_6H_3Me_2\text{-}2,6)_4(NMe_2)]$ and $[Ti(SBu^t)_3(NEt_2)]$ have been synthesised and structurally characterised. Preliminary vapour phase thin-film studies indicate that **3/4** can serve as a precursor to TiS_2 whereas **1** did not produce TaS_2 under the same conditions. More detailed CVD

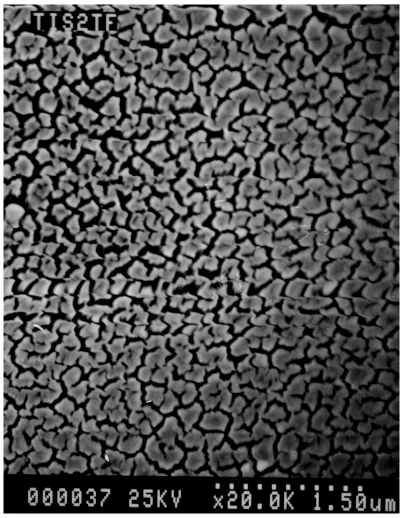


Fig. 5 SEM of the film produced by the decomposition of **3**/**4**.

studies are currently being carried out and will be described in a future publication.

Experimental

General procedures

All manipulations were performed under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in a Mbraun Unilab glove box. All solvents were distilled from appropriate drying agents prior to use (sodium for toluene, thf and hexanes; CaH_2 for CH_2Cl_2). $Ti(NEt_2)_4$[23] and $Ta(NMe_2)_5$[24] were prepared by literature methods. All other reagents were procured commercially from Aldrich and used without further purification. Microanalytical data were obtained at University College London (UCL).

Physical measurements

^1H and ^{13}C NMR spectra were recorded on Brüker AMX300 or DRX500 spectrometers at UCL, referenced to CD_2Cl_2, which was degassed and dried over molecular sieves prior to use; ^1H and ^{13}C chemical shifts are reported relative to $SiMe_4$ (δ 0.00). Mass spectra (CI) were run on a micromass ZABSE instrument, and IR spectra on a Nicolet 205 instrument. EDAX/SEM results were obtained on an Hitachi S570 instrument using the KEVEX system. Raman spectra were acquired on a Renishaw Raman System 1000 using a helium–neon laser of wavelength 632.8 nm. The Raman system was calibrated against the emission lines of neon. TGA of the compounds were obtained from the Thermal Methods Laboratory at Birkbeck college (ULIRS). Melting points were obtained in sealed glass capillaries under nitrogen and are uncorrected.

Preparations

$[Ta(SC_6H_3Me_2\text{-}2,6)_4(NMe_2)]$ 1. The dropwise addition of 2,6-$Me_2C_6H_3SH$ (0.66 cm^3, 4.98 mmol) to a pale yellow solution of $Ta(NMe_2)_5$ (0.20 g, 0.499 mmol) in toluene (20 cm^3) at room temperature resulted in a colour change to dark orange-red. The reaction mixture was allowed to stir for 2 h, after which the solvent was removed *in vacuo*. The resulting dark red-orange oil was redissolved in CH_2Cl_2 (15 cm^3) and filtered through Celite. A dark orange-red solution resulted and a hexanes overlayer (7 cm^3) was added carefully. Solvent diffusion at room temperature over a period of days produced bright red crystals of **1** in a 50% yield. Calc. for $C_{34}H_{42}NS_4Ta$: C, 52.77; H, 5.47; N, 1.81. Found C, 52.0; H, 5.82; N, 2.15%. ^1H NMR (CD_2Cl_2): δ 2.45 [s, 24H, 2,6-$(CH_3)_2C_6H_3$], 2.76 (s, 6H, NCH_3), 6.78–7.18 [m, 12H, 2,6-$(CH_3)_2C_6H_3$]. $^{13}C\text{-}\{^1H\}$ NMR (CD_2Cl_2): δ 22.4 [s, 2,6-$(CH_3)_2C_6H_3$], 39.7 (NCH_3), 125.9, 137.9, 143.8 [s, 2,6-$(CH_3)_2C_6H_3$].

$[Ti(SBu^t)_4]$ 3 and $[Ti(SBu^t)_3(NEt_2)]$ 4. The compound Bu^tSH (1.90 cm^3, 16.85 mmol) was added dropwise to an orange solution of $Ti(NEt_2)_4$ (0.60 cm^3, 1.66 mmol) in toluene (20 cm^3) at room temperature. The solution turned dark red over a period of 30 minutes and was allowed to stir for a further 2 h, after which time the solvent was removed *in vacuo*. The resulting dark red oil was redissolved in hexanes (15 cm^3) and filtered through Celite to give a dark red solution which was concentrated to a volume of approx. 5 cm^3. Cooling of this solution to −20 °C overnight afforded a mixture of **3** and **4**. Single crystals of **4**, suitable for crystallography, were produced by fractional crystallisation of a concentrated hexanes (2 cm^3) solution of this mixture. Calc. for $C_{16}H_{36}S_4Ti$: C, 47.50; H, 8.97; N, 0. Calc. for $C_{16}H_{37}NS_3Ti$: C, 49.59; H, 9.62; N, 3.61. Found C, 47.70; H, 9.73; N, 2.78%. ^1H NMR (CD_2Cl_2): δ 1.21 (t, NCH_2CH_3), 1.55 [s, $SC(CH_3)_3$], 1.64 [s, $SC(CH_3)_3$], 4.12 (q, NCH_2CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 13.9 (NCH_2CH_3), 30.7 (NCH_2CH_3), 36.4 [$SC(CH_3)_3$], 36.6 [$SC(CH_3)_3$], 57.8 [$SC(CH_3)_3$], 59.2 [$SC(CH_3)_3$].

Tube furnace reactions

A sample of compound **1** (0.3 g) was loaded into a glass ampoule (40 cm length × 9 mm diameter) in the glovebox. The ampoule was then placed in a furnace such that 30 cm was inside the furnace and the end containing the sample protruded by 4 cm. The ampoule was heated to a temperature of 450 °C under dynamic vacuum, except for the section of the tube containing the sample. The ampoule was slowly drawn into the furnace over a period of a few minutes until **1** started to melt. Once all of the compound had decomposed the furnace was allowed to cool to room temperature. A black film resulted on the inside wall of the ampoule where the tube was in the furnace. The film was analysed by EDAX/SEM and Raman spectroscopy. The same procedure was used to investigate the decomposition of **3**/**4** which resulted in the formation of a purple film.

X-Ray crystallography

Crystals of compound **1** were grown from CH_2Cl_2–hexanes mixtures at room temperature whereas crystals of **4** were grown from hexanes solution at −20 °C.

Crystal data for 1. $C_{34}H_{42}NS_4Ta$, $M = 773.9$, tetragonal, $I4_1/a$ (no. 88), $a = 32.088(7)$, $c = 13.126(3)$ Å, $V = 13515(6)$ Å^3, $Z = 16$, $D_c = 1.521$ g cm^{-3}, μ(Mo-Kα) = 3.52 mm^{-1}, $T = 203$ K, orange-red blocks; 5949 independent measured reflections, F^2 refinement, $R_1 = 0.037$, $wR_2 = 0.069$, 4529 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 50°$], 362 parameters.

Crystal data for 4. $C_{16}H_{37}NS_3Ti$, $M = 387.6$, orthorhombic, $Pbca$ (no. 61), $a = 10.145(1)$, $b = 15.861(4)$, $c = 28.332(2)$ Å, $V = 4559(1)$ Å^3, $Z = 8$, $D_c = 1.129$ g cm^{-3}, μ(Cu-Kα) = 5.69 mm^{-1}, $T = 183$ K, red blocks; 3351 independent measured reflections, F^2 refinement, $R_1 = 0.057$, $wR_2 = 0.137$, 2199 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 120°$], 191 parameters.

CCDC reference numbers 165273 and 165274.

See http://www.rsc.org/suppdata/dt/b1/b104888k/ for crystallographic data in CIF or other electronic format.

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