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# Reactivity of tetrakisdimethylamido-titanium(IV) and -zirconium(IV) with thiols

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The reaction of $[M(NMe_2)_4]$ (M = Ti, Zr) with thiols has been investigated. Reaction of $[Ti(NMe_2)_4]$ with an excess of $CF_3CH_2SH$ in hexanes at room temperature resulted in the formation of the ionic complex $[Me_2NH_2]_2[Ti(SCH_2CF_3)_6]$ (**1**). The related reaction between $[Zr(NMe_2)_4]$ and 4 equivalents of $Bu^tSH$ at room temperature resulted in the isolation of the ionic complex $[Me_2NH_2][Zr_2(\mu\text{-}SBu^t)_3(SBu^t)_6]$ (**2**). In contrast, reaction of $[Zr(NMe_2)_4]$ and 4 equivalents of 2-mercaptopyridine ($HSC_5H_4N$) afforded the neutral complex $[Zr(SC_5H_4N)_4]$ (**3**). Compounds **1** and **2** have been characterised by X-ray crystallography. Low pressure CVD of $[Me_2NH_2]_2[Ti(SCH_2CF_3)_6]$ produced purple films of $TiS_2$ on glass substrates at 550 °C.

## Introduction

Early transition metal thiolates, of the type $[M(SR)_n]$ (*e.g.* $n = 4$, M = Ti, Mo; $n = 5$, M = Ta, Nb), have received attention in recent years because of the application of some of these compounds as precursors to metal disulfides ($MS_2$).[1–5] In turn, metal disulfides are of interest due to their layered structure, allowing facile intercalation into the van der Waals gap between layers.[6] This property lends itself to their application as the cathode material in Li rechargeable batteries.[7] The intercalates themselves have shown useful properties, for example an increase in the superconducting transition temperature can occur on intercalation of amines.[8] A large number of studies have focused on the intercalation of guest species into the inter layer gap of $ZrS_2$.[9–11] Guest species include a range of metallocene compounds (where M = Mo, Cr, Co, Ti),[9,10] in addition to ammonia. In all cases the zirconium sulfide used was made from the elements at high temperatures (900 °C) over a number of days.[9–11] Metal disulfides also find application as solid lubricants due to weak van der Waals interactions between adjacent layers of the $MS_2$ lattice.[6,12]

Early transition metal thiolate complexes represent a class of compound that have only been studied to a limited extent.[13] Early preparative routes to titanium thiolates involved the reaction of $[Ti(NR_2)_4]$ (R = Me or Et) and R′SH (R = Me, Et or $Pr^i$) resulting in the formation of complexes of the type $[Ti(SR')_4(HSR')_x(NHR_2)_y]$ (where $(x + y)$ varied from 0.8 to 1.33).[14] We have recently shown that the reaction of $[Ti(NEt_2)_4]$ with $C_6F_5SH$ and $PhCH_2SH$, resulted in the formation of ionic complexes of the type $[Et_2NH_2][Ti(SC_6F_5)_4(NEt_2)]$ and $[Et_2NH_2][Ti_2(\mu\text{-}SCH_2Ph)_3(SCH_2Ph)_6]$, respectively.[4,15] There have been few reports of crystallographically characterised zirconium thiolate complexes. However, the synthesis of zirconium thiolates has been reported from zirconium amides,[16,17] cyclopentadienyl zirconium chloride,[18–21] in addition to reports of adduct formation, *e.g.* $[ZrCl_4(SMe_2)_2]$.[22] Cluster formation is highly favoured in zirconium thiolate chemistry. Clusters have been obtained from the reaction of 2-methyl-2-propanethiol and $[Zr(BH_4)_4]$ resulting in the formation of $[Zr_3S_3(Bu^tS)_2(BH_4)_4(thf)_2]$ or $[Zr_6S_6(Bu^tS)_4(BH_4)_8(thf)_2]$.[23,24] In contrast, reaction of the same thiol with $[Zr(CH_2Ph)_4]$ afforded $[Zr_3(S)(SBu^t)_{10}]$.[25]

In this paper the reactivity of $[M(NMe_2)_4]$ (M = Ti, Zr) with thiols is described. The synthesis and structures of two new ionic titanium(IV) and zirconium(IV) thiolate complexes, $[Me_2NH_2]_2[Ti(SCH_2CF_3)_6]$ (**1**) and $[Me_2NH_2][Zr_2(SBu^t)_3(\mu\text{-}SBu^t)_6]$ (**2**) are also reported. The thermal decomposition of **1** and **2** have also been studied.

## Results and discussion

The reaction between $[Ti(NMe_2)_4]$ and 6 equivalents of $CF_3CH_2SH$ in hexanes at room temperature resulted in an immediate colour change from orange to dark red. Work-up of the reaction mixture yielded a dark red precipitate in a 82% yield. Crystallisation from dichloromethane/hexane layers resulted in the isolation of dark red needle-like crystals. Analytical and spectroscopic data for these crystals were consistent with the formation of the ionic species $[Me_2NH_2]_2[Ti(SCH_2CF_3)_6]$ (**1**) (Scheme 1).

An X-ray analysis of crystals of **1** revealed the structure to comprise the homoleptic [hexa(trifluoroethanethiolate) titanium(IV)]$^{2-}$ complex anion shown in Fig. 1, together with two dimethylammonium monocations. Selected bond lengths and angles for **1** are presented in Table 1. Compound **1** crystallises into the triclinic space group $P\bar{1}$. The geometry at titanium is octahedral, with the central titanium ion in **1** located on the crystallographic inversion centre. The *cis* S–Ti–S bond angles range from 83.86(4) to 96.37(5)° and the Ti–S bond distances are typical for metal–sulfur bonds in transition metal thiolate complexes (Ti–S 2.4183(14)–2.4267(13) Å).[3,4,15]

The formation of **1** is in contrast to related titanium thiolate complexes formed from the reaction of $[Ti(NR_2)_4]$ (R = Me or Et) and R′SH. We have shown previously that reaction of $[Ti(NR_2)_4]$ with excess $Bu^tSH$ affords the neutral complexes $[Ti(SBu^t)_4]$ and $[Ti(SBu^t)_3(NR_2)]$.[1,3] However, reaction of $[Ti(NR_2)_4]$ with MeSH or $PhCH_2SH$ afforded ionic complexes of the type $[R_2NH_2][Ti_2(\mu\text{-}SR')_3(SR')_6]$ (R = Me or $CH_2Ph$).[15,26] Reaction of pentafluorothiophenol with $[Ti(NEt_2)_4]$ in a 4 : 1 and 10 : 1 ratio resulted in the formation of $[Et_2NH_2][Ti(SC_6F_5)_4(NEt_2)]$ and $[Et_2NH_2]_3[Ti(SC_6F_5)_5][(SC_6F_5)]_2$, respectively.[4] Therefore, the product obtained from the reaction of $[Ti(NR_2)_4]$ (R = Me or Et) and R′SH appears to be sensitive to the ratio of reagents used and the size of the

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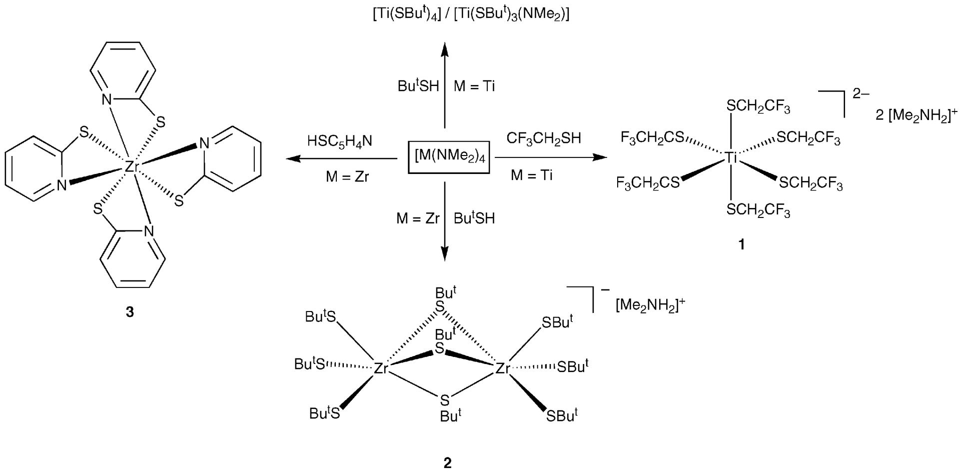

**Scheme 1**

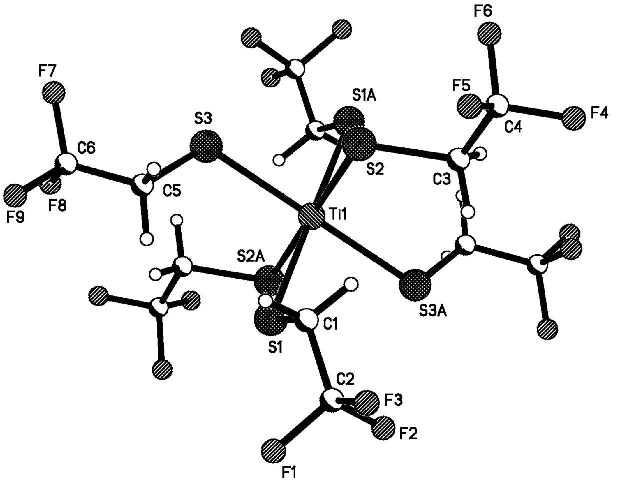

**Fig. 1** Structure of the anion in **1**.

thiolate ligand. The hexathiolate anion, $[Ti(SR')_6]^{2-}$ in **1** may be the result of using a 1 : 6 ratio of $[Ti(NMe_2)_4]$ and $CF_3CH_2SH$, since a larger excess of thiol was employed for the isolation of $[Ti_2(\mu\text{-}SR')_3(SR')_6]^-$ anions, in related systems.[15,26] A hexathiolate anion, $[Ti(SPh)_6]^{2-}$ has been reported previously and was isolated from the reaction of $TiCl_4$ with 6 equivalents of NaSPh and 2 equiv. of $Et_4NBr$.[27] The formation of **1** represents a more facile preparation of homoleptic titanium thiolate anions, which can be obtained in high yield. The $^1H$ NMR of **1** shows single sets of resonances at room temperature with peaks corresponding to the $[Me_2NH_2]^+$ cation at $\delta$ 2.55 and 6.20 (Me and $NH_2$, respectively) and a quartet for the $SCH_2CF_3$ group at $\delta$ 4.10.

The synthesis of a zirconium thiolate using 2-methyl-2-propanethiol from the tetrakisdimethylamido zirconium was also attempted. This ligand was chosen due to previous reports of successful syntheses of monomeric species, such as $[Ti(SBu^t)_4]$ and $[Ti(SBu^t)_3(NR_2)]$, and their subsequent use to form $TiS_2$ thin films.[1,3] The addition of 4 equivalents of $Bu^tSH$ to a solution of $[Zr(NMe_2)_4]$ in dichloromethane at room temperature afforded an orange coloured solution. Bright yellow crystals were obtained in a 62% yield after concentrating the orange solution and cooling to −20 °C. It was initially thought that the monomeric zirconium thiolate $[Zr(SBu^t)_4]$, would be formed by this route.[3,4] However, analytical and spectroscopic data revealed that the ionic species $[Me_2NH_2][Zr_2(\mu\text{-}SBu^t)_3(SBu^t)_6]$ (**2**) had formed (Scheme 1). The structure of **2** was confirmed by X-ray crystallography, the results of which are shown in Fig. 2; selected bond lengths and angles are presented in Table 2. Complex **2** crystallises into the monoclinic space group $P2_1/c$. The structure of **2** is ionic comprising $[Me_2NH_2]^+$ cations and $[Zr_2(\mu\text{-}SBu^t)_3(SBu^t)_6]^-$ anions with no close inter-ionic contacts between ions or the lattice dichloromethane molecules. In the anion in **2** the two zirconium atoms are each coordinated by three terminal (Zr–S 2.4360(8)–2.5451(8) Å) and three bridging (Zr–S 2.6743(7)–2.7336(7) Å) $SBu^t$ ligands. Therefore, the coordination number at each zirconium centre is six and the geometry is approximately octahedral (*trans*-S–Zr–S 147.28(3)–161.84(3)°; *cis*-S–Zr–S 69.03(2)–111.59(3°). The $Zr_2S_9$ framework in **2** adopts a face-sharing bioctahedral arrangement similar to that found in the related titanium anions $[Ti_2(\mu\text{-}SCH_2Ph)_3(SCH_2Ph)_6]^-$ and $[Ti_2(\mu\text{-}SMe)_3(SMe)_6]^-$.[15,26] The Zr–S bond distances are similar to those observed previously in Zr thiolate complexes.[23–25]

In solution compound **2** appears to retain its solid state structure as shown by the $^1H$ NMR of **2** where peaks corresponding to the terminal and bridging $SBu^t$ groups were observed in a 1 : 2 ratio. This is similar to $[Et_2NH_2][Ti_2(\mu\text{-}SCH_2Ph)_3(SCH_2Ph)_6]$, whereas $[Me_2NH_2][Ti_2(\mu\text{-}SMe)_3(SMe)_6]$ showed a complex $^1H$ NMR pattern at room temperature,

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

| | | | |
|---|---|---|---|
| Ti(1)–S(1) | 2.4267(13)) | Ti(1)–S(2) | 2.4183(14) |
| Ti(1)–S(3) | 2.4224(17) | | |
| S(2A)–Ti(1)–S(2) | 180.000(1) | S(2)–Ti(1)–S(3A) | 95.35(3) |
| S(2)–Ti(1)–S(3) | 84.65(3) | S(2)–Ti(1)–S(1A) | 83.63(5) |
| S(2)–Ti(1)–S(1) | 101.32(3) | S(3)–Ti(1)–S(3A) | 180.0(3) |
| S(2)–Ti(1)–S(1) | 96.37(6) | S(3)–Ti(1)–S(1) | 96.14(4) |
| S(3A)–Ti(1)–S(1) | 83.86(4) | S(1A)–Ti(1)–S(1) | 180.000(1) |

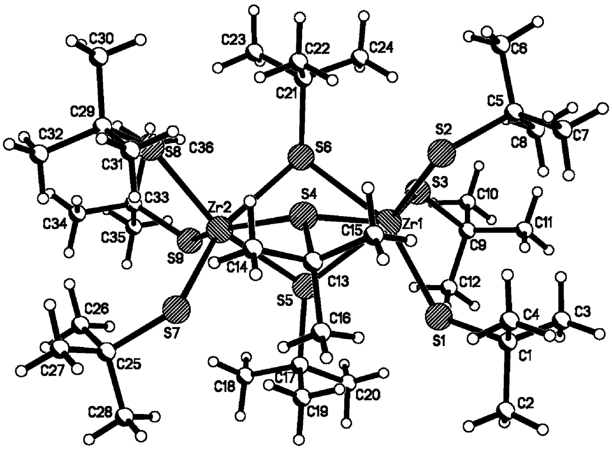

**Fig. 2** The molecular structure of the anion in the structure of **2**.

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

| | | | |
|---|---|---|---|
| Zr(1)–S(1) | 2.4360(8) | Zr(1)–S(2) | 2.4641(8) |
| Zr(1)–S(3) | 2.5489(8) | Zr(1)–S(6) | 2.6842(7) |
| Zr(1)–S(4) | 2.6902(7) | Zr(1)–S(5) | 2.7336(7) |
| Zr(2)–S(8) | 2.4531(9) | Zr(2)–S(7) | 2.4654(8) |
| Zr(2)–S(9) | 2.5451(8) | Zr(2)–S(6) | 2.6743(7) |
| Zr(2)–S(5) | 2.6871(8) | Zr(2)–S(4) | 2.7110(7) |

| | | | |
|---|---|---|---|
| S(1)–Zr(1)–S(2) | 105.38(3) | S(1)–Zr(1)–S(3) | 101.68(3) |
| S(2)–Zr(1)–S(3) | 104.66(3) | S(1)–Zr(1)–S(6) | 152.73(3) |
| S(2)–Zr(1)–S(6) | 101.32(3) | S(3)–Zr(1)–S(6) | 76.49(2) |
| S(1)–Zr(1)–S(4) | 108.01(3) | S(2)–Zr(1)–S(4) | 80.66(2) |
| S(3)–Zr(1)–S(4) | 147.28(3) | S(6)–Zr(1)–S(4) | 70.83(2) |
| S(1)–Zr(1)–S(5) | 83.76(3) | S(2)–Zr(1)–S(5) | 161.84(3) |
| S(3)–Zr(1)–S(5) | 88.39(2) | S(6)–Zr(1)–S(5) | 69.03(2) |
| S(4)–Zr(1)–S(5) | 81.58(2) | S(8)–Zr(2)–S(7) | 103.96(3) |
| S(8)–Zr(2)–S(9) | 89.94(3) | S(7)–Zr(2)–S(9) | 111.59(3) |
| S(8)–Zr(2)–S(6) | 89.88(3) | S(7)–Zr(2)–S(6) | 154.35(3) |
| S(9)–Zr(2)–S(6) | 89.56(2) | S(8)–Zr(2)–S(5) | 154.98(3) |
| S(7)–Zr(2)–S(5) | 100.42(3) | S(9)–Zr(2)–S(5) | 75.83(2) |
| S(6)–Zr(2)–S(5) | 69.87(2) | S(8)–Zr(2)–S(4) | 105.57(3) |
| S(7)–Zr(2)–S(4) | 84.72(2) | S(9)–Zr(2)–S(4) | 154.43(2) |
| S(6)–Zr(2)–S(4) | 70.66(2) | S(5)–Zr(2)–S(4) | 82.06(2) |

dissolving to form [$Ti_3(SMe)_{12}$] and other compounds.[15,26] The formation of **2** is surprising based on related reactions of zirconium compounds with thiols, which suggest that cluster formation, *via* C–S bond cleavage, is favoured.[23–25] Thus, the reaction of $Bu^tSH$ with [$Zr(BH_4)_4$] was reported to form the cluster [$Zr_3S_3(Bu^tS)_2(BH_4)_4(thf)_2$], which dimerises *via* dissociation of a thf molecule to give [$Zr_6S_6(Bu^tS)_4(BH_4)_8(thf)_2$].[23,24] Similarly, the trinuclear cluster [$Zr_3(S)(SBu^t)_{10}$] was isolated from the reaction of [$Zr(CH_2Ph)_4$] and $Bu^tSH$.[25] The formation of these clusters is the result of C–S bond cleavage allowing the inclusion of sulfido ligands in the structure. The reaction of [$Zr(NMe_2)_4$] with $Bu^tSH$ to give **2** does not result in facile C–S bond cleavage hence only thiolate ligands coordinate to the Zr centre in **2**. Therefore, this route represents a facile method for the preparation of homoleptic zirconium thiolate complexes. Salt elimination routes to related zirconium thiolate anions have been published previously and resulted in the formation of [Li(DME)][$Zr(SBu^t)_5$] and [$Li(thf)]_2[Zr(SBu^t)_6$].[28]

A neutral homoleptic zirconium thiolate has been isolated. Thus, reaction of [$Zr(NMe_2)_4$] and four equivalents of 2-mercaptopyridine ($HSC_5H_4N$) was carried out in dichloromethane at room temperature. An immediate colour change from colourless to bright yellow occurred on addition of the thiol. A yellow microcrystalline solid formed in a 52% yield on cooling a concentrated dichloromethane solution to −20 °C. Unfortunately, it was not possible to obtain a single crystal structure of the product. However, analytical and spectroscopic data for the yellow crystalline solid indicated that the homoleptic compound [$Zr(SC_5H_4N)_4$] (**3**) had formed. The structure of **3** is expected to be eight-coordinate (Scheme 1), based on related Zr monothiocarbamate complexes (*e.g.* [$Zr(SOCNEt_2)_4$]), in which the four S atoms are clustered in all-*cis* positions on one side of the coordination polyhedron.[29] The $^1H$ NMR data of **3** shows that there is one ligand environment present corresponding to 2-mercaptopyridine. The absence of $NMe_2$ groups in the $^1H$ NMR of **3** was noted, indicating that all of the amido groups had been exchanged for thiolate ligands.

## Thermal analysis and CVD studies

Since early transition metal thiolates are of interest as precursors to $MS_2$ materials, the thermal decomposition of some of the compounds was investigated. The TGA of **1** shows one distinct mass loss which is almost complete at 200 °C (74.8% mass loss). The total mass loss of 81% is close to the 86% required for complete decomposition of **1** to $TiS_2$, suggesting that this compound would make a good precursor and could deposit films at low temperatures (<400 °C). The sharp endotherm at 74 °C in the DSC of **1** signifies a melting point suggesting that the precursor could be volatilised at a low temperature. The TGA for **2** shows a total mass loss of 60% at 500 °C, much lower than the 85% required for formation of $ZrS_2$. Furthermore, the DSC shows a broad endotherm at 72 °C corresponding to a decomposition of the complex. This decomposition is at a lower temperature than the melting point of 125 °C signified by the sharp endotherm. This means that carry over of the precursor to the substrate would not be possible without decomposition using conventional CVD thermal volatilisation methods.

Compound **1** showed a clean decomposition and gave the best deposition characteristics, therefore LPCVD of **1** was investigated. The details of the LPCVD are described in the Experimental section.[30] A dark purple film was deposited on glass substrates from **1** over 6 h at 600 °C and 0.03 mm Hg. Energy dispersive X-ray analysis showed that films deposited from **1** were composed of titanium and sulfur with elemental ratios close to 1 : 2. Some slight deviations were noted from this composition for thinner films where breakthrough to the underlying glass was observed. No evidence of carbon or fluorine contamination was noted to the detection limits of the instrument. The Raman pattern measured was characteristic of $TiS_2$ with a large peak at 330 $cm^{-1}$ and a shoulder at 367 $cm^{-1}$.[1] No other Raman peaks were observed showing that $TiO_2$ or graphitic carbon were not present. The SEM image (Fig. 3) shows that the films have a needle-like morphology with needles of *ca.* 0.4 µm in length. This morphology matches well with previous reported results from the LPCVD of [$Ti(SBu^t)_4$] and also with atmospheric pressure (AP)CVD films at 600 °C from $TiCl_4$ and thiols.[5,31] The films studied in this work were amorphous by glancing angle X-ray diffraction, in agreement with results obtained for low pressure films produced from the single-source precursor [$Ti(SBu^t)_4$].[3,5] The purple colour of the $TiS_2$ films produced from **1** is similar to those described previously from the LPCVD of [$Ti(SBu^t)_4$] and [$Ti(SBu^t)_3(NEt_2)$].[3,32]

In summary, three new group(IV) thiolate complexes have been synthesised *via* amide/thiolate exchange. Two of the complexes, [$Me_2NH_2]_2[Ti(SCH_2CF_3)_6$] and [$Me_2NH_2$] [$Zr_2(SBu^t)_3(\mu\text{-}SBu^t)_6$] have been structurally characterised. $TiS_2$ thin films have been deposited on glass substrates *via* LPCVD

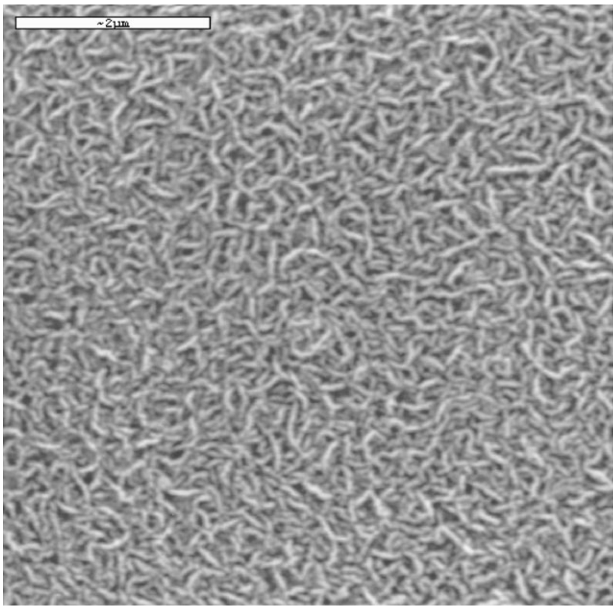

**Fig. 3** SEM of a film grown from **1**.

from $[Me_2NH_2]_2[Ti(SCH_2CF_3)_6]$. The low decomposition temperature of $[Me_2NH_2]_2[Ti(SCH_2CF_3)_6]$ is surprising given the ionic nature of this complex.

## Experimental

### General procedures

All manipulations were carried out under a dry, oxygen-free dinitrogen atmosphere using either standard Schlenk techniques or in a MBraun Unilab glove box. Dichloromethane was distilled from $CaH_2$ prior to use and hexanes were dried using sodium/benzophenone. $[Ti(NMe_2)_4]$ was obtained from Epichem Ltd and used as received. $[Zr(NMe_2)_4]$ was made following literature methods.[33] All thiols were procured commercially from Aldrich and were dried over molecular sieves and degassed before use. Microanalytical data were obtained at University College London (UCL).

### Physical measurements

NMR spectra were recorded on a Brüker AMX400 spectrometer at UCL, referenced to $CD_2Cl_2$, which was dried and degassed over molecular sieves prior to use; $^1$H and $^{13}$C chemical shifts are reported relative to $SiMe_4$ ($\delta$ 0.00). FT-IR spectra were recorded on a Shimadzu FTIR-8200 instrument. Mass spectra were recorded on a Micromass VG 70-SE spectrometer. Thermal gravimetric analysis (TGA) was performed under a dinitrogen atmosphere with a heating rate of 10 °C min$^{-1}$ and obtained from the Thermal Methods Laboratory at Birkbeck College London. 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. EDXA was obtained on a JOEL 25 and SEM was obtained on a Hitachi S570 instrument using the KEVEX system. UV-Vis spectra were recorded in the range 200–1100 nm using a Helios double beam instrument.

**Synthesis of 1.** 2,2,2-Trifluoroethanethiol (0.3 cm$^3$, 3.38 mmol) was added to a solution of $[Ti(NMe_2)_4]$ (0.2 cm$^3$, 0.85 mmol) in hexanes (30 cm$^3$) with an immediate colour change to dark red. Stirring was continued for 3 h whereby a dark red precipitate had formed. The solution was removed by filtration and the precipitate was washed with 2 × 5 cm$^3$ of hexanes and dried *in vacuo*. Dark red needle like crystals (0.58 g, 82%) were obtained by cooling a concentrated solution of the precipitate in dichloromethane with an overlayer of hexanes to −20 °C for 3 d. $^1$H NMR ($CD_2Cl_2$) $\delta$ 2.55 (s, 12H, $H_2NMe_2$), 4.1 (quartet, 12H, $SCH_2CF_3$), 6.2 (s, 4H, $H_2NMe_2$). $^{13}$C{$^1$H} NMR ($CD_2Cl_2$) $\delta$ 36.9 ($H_2NMe_2$), 38.6 ($SCH_2CF_3$) 45.3 ($SCH_2CF_3$). Anal. calc. for $C_{16}H_{28}F_{18}N_2S_6Ti$ C, 23.2; H, 3.4; N, 3.4. Found C, 23.9; H, 3.8; N, 3.1%. Melting point: 74 °C.

**Synthesis of 2.** 2-Methyl-2-propanethiol (0.2 cm$^3$, 1.50 mmol) was added to $Zr(NMe_2)_4$ (0.1 g, 0.37 mmol) in dichloromethane (30 cm$^3$) producing an orange solution. Stirring was continued for 3 h and the solution was concentrated *in vacuo* to approximately 1 cm$^3$. Yellow crystals suitable for X-ray analysis were isolated on cooling to −20 °C overnight. Yield = 62%, melting point 125 °C. $^1$H NMR ($CD_2Cl_2$) $\delta$ 1.40 (s, 54H, $SC(CH_3)_3$), 1.60 (s, 27H, μ-$SC(CH_3)_3$), 2.75 (s, 6H, $H_2NMe_2$), 2.8 (s, 2H, $H_2NMe_2$). $^{13}$C NMR ($CD_2Cl_2$) $\delta$ 35.0 ($SC(CH_3)_3$), 42.0 ($SC(CH_3)_3$). Anal. Calc. For $C_{38}H_{89}NS_9Zr_2$ C, 44.3; H, 8.7; N, 1.4. Found C, 44.8; H, 8.9; N, 1.4%.

**Synthesis of 3.** 2-Mercaptopyridine (0.17 g, 1.50 mmol) was added to a stirred solution of $[Zr(NMe_2)_4]$ (0.1 g, 0.37 mmol) in dichloromethane (30 cm$^3$). Stirring was continued for 1 h giving a bright yellow solution. This was concentrated to approximately 2 cm$^3$ *in vacuo* and was cooled to −20 °C. A yellow microcrystalline solid formed (0.10 g, yield 52%). $^1$H NMR ($CD_2Cl_2$) $\delta$ 6.90 (m, 4H, m-$SC_5H_4N$), 7.10 (m, 4H, p-$SC_5H_4N$), 7.46 (m, 4H, m-$SC_5H_4N$), 8.00 (m, 4H, o-$SC_5H_4N$). $^{13}$C{$^1$H} NMR ($CD_2Cl_2$) $\delta$ 118.4 (m-$SC_5H_4N$), 128.4 (m-$SC_5H_4N$), 138.5 (p-$SC_5H_4N$), 144.2 (o-$SC_5H_4N$), 173.5 (o-$SC_5H_4N$). Anal. calc. for $C_{20}H_{16}N_4S_4Zr(CH_2Cl_2)_{0.3}$ C, 43.7; H, 3.0; N, 10.0. Found C, 43.3; H, 3.1; N, 9.9%.

### Single crystal X-ray analysis

Crystals of **1** were obtained at −20 °C from dichloromethane–hexanes layers, whereas crystals of **2** were isolated from dichloromethane at −20 °C.

### Low pressure CVD

Approximately 1.0 g of compound **1** was loaded into the sealed end of a glass tube (400 mm length × 16 mm diameter) in the glovebox. Uncoated glass substrates of 8 cm × 1 cm were used and were cleaned prior to use by washing with petroleum ether (40–60 °C) and propan-2-ol and then dried in air. The tube was then placed in a furnace such that 35 cm was inside the furnace and the end containing the sample protruded by 5 cm. The tube was heated to a temperature of 550 °C under dynamic vacuum (0.3 mmHg). The tube was slowly drawn into the furnace, *ca.* 1–2 cm h$^{-1}$ until the sample started to melt. It was then held at that point until the precursor had decomposed. Once the compound had decomposed the furnace was allowed to cool to room temperature. Coated substrates were handled in air but stored under an inert atmosphere in a Mbraun Unilab glove box. Purple films were deposited from **1** which were analysed by EDAX/SEM, Raman spectroscopy and UV/visible.

**Crystal data for 1.** $C_{20}H_{36}F_{18}N_2S_6Ti$, $M$ = 886.77, triclinic, $P\bar{1}$, $a$ = 8.173(5), $b$ = 10.794(7), $c$ = 10.913(7) Å, $\alpha$ = 69.484(13), $\beta$ = 85.759(13), $\gamma$ = 82.043(13)°, $V$ = 894.7(11) Å$^3$, $Z$ = 1, $D_c$ = 1.646 g cm$^{-3}$, μ(Mo-Kα) = 0.701 mm$^{-1}$, $T$ = 150(2) K, red needles 0.46 × 0.22 × 0.08 mm; 7839 reflections collected on a Bruker SMART APEX diffractometer; 4106 independent reflections ($R_{int}$ = 0.0289) refined on $F^2$ to, $R_1$ = 0.0468, $wR_2$ = 0.1107, (3675 reflections with $|F_o| > 4\sigma|F_o|$ gave $R_1$ = 0.0416, $R$ = 0.1064). The final refinement included 216 parameters and the largest residual was 0.763 eÅ$^3$. CCDC 248661.†

**Crystal data for 2.** $C_{40}H_{93}Cl_4NS_9Zr_2$, $M$ = 1200.93, monoclinic, $P2_1/c$, $a$ = 11.8588(6), $b$ = 18.7448(10), $c$ = 27.2112(14) Å, $\beta$ = 94.2710(10)°, $V$ = 6032.0(5) Å$^3$, $Z$ = 4, $D_c$ = 1.322 g cm$^{-3}$, μ(Mo-Kα) = 0.861 mm$^{-1}$, $T$ = 150(2) K, yellow prisms 0.49 × 0.44 × 0.32 mm; 52874 reflections collected on a Bruker SMART APEX diffractometer; 14128 independent reflections ($R_{int}$ = 0.0318) refined on $F^2$, $R_1$ = 0.0584, $wR_2$ = 0.1127, (12313 reflections with $|F_o| > 4\sigma|F_o|$ gave $R_1$ = 0.0494, $R$ = 0.1086). The final refinement included 505 parameters and the largest residual was 1.68 eÅ$^3$, closed to a lattice dichloromethane molecule. CCDC 248662.†

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† CCDC reference numbers 248661 and 248662. See http://www.rsc.org/suppdata/nj/b4/b413060j/ for crystallographic data in .cif or other electronic format.

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