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Hard/soft interactions in early transition metal chemistry: synthesis, properties and structures of thioether and selenoether complexes of titanium(IV)

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Reaction of $TiCl_4$ with L–L [L–L = $MeE(CH_2)_nEMe$; E = S or Se, $n = 2$ or 3, $PhE(CH_2)_2EPh$ or o-$C_6H_4(EMe)_2$] in anhydrous n-hexane solution under an N_2 atmosphere results in the rapid formation of [$TiCl_4$(L–L)] as yellow, orange or red solids. Analogous bromo and iodo species, [TiX_4(L–L)] [X = Br; L–L = $MeE(CH_2)_nEMe$ or o-$C_6H_4(EMe)_2$; X = I; L–L = $MeSe(CH_2)_2SeMe$ or o-$C_6H_4(SeMe)_2$], were obtained as intense orange or red coloured solids by treatment of TiX_4 with L–L in CH_2Cl_2 solution. Crystallographic studies on [$TiCl_4${$MeS(CH_2)_2SMe$}], [$TiCl_4${$MeS(CH_2)_3SMe$}], [$TiCl_4${$MeSe(CH_2)_3SeMe$}] and [$TiCl_4${o-$C_6H_4(SeMe)_2$}] reveal a distorted octahedral arrangement with the coordinated group 16 donor ligand adopting the DL form in the first three cases and the *meso* form in the fourth example. These studies also reveal a *trans* influence series of Cl > S ≈ Se on Ti(IV). Solution NMR studies show that the chloro-compounds undergo rapid pyramidal inversion at ambient temperature, while the bromo and iodo species also undergo rapid ligand dissociation/chelate ring-opening. At low temperature these processes are slowed significantly, such that in most of the chloro and bromo species it is possible to identify both the *meso* and DL invertomers, although ligand exchange is still rapid at 200 K for the iodo species. The potential of these compounds as sources of titanium sulfide or titanium selenide phases *via* controlled decomposition is also discussed briefly. Finally, the dinuclear species, [Cl_3Ti{$MeS(CH_2)_2SMe$}]$_2$(μ-O), formed by partial hydrolysis of [$TiCl_4${$MeS(CH_2)_2SMe$}], has also been identified crystallographically.

Introduction

The coordination chemistry of thio- and seleno-ether ligands with transition metal centres is dominated by complexes involving middle and late transition metals in medium or high oxidation states, although a number of low-valent early transition metal carbonyl complexes involving seleno- and telluro-ether ligands have been reported.[1,2] We have investigated the synthesis and properties of group 16 donor ligands and their coordination to a wide range of transition metal and p-block ions in order to exploit the versatile nature of these ligands towards both high and low oxidation state metals. We are particularly interested in developing the coordination chemistry of the group 4 and group 5 metals with thio- and seleno-ethers as potential single source precursors to metal chalcogenide materials. Transition metal sulfides and selenides represent an important class of inorganic materials with diverse applications ranging from, for example, cathode materials in rechargeable Li batteries, to semiconductors and semimetals.[3] The use of single source precursors to these materials is attractive since applications often require that the materials are deposited as thin films and these are not easily obtained with conventional methods. Here we report on our investigation of the preparation, structural features and properties of Ti(IV) halide compounds with a range of bidentate thio- and seleno-ether ligands. There are scattered reports in the literature on Ti(IV) thio- and seleno-ether compounds, but generally their characterisation is very limited and there have been no systematic studies of their properties.[4] Very recently Winter and coworkers have structurally characterised some complexes with monodentate thio- and seleno-ethers, although these were mainly obtained indirectly as metal-mediated decomposition products.[5] We report here on the preparation and spectroscopic characterisation of a series of TiX_4 (X = Cl, Br or I) complexes with bidentate thioether or seleno ether ligands. The bromo and iodo species were included since the volatility and decomposition behaviour of this class of compound is expected to vary with halogen. There are very few well characterised TiI_4 complexes in the literature,[6] and no thio- or seleno-ether derivatives. The group 16 donor ligands which we have used includes a range of C-functionalities since this is expected to permit some tuning of the deposition characteristics at the next stage of this work. The crystal structures of [$TiCl_4${$MeS(CH_2)_2SMe$}], [$TiCl_4${$MeS(CH_2)_3SMe$}], [$TiCl_4${$MeSe(CH_2)_3SeMe$}], [$TiCl_4${o-$C_6H_4(SeMe)_2$}] and [{$MeS(CH_2)_2SMe$}Cl_3Ti(μ-O)$TiCl_3${$MeS(CH_2)_2SMe$}] are also described.

Results and discussion

Reaction of $TiCl_4$ with L–L [L–L = $MeE(CH_2)_nEMe$, E = S or Se, $n = 2$ or 3, $PhE(CH_2)_2EPh$, o-$C_6H_4(EMe)_2$] in rigorously anhydrous n-hexane solution at room temperature results in the immediate precipitation of a yellow, orange or red solid, [$TiCl_4$(L–L)]. The bromo and iodo derivatives, [$TiBr_4$(L–L)] [L–L = $MeE(CH_2)_nEMe$ or o-$C_6H_4(EMe)_2$] and [TiI_4(L–L)] [L–L = $MeSe(CH_2)_2SeMe$ or o-$C_6H_4(SeMe)_2$], were prepared by dissolving $TiBr_4$ or TiI_4 in rigorously anhydrous CH_2Cl_2 with L–L, and precipitating the resulting deep orange or red products with n-hexane. The iodo derivatives proved to be particularly difficult to isolate as powdered solids, and typically the yields of these products were considerably lower than for the chloro and bromo species. All of the complexes are extremely readily hydrolysed, rapidly decolorising and liberating L–L upon exposure to moist air. Therefore, the compounds were routinely stored in a dry, N_2-purged glove-box and under these conditions the solids do not exhibit any appreciable decomposition over a period of a few weeks.

IR spectroscopy reveals up to four bands in the region 420–370 or 330–290 cm^{-1}, tentatively attributed to ν(Ti–Cl) or ν(Ti–Br) respectively, indicative of *cis*-[TiX_4(L–L)] (theory $2a_1 + b_1 + b_2$). These data, together with microanalyses,

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indicate that the products are *cis*-[TiX_4(L–L)]. Electronic spectra were recorded by diffuse reflectance owing to the extreme sensitivity of the compounds. The spectra of these d^0 Ti(IV) compounds show several broad and intense charge transfer (CT) transitions. The bromide species generally show broad, ill-defined overlapping transitions. This is not surprising since on electronegativity grounds $\pi(Br) \longrightarrow Ti(t_{2g})$ is unlikely to be very different from $\pi(Se\ or\ S) \longrightarrow Ti(t_{2g})$. Analysis of the spectra shows that the $\pi(Cl) \longrightarrow Ti(t_{2g})$ transitions occur at *ca.* 28500 cm^{-1}, $\pi(Br) \longrightarrow Ti(t_{2g})$ at *ca.* 22500 cm^{-1}, $\pi(S) \longrightarrow Ti(t_{2g})$ at *ca.* 22000 cm^{-1} and $\pi(Se) \longrightarrow Ti(t_{2g})$ at *ca.* 21000 cm^{-1}. These values compare with *ca.* 28000 and 22000 cm^{-1} for the lowest energy $\pi(X) \longrightarrow Ti(t_{2g})$ CT transitions in $[TiX_6]^{2-}$ for X = Cl and Br respectively,[7] and serve to confirm the donor types present.

The solution behaviour of these species was investigated *via* ^1H, $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectroscopy in chlorocarbon solvents. The ^1H NMR spectra are rather less informative than either the $^{13}C\{^1H\}$ or $^{77}Se\{^1H\}$ spectra, however they confirm the presence of the dithio- or diseleno-ether ligand. For the $TiCl_4$ adducts sharp ^1H resonances are observed, these broaden significantly in the $TiBr_4$ adducts, indicating that ligand dissociation and/or fast pyramidal inversion is occurring at 300 K (see below). Resonances for the individual invertomers are not observed at this temperature. At 300 K the $^{13}C\{^1H\}$ NMR spectra of the $TiCl_4$/dithioether systems generally show sharp ligand resonances consistent with the high temperature limiting case, while those of the selenoether complexes are very much broader, suggesting that inversion is slower for these species. Cooling to *ca.* 220 K reveals sharp resonances associated with the presence of both the *meso* and DL forms in varying ratios. Similar behaviour is observed by $^{77}Se\{^1H\}$ NMR spectroscopy. Thus, at 300 K no resonances are seen in any of the $^{77}Se\{^1H\}$ NMR spectra. However, two resonances of unequal intensity are clearly observed to high frequency of the free diselenoether upon cooling to 200 K. Addition of $MeS(CH_2)_2SMe$ to a solution of [$TiCl_4\{MeS(CH_2)_2SMe\}$] at 300 K results in very broad, but discrete, $^{13}C\{^1H\}$ resonances for 'free' and coordinated $MeS(CH_2)_2SMe$. Cooling this system to 250 K results in sharp resonances associated with both constituents and with the same chemical shifts as the individual species. This result indicates that intermolecular exchange is slow at 250 K, becoming detectable (but not fast) at room temperature for this $TiCl_4$ system. These results also indicate that eight-coordinate species do not form under these conditions. The susceptibility of these compounds to hydrolysis is demonstrated by the observation that the deliberate addition of wet CH_2Cl_2 to a sample of [$TiCl_4\{MeS(CH_2)_2SMe\}$] results in an immediate decolorisation and the $^{13}C\{^1H\}$ NMR spectrum shows resonances associated with uncoordinated $MeS(CH_2)_2SMe$ only.

The solution behaviour of the $TiBr_4$/dithioether and $TiBr_4$/diselenoether systems are more complex. At 300 K only very broad resonances are observed in the $^{13}C\{^1H\}$ NMR spectra. Similarly, no $^{77}Se\{^1H\}$ resonances are evident at 300 K. $^{13}C\{^1H\}$ NMR spectra of [$TiBr_4\{MeE(CH_2)_2EMe\}$] and [$TiBr_4\{o\text{-}C_6H_4(EMe)_2\}$] at 200 K reveal resonances due to 'free' dithioether or diselenoether, as well as weak resonances attributed to the *meso* and DL forms of the coordinated ligand. For example, at 200 K the $^{13}C\{^1H\}$ NMR spectrum of [$TiBr_4\{o\text{-}C_6H_4(SeMe)_2\}$] shows a 'free' : coordinated selenoether ratio of *ca.* 1 : 2 and a (coordinated) *meso* : DL ratio of *ca.* 1 : 1. $^{77}Se\{^1H\}$ NMR spectroscopy at 200 K shows that [$TiBr_4\{MeSe(CH_2)_3SeMe\}$] is extensively dissociated in solution, revealing a strong resonance for free ligand, with no obvious sign of resonances from coordinated selenoether. The limited solubilities of [$TiBr_4\{MeSe(CH_2)_2SeMe\}$] and [$TiBr_4\{o\text{-}C_6H_4(SeMe)_2\}$] prevented us from observing $^{77}Se\{^1H\}$ NMR resonances even at 200 K. The iodo complexes show sharp $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$ NMR resonances to high frequency of the group 16 donor ligand itself even at 200 K with no evidence for individual invertomers. This is consistent with ligand exchange still occurring rapidly even under these low temperature conditions.

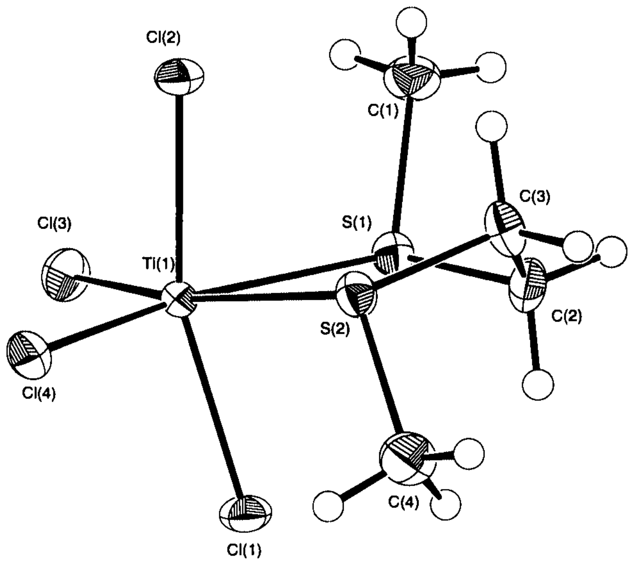

Fig. 1 View of the structure of [$TiCl_4\{MeS(CH_2)_2SMe\}$] with the numbering scheme adopted. Ellipsoids are drawn at the 40% probability level.

The NMR data indicate the relative Lewis acid ability of the Ti(IV) tetrahalides as $TiCl_4 > TiBr_4 > TiI_4$. Thus, while the $TiCl_4$ adducts are undergoing fast inversion at room temperature on the NMR timescale, dissociation is slow (see above); inversion is slow at low temperature. In contrast for the $TiBr_4$ derivatives, both ligand dissociation and pyramidal inversion are fast at room temperature. Both of these dynamic processes are slowed considerably at 200 K, but for those systems at the low temperature limit, a mixture of [$TiBr_4$(L–L)], L–L and $TiBr_4$ are present in varying amounts (see above). The iodide complexes undergo rapid exchange even at 200 K.

Unfortunately, unlike in our previous studies on SnX_4 complexes with group 16 donor ligands,[8] where ^{119}Sn NMR spectra proved very useful in understanding the solution behaviour of the new compounds, we were unable to observe the metal nucleus (in this case $^{47/49}Ti$ †) NMR spectra for the compounds in this work. We were easily able to observe $^{47/49}Ti$ NMR resonances for [$(\eta^5\text{-}C_5H_5)_2TiCl_2$] in CH_2Cl_2 at 300 K. Cooling this solution resulted in significant broadening and eventual loss of the signal, presumably due to the quadrupole. Since for the thio- and seleno-ether systems we were unable to observe $^{47/49}Ti$ NMR spectra either at room temperature or on cooling, and as these nuclei have similar receptivities to ^{13}C (although both are lower frequency and quadrupolar), the absence of $^{47/49}Ti$ resonances is consistent with the occurrence of dynamic processes in solution (see above).

In view of the paucity of well characterised thio- and selenoether complexes of Ti(IV) and in order to establish unequivocally the coordination geometry at Ti(IV), single crystal X-ray structure analyses were undertaken on [$TiCl_4\{MeS(CH_2)_2SMe\}$], [$TiCl_4\{MeS(CH_2)_3SMe\}$], [$TiCl_4\{MeSe(CH_2)_3SeMe\}$] and [$TiCl_4\{o\text{-}C_6H_4(SeMe)_2\}$]. Crystals were obtained by slow evaporation from CH_2Cl_2 solutions of the complexes. The structure of [$TiCl_4\{MeS(CH_2)_2SMe\}$] shows (Fig. 1, Table 1) a distorted octahedral geometry at Ti(IV) derived from four chloro ligands and two mutually *cis* S-donors from a chelating dithioether in the DL form. The two mutually *trans* Cl ligands lean towards the dithioether ligand [Cl(1)–Ti(1)–Cl(2) 162.91(3)°]. A similar arrangement was observed previously for Sn(IV)–tetrahalo derivatives incorporating bidentate dithio-,

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† Unusually both ^{47}Ti and ^{49}Ti resonances occur within the same spectral range.

Table 1 Selected bond lengths (Å) and angles (°) for [$TiCl_4${MeS-$(CH_2)_2$SMe}]

Ti(1)–Cl(1)	2.2907(8)	Ti(1)–Cl(4)	2.2253(9)
Ti(1)–Cl(2)	2.2926(8)	Ti(1)–S(1)	2.6106(9)
Ti(1)–Cl(3)	2.2358(8)	Ti(1)–S(2)	2.6010(8)
Cl(1)–Ti(1)–Cl(2)	162.91(3)	Cl(4)–Ti(1)–S(1)	167.45(3)
Cl(1)–Ti(1)–Cl(3)	95.68(3)	Cl(4)–Ti(1)–S(2)	88.03(3)
Cl(1)–Ti(1)–Cl(4)	94.75(3)	S(1)–Ti(1)–S(2)	80.34(3)
Cl(1)–Ti(1)–S(1)	80.02(3)	Cl(1)–Ti(1)–S(2)	86.98(3)
Cl(2)–Ti(1)–Cl(3)	95.20(3)	Cl(2)–Ti(1)–Cl(4)	94.95(3)
Cl(2)–Ti(1)–S(1)	87.58(3)	Cl(2)–Ti(1)–S(2)	79.33(3)
Cl(3)–Ti(1)–Cl(4)	105.66(3)	Cl(3)–Ti(1)–S(1)	86.30(3)
Cl(3)–Ti(1)–S(2)	165.73(3)		

Table 2 Selected bond lengths (Å) and angles (°) for [$TiCl_4${MeS-$(CH_2)_3$SMe}]

Ti(1)–Cl(1)	2.235(2)	Ti(1)–Cl(2)	2.285(2)
Ti(1)–S(1)	2.644(2)		
Cl(1)–Ti(1)–Cl(1*)	102.8(1)	Cl(2)–Ti(1)–S(1)	82.24(9)
Cl(1)–Ti(1)–Cl(2)	96.53(9)	Cl(2)–Ti(1)–S(1*)	86.44(9)
Cl(1)–Ti(1)–Cl(2*)	92.73(9)	Cl(1)–Ti(1)–S(1)	88.37(7)
Cl(1)–Ti(1)–S(1*)	168.3(1)	S(1)–Ti(1)–S(1*)	80.8(1)
Cl(2)–Ti(1)–Cl(2*)	165.1(1)		

Table 3 Selected bond lengths (Å) and angles (°) for [$TiCl_4${MeSe-$(CH_2)_3$SeMe)]

Ti(1)–Cl(1)	2.278(3)	Ti(1)–Se(1)	2.755(3)
Ti(1)–Cl(2)	2.247(4)		
Cl(2)–Ti(1)–Cl(2*)	104.1(2)	Cl(2)–Ti(1)–Se(1)	87.50(11)
Cl(2)–Ti(1)–Cl(1)	94.19(14)	Cl(1)–Ti(1)–Se(1)	81.58(11)
Cl(2)–Ti(1)–Cl(1*)	95.79(13)	Cl(1)–Ti(1)–Se(1*)	86.07(11)
Cl(1)–Ti(1)–Cl(1*)	163.7(2)	Se(1)–Ti(1)–Se(1*)	81.12(12)
Cl(2)–Ti(1)–Se(1*)	168.09(14)		

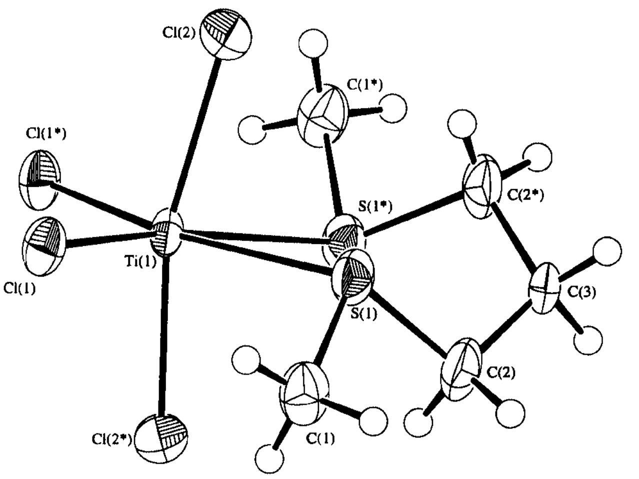

Fig. 2 View of the structure of [$TiCl_4${$MeS(CH_2)_3SMe$}] with the numbering scheme adopted. Ellipsoids are drawn at the 40% probability level.

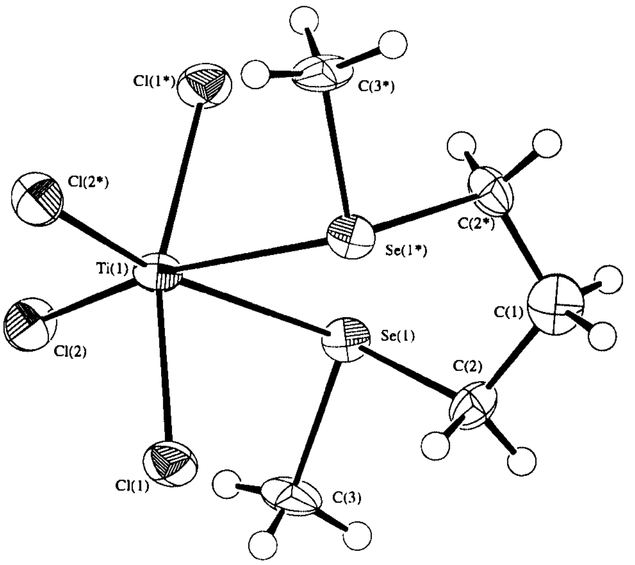

Fig. 3 View of the structure of [$TiCl_4${$MeSe(CH_2)_3SeMe$)] with the numbering scheme adopted. Ellipsoids are drawn at the 40% probability level.

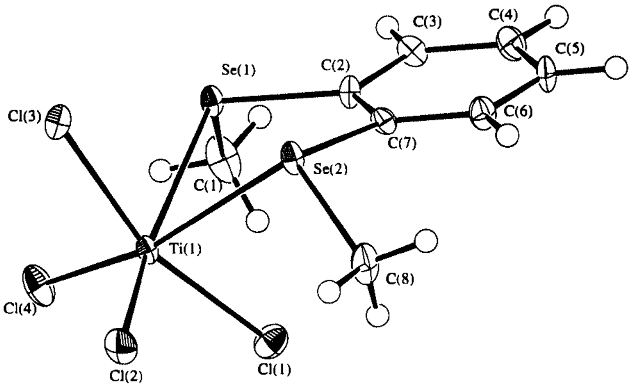

Fig. 4 View of the structure of [$TiCl_4${o-$C_6H_4(SeMe)_2$}] with the numbering scheme adopted. Ellipsoids are drawn at the 40% probability level.

diseleno- and ditelluro-ether ligands, which are also derived from a tetrahedral metal precursor, in this case SnX_4.[8] Indeed, all of the Cl–Ti–S bond angles are less than the 90° expected for a regular octahedron. The Ti–S bond distances of 2.6106(9) and 2.6010(8) Å in this complex are similar to those observed in the disulfide species [$TiCl_4(H_8C_4SSC_4H_8)$], 2.626(7), 2.625(7) Å,[5] and are only slightly longer than those in the imido species, [$TiCl_2(NBu^t)$([9]aneS_3)] ([9]aneS_3 = 1,4,7-trithiacyclononane), Ti–$S_{trans\mathrm{Cl}}$ = 2.575(1), 2.591(1), Ti–$S_{trans\mathrm{N}}$ = 2.750(1) Å.[9] The Ti–$Cl_{trans\mathrm{S}}$ bond distances, 2.2358(8) and 2.2253(9) Å, are significantly shorter than those for the mutually *trans* Cl ligands, 2.2907(8), 2.2926(8) Å, consistent with the preference of the hard Ti(IV) centre for hard Cl ligands. This suggests a *trans* influence order on Ti(IV) of Cl > S. [$TiCl_4${$MeS(CH_2)_3SMe$}] (Fig. 2, Table 2) adopts a similar structure, with the dithioether adopting the DL configuration and the Cl ligands *cis* to the S atoms tilted towards the dithioether [Cl(2)–Ti(1)–Cl(2*) 165.1(1)°]. The Ti–S and Ti–Cl bond distances are comparable with, and exhibit the same trends as, those in [$TiCl_4${MeS-$(CH_2)_2$SMe}] above. The selenoether complex [$TiCl_4${MeSe-$(CH_2)_3$SeMe}] (Fig. 3, Table 3) is not isomorphous, but adopts a very similar molecular structure to [$TiCl_4${$MeS(CH_2)_3SMe$}] above, although the structure of the former was obtained from a twinned crystal (see Experimental section). Thus, this species adopts a distorted octahedral geometry with the diselenoether ligand chelating and in the DL form. The compound has crystallographic two-fold symmetry, with Ti–Cl 2.278(3), 2.247(4) Å and Ti–Se 2.755(3) Å. The Ti–Se distances are longer than *d*(Ti–S) in the thioether species above as expected, and comparable with those in *cis*-[$TiCl_4(SeR_2)_2$] [R = Me, Ti–Se 2.777(4), 2.743(4); R = Et, Ti–Se 2.740(2), 2.763(2) Å] and similar also to those in the diselenide complex [$TiCl_4$(Et-SeSeEt)] [2.796(2) Å].[5] The complex [$TiCl_4${o-$C_6H_4(SeMe)_2$}] (Fig. 4, Table 4) shows similar Ti–Cl and Ti–Se bond distances, although this species adopts the *meso* form, with both Se-bound Me groups lying on the same side of the $TiCl_2Se_2$ plane.

During our initial attempts to obtain crystals of [$TiCl_4$-{$MeS(CH_2)_2SMe$}] we grew crystals of the dinuclear species,

Table 4 Selected bond lengths (Å) and angles (°) for $[TiCl_4\{o\text{-}C_6H_4(SeMe)_2\}]$

Se(1)–Ti(1)	2.727(1)	Ti(1)–Cl(3)	2.308(2)
Ti(1)–Cl(4)	2.239(2)	Se(2)–Ti(1)	2.744(1)
Ti(1)–Cl(1)	2.267(2)	Ti(1)–Cl(2)	2.231(2)
Cl(1)–Ti(1)–Cl(3)	163.11(7)	Cl(1)–Ti(1)–Cl(4)	96.42(7)
Cl(2)–Ti(1)–Cl(3)	93.14(6)	Cl(2)–Ti(1)–Cl(4)	109.28(7)
Cl(3)–Ti(1)–Cl(4)	94.87(6)	Se(1)–Ti(1)–Se(2)	74.42(3)
Se(1)–Ti(1)–Cl(1)	87.20(5)	Se(1)–Ti(1)–Cl(2)	162.48(6)
Se(1)–Ti(1)–Cl(3)	80.74(5)	Se(1)–Ti(1)–Cl(4)	87.69(5)
Se(2)–Ti(1)–Cl(1)	84.41(5)	Se(2)–Ti(1)–Cl(2)	88.46(5)
Se(2)–Ti(1)–Cl(3)	81.00(4)	Se(2)–Ti(1)–Cl(4)	162.05(6)
Cl(1)–Ti(1)–Cl(2)	94.94(6)		

Table 5 Selected bond lengths (Å) and angles (°) for $[\{MeS(CH_2)_2SMe\}Cl_3Ti(\mu\text{-}O)TiCl_3\{MeS(CH_2)_2SMe\}]$

Ti(1)–S(1)	2.653(2)	Ti(1)–Cl(3)	2.295(2)
Ti(1)–S(2)	2.624(2)	Ti(1)–Cl(5)	2.255(2)
Ti(1)–Cl(2)	2.300(2)	Ti(1)–O(1)	1.788(1)
Cl(2)–Ti(1)–Cl(3)	160.80(7)	S(1)–Ti(1)–S(2)	80.54(6)
Cl(2)–Ti(1)–Cl(5)	96.79(7)	S(1)–Ti(1)–O(1)	165.39(7)
Cl(2)–Ti(1)–S(1)	77.82(6)	S(2)–Ti(1)–O(1)	86.40(5)
Cl(2)–Ti(1)–S(2)	87.94(6)	Cl(2)–Ti(1)–O(1)	95.27(6)
Cl(3)–Ti(1)–Cl(5)	94.12(7)	Cl(3)–Ti(1)–S(1)	86.28(6)
Cl(3)–Ti(1)–S(2)	78.80(6)	Cl(3)–Ti(1)–O(1)	97.66(6)
Cl(5)–Ti(1)–S(1)	90.92(6)	Ti(1)–O(1)–Ti(1*)	180.00
Cl(5)–Ti(1)–S(2)	169.18(7)	Cl(5)–Ti(1)–O(1)	102.77(6)

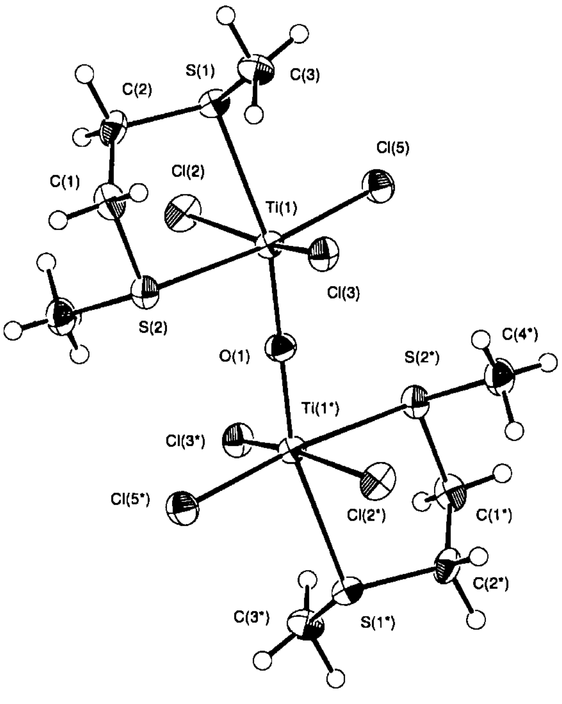

Fig. 5 View of the structure of $[\{MeS(CH_2)_2SMe\}Cl_3Ti(\mu\text{-}O)TiCl_3\{MeS(CH_2)SMe)]$ with the numbering scheme adopted. Ellipsoids are drawn at the 40% probability level. Atoms marked * are related by a crystallographic inversion centre.

$[\{MeS(CH_2)_2SMe\}Cl_3Ti(\mu\text{-}O)TiCl_3\{MeS(CH_2)_2SMe\}]$, obviously formed by partial hydrolysis of $[TiCl_4\{MeS(CH_2)_2SMe\}]$ in 'wet' CH_2Cl_2–hexane. The structure of this species shows (Fig. 5, Table 5) two distorted octahedral Ti(IV) centres linked by a bridging oxo-ligand which occupies a crystallographic inversion centre, and hence imposes a 180° angle for the Ti–O–Ti unit. Once again the dithioether ligands adopt the DL form. In this species all three Cl ligands bend away from the oxo-ligand, O–Ti–Cl 95.27(6)–102.77(6)°. The Ti–S distances in this dinuclear species, 2.653(2), 2.624(2) Å, are longer than those observed in the mononuclear species above. Related oxo-bridged dinuclear Ti species are known, *e.g.* $[PPh_4]_2[\{TiCl_3(NCMe)_2\}_2(\mu\text{-}O)]$ (μ-O occupies an inversion centre), $[Mg(MeCN)_6][\{TiCl_4(MeCN)\}_2(\mu\text{-}O)]\cdot 4MeCN$ [Ti–O–Ti 174.7(3)°] and $[\{(\eta^5\text{-}C_5H_5)TiCl_2\}_2(\mu\text{-}O)]$ (μ-O occupies an inversion centre).[10] The EI mass spectrum of $[\{MeS(CH_2)_2SMe\}Cl_3Ti(\mu\text{-}O)TiCl_3\{MeS(CH_2)_2SMe\}]$ shows major peaks with the correct isotopic distributions corresponding to the dicationic species $[Ti_2Cl_5O\{MeS(CH_2)_2SMe\}_2]^{2+}$, together with fragments corresponding to sequential loss of halide. Microanalytical data confirm that the dinuclear species identified crystallographically is representative of the bulk sample recrystallised in this way.

Conclusions

These results show that thioether and selenoether ligands involving different C-functionalities (terminal substituents and interdonor linkages) readily form complexes with Ti(IV) tetrahalides, to yield intensely coloured species that are highly hydrolytically unstable. Several of the complexes have been crystallographically authenticated, and these studies have also revealed an unusual oxo-bridged dinuclear species formed by partial hydrolysis. NMR spectroscopic studies reveal that the Lewis acidity of TiX_4 increases in the order $X = I < Br < Cl$, and that both ligand dissociation and pyramidal inversion are slowed significantly at *ca.* 200 K. Also, the thioether species are less dissociated than the selenoether complexes; a similar trend to that seen for the Sn(IV) (hard acid) adducts.[8]

Detailed studies of the decomposition behaviour of these compounds will be the basis of a later paper, however, preliminary studies show that the aliphatic derivatives are volatile in high vacuum and may be sublimed with minimal decomposition. Dealkylation is also shown to occur readily for some compounds in solution (*e.g.* $[TiCl_4\{PhSe(CH_2)_2SePh\}]$ undergoes elimination in anhydrous $CHCl_3$ solution upon standing, to yield PhSeSePh as shown by $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$ NMR studies) and more generally on passing the vaporised material through a hot tube.

Experimental

IR were measured as Nujol mulls using a Perkin-Elmer 983G spectrometer over the range 200–4000 cm^{-1}. Mass spectra were run by electron impact (EI) using a VG Analytical 70–250-SE Normal Geometry Double Focusing Mass Spectrometer. UV–visible spectra were recorded by diffuse reflectance using $BaSO_4$ as dilutant on a Perkin Elmer Lambda19 UV/visible spectrometer. ^1H NMR spectra were recorded in $CDCl_3$ using a Bruker AM300 spectrometer operating at 300 MHz. $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectra were obtained using a Bruker AM360 spectrometer operating at 90.6 and 68.7 MHz and are referenced to $SiMe_4$ and external neat $SeMe_2$ respectively. The thioether and selenoether ligands were prepared by the literature methods.[11–14] TiX_4 were used as received from Aldrich.

Preparations

All preparations were conducted using standard Schlenk techniques under a dinitrogen atmosphere and rigorously dry solvents. One representative synthesis of a $TiCl_4$, $TiBr_4$ and TiI_4 complex is detailed.

$[TiCl_4\{MeS(CH_2)_2SMe\}]$. To a solution of $MeS(CH_2)_2SMe$ (0.11 g, 0.91 mmol) in dry, degassed hexane (20 cm^3) was added $TiCl_4$ (0.10 cm^3, 0.91 mmol) *via* syringe. This resulted in the immediate precipitation of a bright yellow solid which was filtered *in vacuo*, washed with hexane and dried *in vacuo*. Yield 0.26 g, 91%. Calc. for $C_4H_{10}Cl_4S_2Ti$: C, 15.4; H, 3.2. Found: C, 15.3; H, 3.2%. ^1H NMR: δ 2.92 (br s, CH_2, 4 H), 2.38 (br s, CH_3, 6H). $^{13}C\{^1H\}$ NMR (300 K): δ 38.9 (CH_2), 23.2 (CH_3); (200 K): 39.4, 39.1 (CH_2), 23.5, 22.2 (CH_3). IR (ν_{TiCl})/cm^{-1}: 420, 406, 397, 383. Electronic spectrum (10^{-3} ν_{max}/cm^{-1}): 23.8, 29.5 (sh), 33.3 (sh).

[$TiCl_3\{MeS(CH_2)_2SMe\}]_2(\mu$-O). Method as above, but using 'wet' CH_2Cl_2–hexane. Yellow crystals. Required for $C_8H_{20}Cl_6OS_4Ti_2$: C, 12.7; H, 2.7. Found: C, 13.0; H, 2.8%. EI mass spectrum: found *m*/*z* 342, 325, 267, 249; calc. for $[^{48}Ti_2{}^{35}Cl_3O\{MeS(CH_2)_2SMe\}]^+$ *m*/*z* 339, $[^{48}Ti_2{}^{35}Cl_6O]^+$ *m*/*z* 322, $[^{48}Ti_2{}^{35}Cl_5O\{MeS(CH_2)_2SMe\}_2]^{2+}$ *m*/*z* 265.5, $[^{48}Ti_2{}^{35}Cl_4O\{MeS(CH_2)_2SMe\}_2]^{2+}$ *m*/*z* 248.

[$TiCl_4\{MeS(CH_2)_3SMe\}$]. Orange solid. Yield 88%. Required for $C_5H_{12}Cl_4S_2Ti$: C, 18.4; H, 3.7. Found: C, 17.9; H, 3.6%. ^1H NMR: δ 3.10 (t, SCH_2, 4H), 2.53 (s, CH_3, 6H), 2.24 (qnt, CH_2, 2H). $^{13}C\{^1H\}$ NMR (300 K): δ 36.4 (SCH_2), 24.0 (CH_3), 22.0 (CH_3); (200 K): 37.6, 35.1 (SCH_2), 24.4 (CH_2), 22.8, 22.0 (CH_3). IR (ν_{TiCl})/cm^{-1}: 408, 398, 387, 378. Electronic spectrum (10^{-3} ν_{max}/cm^{-1}): 22.5, 27.0 (sh), 31.3 (sh).

[$TiCl_4\{PhS(CH_2)_2SPh\}$]. Red solid. Yield 85%. Required for $C_{14}H_{14}Cl_4S_2Ti$: C, 38.6; H, 3.2. Found: C, 38.2; H, 3.5%. ^1H NMR: δ 7.32–7.46 (m, Ph, 10H), 3.58 (s, CH_2, 4H). $^{13}C\{^1H\}$ NMR (300 K): δ 127–130 (Ph), 34.6 (CH_2); (200 K): 126–132 (Ph), 35.9, 33.0 (CH_2). IR (ν_{TiCl})/cm^{-1}: 413, 400, 386, 378. Electronic spectrum (10^{-3} ν_{max}/cm^{-1}): 20.5 (br), 28.5 (sh).

[$TiCl_4\{o$-$C_6H_4(SMe)_2\}$]. Orange solid. Yield 55%. Required for $C_8H_{10}Cl_4S_2Ti$: C, 26.7; H, 2.8. Found: C, 26.5; H, 3.0%. ^1H NMR: δ 7.14–7.25 (m, *o*-C_6H_4, 4H), 2.47 (s, CH_3, 6H). $^{13}C\{^1H\}$ NMR (300 K): δ 129–134 (*o*-C_6H_4), 26.8 (CH_3); (200 K): 128–134 (*o*-C_6H_4), 28.0, 27.0 (CH_3). IR (ν_{TiCl})/cm^{-1}: 405, 396, 387, 382.

[$TiCl_4\{MeSe(CH_2)_2SeMe\}$]. Orange solid. Yield 90%. Required for $C_4H_{10}Cl_4Se_2Ti$: C, 11.8; H, 2.5. Found: C, 11.5; H, 2.0%. ^1H NMR: δ 3.30 (br s, CH_2, 4H), 2.60 (br s, CH_3, 6H). $^{13}C\{^1H\}$ NMR (300 K): δ 34.2 (CH_2), 14.5 (CH_3); (200 K): 34.4, 34.2 (CH_2), 14.9, 14.6 (CH_3). $^{77}Se\{^1H\}$ NMR (200 K): δ 313, 307. IR (ν_{TiCl})/cm^{-1}: 414, 402, 393, 380. Electronic spectrum (10^{-3} ν_{max}/cm^{-1}): 23.0, 24.0, 29.5 (sh), 34.0.

[$TiCl_4\{MeSe(CH_2)_3SeMe\}$]. Bright red solid. Yield 84%. Required for $C_5H_{12}Cl_4Se_2Ti$: C, 14.3; H, 2.9. Found: C, 14.2; H, 3.0%. ^1H NMR: δ 2.90 (s, $SeCH_2$, 4H), 2.28 (s, CH_3, 6H), 2.22 (s, CH_2, 2H). $^{13}C\{^1H\}$ NMR (300 K): no spectrum; (200 K): δ 34.3, 32.1 ($SeCH_2$), 30.8 (CH_2), 17.0, 15.8 (CH_3). $^{77}Se\{^1H\}$ NMR (200 K): δ 183, 180. IR (ν_{TiCl})/cm^{-1}: 396, 384, 378, 373. Electronic spectrum (10^{-3} ν_{max}/cm^{-1}): 20.1, 24.5, 29.0 (sh), 32.2 (sh).

[$TiCl_4\{PhSe(CH_2)_2SePh\}$]. Dark red solid. Yield 79%. Required for $C_{14}H_{14}Cl_4Se_2Ti$: C, 31.7; H, 2.7. Found: C, 32.0; H, 2.8%. ^1H NMR: δ 7.9–8.2 (m, Ph, 10H), 3.7 (br s, CH_2, 4H). $^{13}C\{^1H\}$ NMR (300 K): δ 128.1–133.8 (Ph), 31.0 (CH_2); (200 K): 129.2–133.6 (Ph), 32.6, 32.2 (CH_2). $^{77}Se\{^1H\}$ NMR (200 K): δ 441, 436. IR (ν_{TiCl})/cm^{-1}: 405, 385, 377, 373. Electronic spectrum (10^{-3} ν_{max}/cm^{-1}): 20.4, 31.6 (br).

[$TiCl_4\{o$-$C_6H_4(SeMe)_2\}$]. Orange red solid. Yield 76%. Required for $C_8H_{10}Cl_4Se_2Ti$: C, 21.2; H, 2.2. Found: C, 21.0; H, 2.3%. ^1H NMR: δ 7.28–7.46 (m, *o*-C_6H_4, 4H), 2.58 (s, CH_3, 6H). $^{13}C\{^1H\}$ NMR (300 K): δ 131.0, 134.9 (*o*-C_6H_4), 21.7 (CH_3); (200 K): 134.8, 131.1 (*o*-C_6H_4), 23.5, 22.9 (CH_3). $^{77}Se\{^1H\}$ NMR (200 K): δ 399, 390. IR (ν_{TiCl})/cm^{-1}: 390, 386, 382, 379. Electronic spectrum (10^{-3} ν_{max}/cm^{-1}): 21.6, 28.5 (sh), 34.6 (sh).

[$TiBr_4\{MeS(CH_2)_2SMe\}$]. $TiBr_4$ (0.31 g, 0.84 mmol) was dissolved in refluxing, dry CH_2Cl_2 (40 cm^3) under N_2. After cooling to room temperature $MeS(CH_2)_2SMe$ (0.11 g, 0.84 mmol) was added. The resulting red solution was stirred for *ca.* 30 min then concentrated *in vacuo* to *ca.* 5 cm^3. Dry hexane (20 cm^3) was then added to afford an orange red solid which was filtered off and dried *in vacuo*. Yield 0.24 g, 58%. Required for $C_4H_{10}Br_4S_2Ti$: C, 9.8; H, 2.1. Found: C, 10.1; H, 2.0%. ^1H NMR: δ 2.8 (s, CH_2, 4H), 2.2 (s, CH_3, 6H). IR (ν_{TiBr})/cm^{-1}: 332, 325, 319, 311. Electronic spectrum (10^{-3} ν_{max}/cm^{-1}): 22.2 (v br), 33.0 (sh).

[$TiBr_4\{MeS(CH_2)_3SMe\}$]. Bright red solid. Yield 61%. Required for $C_5H_{12}Br_4S_2Ti$: C, 11.9; H, 2.4. Found: C, 12.2; H, 2.5%. ^1H NMR: δ 2.76 (s, SCH_2, 4H), 2.27 (s, CH_3, 6H), 1.95 (m, CH_2, 2H). IR (ν_{TiBr})/cm^{-1}: 325, 321, 317, 311. Electronic spectrum (10^{-3} ν_{max}/cm^{-1}): 20.4, 22.5 (sh), 31.5 (sh).

[$TiBr_4\{o$-$C_6H_4(SMe)_2\}$]. Orange solid. Yield 64%. Required for $C_8H_{10}Br_4S_2Ti$: C, 17.9; H, 1.9. Found: C, 18.2; H, 2.2%. ^1H NMR: δ 7.29–7.44 (m, *o*-C_6H_4, 4H), 2.73 (s, CH_3, 6H). IR (ν_{TiBr})/cm^{-1}: 327, 317, 310, 304. Electronic spectrum (10^{-3} ν_{max}/cm^{-1}): 23.3.

[$TiBr_4\{MeSe(CH_2)_2SeMe\}$]. Red solid. Yield 51%. Required for $C_4H_{10}Br_4Se_2Ti$: C, 8.2; H, 1.7. Found: C, 8.6; H, 1.9%. ^1H NMR: δ 2.86 (s, CH_2, 4H), 2.10 (s, Me, 6H). $^{13}C\{^1H\}$ NMR (300 K): no spectrum; (200 K): δ 35.2, 35.0 (CH_2 coordinated diselenoether), 24.3 (CH_2 'free' diselenoether), 14.8, 14.6 (CH_3 coordinated diselenoether), 4.0 (CH_3 free diselenoether). IR (ν_{TBr})/cm^{-1}: 317, 312, 300, 294. Electronic spectrum (10^{-3} ν_{max}/cm^{-1}): 20.5, 26.0, 39.2.

[$TiBr_4\{MeSe(CH_2)_3SeMe\}$]. Dark red solid. Yield 52%. Required for $C_5H_{12}Br_4Se_2Ti$: C, 10.5; H, 2.0. Found: C, 10.3; H, 2.2%. ^1H NMR: δ 2.68 (s, $SeCH_2$, 4H), 2.05 (s, CH_3, 6H), 2.00 (s, CH_2, 2H). $^{13}C\{^1H\}$ NMR (300 K): no spectrum. IR (ν_{TiBr})/cm^{-1}: 327, 317, 308, 300. Electronic spectrum (10^{-3} ν_{max}/cm^{-1}): 21.8 (br).

[$TiBr_4\{o$-$C_6H_4(SeMe)_2\}$]. Orange brown solid. Yield 57%. Required for $C_8H_{10}Br_4Se_2Ti$: C, 15.2; H, 1.6. Found: C, 15.8; H, 1.8%. ^1H NMR: δ 7.20–7.42 (m, *o*-C_6H_4, 4H), 2.47 (s, CH_3, 6H). $^{13}C\{^1H\}$ NMR (300 K): no spectrum; (200 K): δ 127–134 (*o*-C_6H_4 from both 'free' and coordinated ligand), 25.9, 25.5 (CH_3, coordinated ligand), 8.1 (CH_3, 'free' ligand). IR (ν_{TiBr})/cm^{-1}: 326, 321, 305, 299. Electronic spectrum (10^{-3} ν_{max}/cm^{-1}): 20.5 (br), 29.0 (sh).

[$TiI_4\{MeSe(CH_2)_2SeMe\}$]. TiI_4 (0.20 g, 0.36 mmol) was dissolved in refluxing anhydrous CH_2Cl_2 (80 cm^3) under N_2. After cooling to room temperature, the solution was allowed to settle and the remaining solid was removed by filtration. To this purple solution was added $MeSe(CH_2)_2SeMe$ (0.09 g, 0.36 mmol), resulting in an immediate change to an orange–red solution. This solution was stirred at room temperature for *ca.* 30 min and then concentrated *in vacuo* to *ca.* 5 cm^3. Dry hexane (20 cm^3) was then added and this mixture was then concentrated to *ca.* 5 cm^3 *in vacuo* to afford a dark red–purple solid which was collected by filtration. Yield 0.05 g, 19%. Required for $C_4H_{10}I_4Se_2Ti$: C, 6.2; H, 1.3. Found: C, 6.5; H, 1.5%. ^1H NMR: δ 3.0 (s, $SeCH_2$, 4H), 2.3 (s, CH_3, 6H).

[$TiI_4\{o$-$C_6H_4(SeMe)_2\}$]. Red–brown solid. Yield 30%. Required for $C_8H_{10}I_4Se_2Ti$: C, 11.7; H, 1.2. Found: C, 11.3; H, 1.1%. ^1H NMR: δ 7.2–7.4 (*m*, *o*-C_6H_4, 4H), 2.90 (s, CH_3, 6H).

X-Ray crystallographic studies

Details of the crystallographic data collection and refinement parameters are given in Table 6. Crystals were obtained from slow evaporation from a solution of the appropriate complex in CH_2Cl_2 (except $[\{TiCl_3\{MeS(CH_2)_2SMe\}\}_2(\mu\text{-}O)]$ which were

Table 6 Crystallographic data

	$[TiCl_4\{MeS(CH_2)_2SMe\}]$	$[TiCl_4\{MeS(CH_2)_3SMe\}]$	$[TiCl_4\{MeSe(CH_2)_3SeMe\}]$	$[TiCl_4\{o\text{-}C_6H_4(SeMe)_2\}]$	$[\{MeS(CH_2)_2SMe\}Cl_3Ti]_2(\mu\text{-}O)$
Formula	$C_4H_{10}Cl_4S_2Ti$	$C_5H_{12}Cl_4S_2Ti$	$C_5H_{12}Cl_4Se_2Ti$	$C_8H_{10}Cl_4Se_2Ti$	$C_8H_{20}Cl_6OS_4Ti_2$
M	311.95	325.98	449.77	453.80	569.00
Crystal system	Monoclinic	Tetragonal	Tetragonal	Triclinic	Monoclinic
Space group	$P2_1/n$	$I\bar{4}2d$	$I4_1/a$	$P\bar{1}$	$P2_1/n$
a/Å	6.922(2)	10.071(1)	10.029(6)	8.2588(9)	8.963(1)
b/Å	13.335(1)	10.071(1)	10.029(6)	11.091(2)	10.672(2)
c/Å	12.678(1)	24.542(3)	25.698(14)	8.232(1)	11.196(1)
α/°	90	90	90	90.74(1)	90
β/°	95.17(1)	90	90	97.72(1)	90.36(1)
γ/°	90	90	90	108.93(1)	90
U/Å^3	1165.4(3)	2489.1(7)	2585(3)	705.5(2)	1070.8(3)
Z	4	8	8	2	2
μ(Mo-Kα)/cm^{-1}	19.51	18.41	70.74	64.42	18.77
Unique obs. reflections	2151	683	1145	2478	2013
Obs. reflections $[I_o > 2\sigma(I_o)]$	1755	525	792	1972	1412
R^a	0.023	0.041	0.054^c	0.031	0.049
$R_w{}^b$	0.029	0.041	0.142^d	0.035	0.060

[a] $R = \Sigma(|F_o|_i - |F_c|_i)/\Sigma|F_o|_i$. [b] $R_w = [\Sigma w_i(|F_o|_i - |F_c|_i)^2/\Sigma w_i|F_o|_i^2]^{\frac{1}{2}}$. [c] $R1$ $[I > 2\sigma(I)]$. [d] $wR2$ $[I > 2\sigma(I)]$.

obtained by slow evaporation from a solution of $[TiCl_4\{MeS(CH_2)_2SMe\}]$ in CH_2Cl_2–hexane. The data were corrected for absorption using ψ-scans. Structure solution and refinement were routine,[15–19] except for $[TiCl_4\{MeSe(CH_2)_3SeMe\}]$, for which the diffraction data were apparently in the Laue group 4/*mmm* but with systematic absences not fitting any appropriate space group. The structure was therefore solved in space group $I4_1/a$ (no. 88, Laue group 4/*m*) with twinning from two equal components (TWIN 010 100 00-1 in SHELXL 97[18]). The molecule has crystallographic two-fold symmetry with atoms Ti(1) and C(1) occupying 8e sites. Selected bond lengths and angles for the structures are presented in Tables 1–5.

CCDC reference number 186/2090.

See http://www.rsc.org/suppdata/dt/b0/b002792h/ for crystallographic files in .cif format.

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