

# Reactions of $[\text{Cp}_2\text{Ti}(\text{N}^t\text{Bu})(\text{py})]$ with S–H bonds and synthesis of $[\text{Cp}_2\text{Ti}(\mu\text{-S})_2\text{TiCp}_2]$ <sup>1</sup>

Philip Mountford \*

Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK

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## Abstract

The imidotitanocene complex  $[\text{Cp}_2\text{Ti}(\text{N}^t\text{Bu})(\text{py})]$  reacts with an excess of  $\text{H}_2\text{S}$  or  $\text{MeSH}$  to form  $[\text{Cp}_2\text{Ti}(\text{SR})_2]$  ( $\text{R} = \text{H}$  or  $\text{Me}$ ). The labile bis( $\mu$ -sulfido) complex  $[\text{Cp}_2\text{Ti}(\mu\text{-S})_2\text{TiCp}_2]$ , formed as an intermediate in the reaction of  $[\text{Cp}_2\text{Ti}(\text{N}^t\text{Bu})(\text{py})]$  with  $\text{H}_2\text{S}$ , is also obtained by addition of one equivalent of  $[\text{Cp}_2\text{Ti}(\text{SH})_2]$  to  $[\text{Cp}_2\text{Ti}(\text{N}^t\text{Bu})(\text{py})]$ .

**Keywords:** Titanium; Imido; Cyclopentadienyl; Sulfido; X-ray diffraction; Bimetallic

## 1. Introduction

The study of early transition metal imido complexes is an area of continuing interest [1] and significant advances have been achieved with imido-transition metal fragments supported by bis(cyclopentadienyl) ligand sets [2–5]. However, terminal imidotitanium complexes were first fully characterised only in 1990 [6,7] and their chemistry is underdeveloped by comparison with their zirconium congeners [1]. We have recently reported a new route to mono(cyclopentadienyl) and bis(cyclopentadienyl) imidotitanium complexes and are exploring their potential as entry points to new cyclopentadienyl titanium derivatives [8]. Mid to late transition metal imido complexes can react with the S–H bond(s) of  $\text{H}_2\text{S}$ , thiols and bis(hydrosulfido) metal derivatives giving new routes to terminal sulfido, bis(hydrocarbyl sulfido) and homo- and hetero-bimetallic bis( $\mu$ -sulfido) complexes [9–11]. Reactions of Group 4 imido derivatives towards S–H bonds have not been reported. This contribution describes some S–H bond activation reactions of  $[\text{Cp}_2\text{Ti}(\text{N}^t\text{Bu})(\text{py})]$  and the synthesis of the labile complex  $[\text{Cp}_2\text{Ti}(\mu\text{-S})_2\text{TiCp}_2]$ .

## 2. Results and discussion

When an excess of  $\text{H}_2\text{S}$  was added to a dichloromethane solution of  $[\text{Cp}_2\text{Ti}(\text{N}^t\text{Bu})(\text{py})]$  (**1**) [12] the solution immediately became very dark red and then turned light red after a few moments. Removal of the volatiles under reduced pressure afforded the spectroscopically pure bis(hydrosulfido) complex  $[\text{Cp}_2\text{Ti}(\text{SH})_2]$  (**2**), which has previously been obtained from  $[\text{Cp}_2\text{TiCl}_2]$  and  $\text{H}_2\text{S}$  [13]. It was of interest to identify the dark red intermediate in the reaction of **1** with  $\text{H}_2\text{S}$ . Initial studies were carried out using a series of NMR tube experiments in  $\text{C}_6\text{D}_6$ .

Addition of an excess of  $\text{H}_2\text{S}$  to a  $\text{C}_6\text{D}_6$  solution of  $[\text{Cp}_2\text{Ti}(\text{N}^t\text{Bu})(\text{py})]$  (**1**) gave a light red solution exhibiting resonances assignable to free  $\text{py}$ ,  ${}^t\text{BuNH}_2$  and  $[\text{Cp}_2\text{Ti}(\text{SH})_2]$  (**2**) in an equimolar ratio. No other products were observed. The reaction was then repeated using ca. 1 equivalent of  $\text{H}_2\text{S}$  and the dark red solution formed immediately. The  ${}^1\text{H}$  NMR spectrum showed new resonances assignable to free  ${}^t\text{BuNH}_2$  and  $\text{py}$ , together with a singlet ( $\delta = 6.51$  ppm) assigned to an intermediate species, **3**. No other new resonances were observed. Addition of an excess of  $\text{H}_2\text{S}$  to this mixture gave an equimolar mixture of only free  $\text{py}$ ,  ${}^t\text{BuNH}_2$  and  $[\text{Cp}_2\text{Ti}(\text{SH})_2]$ . Thus the dark red species **3** is very probably an intermediate in the overall formation of **2** from **1** and excess  $\text{H}_2\text{S}$ . The NMR studies showed **3** to

\* Corresponding author.

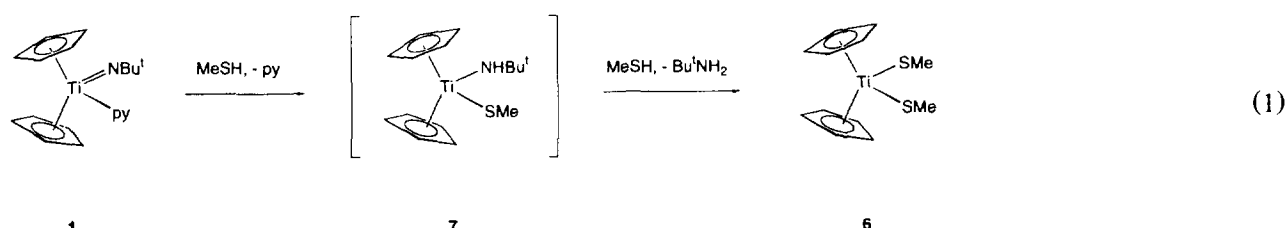
<sup>1</sup> Dedicated to my mentor and teacher, Malcolm L.H. Green FRS, on his 60th birthday.

be labile at room temperature, slowly (1–2 h) decomposing to a number of unknown products.

It is proposed (*vide infra*) that **3** is the new bis( $\mu$ -sulfido) complex  $[\text{Cp}_2\text{Ti}(\mu\text{-S})_2\text{TiCp}_2]$  (Scheme 1). It is likely that the first formed product in the reaction of  $[\text{Cp}_2\text{Ti}(\text{N}^t\text{Bu})(\text{py})]$  (**1**) with  $\text{H}_2\text{S}$  is  $[\text{Cp}_2\text{Ti}(\text{NH}^t\text{Bu})(\text{SH})]$  (**4**, not observed by NMR). The compound **4** could rapidly either (i) eliminate  $^t\text{BuNH}_2$  to form transient  $[\text{Cp}_2\text{Ti}(\text{S})]$  (**5**) which may dimerise via  $\mu\text{-S}$  linkages to form **3**, or (ii) react directly with a second equivalent of  $\text{H}_2\text{S}$  to form the bis(hydrosulfido) complex  $[\text{Cp}_2\text{Ti}(\text{SH})_2]$  (**2**) which also contains reactive S–H bonds; in the absence of sufficient  $\text{H}_2\text{S}$ , **2** can attack unreacted  $[\text{Cp}_2\text{Ti}(\text{N}^t\text{Bu})(\text{py})]$  (**1**), forming **3**.

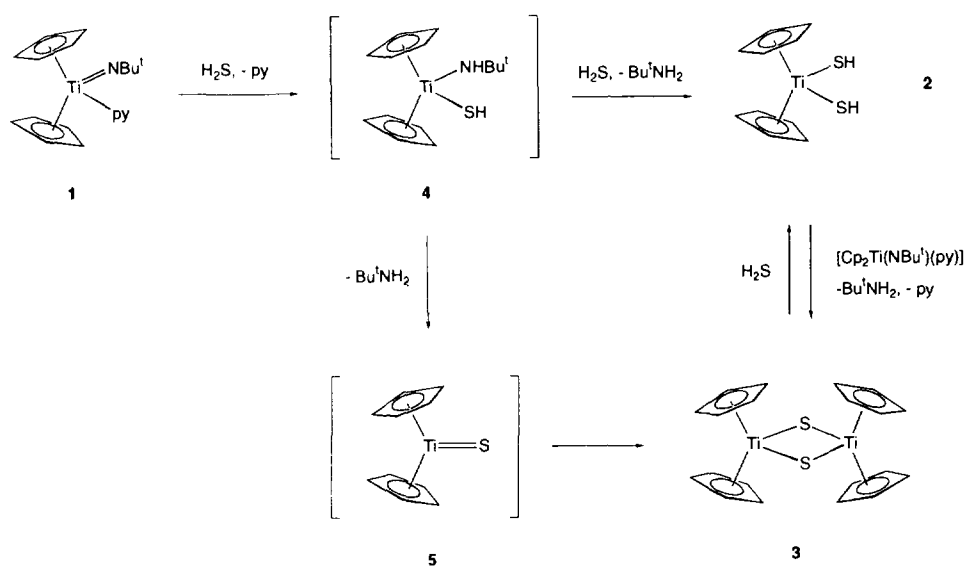
Supporting evidence for the latter possibility is as follows. Firstly, when light red solutions of  $[\text{Cp}_2\text{Ti}(\text{SH})_2]$  (**2**) and  $[\text{Cp}_2\text{Ti}(\text{N}^t\text{Bu})(\text{py})]$  (**1**) (ca. 1:1 molar ratio) in  $\text{C}_6\text{D}_6$  were mixed together, the resultant dark red solution contained free py and  $^t\text{BuNH}_2$  (intensity 9 H), together with a singlet at  $\delta = 6.51$  ppm (intensity 20 H), again assigned to  $[\text{Cp}_2\text{Ti}(\mu\text{-S})_2\text{TiCp}_2]$

(**3**). Thus any  $[\text{Cp}_2\text{Ti}(\text{SH})_2]$  (**2**) formed in the reaction of  $[\text{Cp}_2\text{Ti}(\text{N}^t\text{Bu})(\text{py})]$  (**1**) with  $\text{H}_2\text{S}$  can also attack **1**. Secondly, when a solution of **1** in  $\text{C}_6\text{D}_6$  was treated with ca. 1.1 equivalents of MeSH the resultant spectrum showed resonances attributable to unreacted **1**, the previously described bis(methyl sulfido) derivative  $[\text{Cp}_2\text{Ti}(\text{SMe})_2]$  (**6**) [14] and free py and  $^t\text{BuNH}_2$ . Three additional minor resonances typical of Cp, SMe and  $^t\text{Bu}$  groups (ratio 10 H:3 H:9 H respectively) were consistent with the formation of the mixed sulfide–amide  $[\text{Cp}_2\text{Ti}(\text{N}^t\text{BuNH})(\text{SMe})]$  (**7**) [15]. Assuming these tentative assignments, the relative molar ratio of **1**:**6**:**7** was ca. 3:2:4, and so no attempt was made to isolate **7** on a synthetic scale. Addition of an excess of MeSH to this reaction mixture resulted in the overall quantitative formation of **6** (see Eq. (1)). It is thus very likely that intermediate amido species formed in the reaction of  $[\text{Cp}_2\text{Ti}(\text{N}^t\text{Bu})(\text{py})]$  (**1**) with RSH can themselves rapidly react with further S–H bonds, forming  $[\text{Cp}_2\text{Ti}(\text{SR})_2]$ . Related observations have been made in the reaction of a molybdenum imido system with  $^t\text{BuOH}$  [16].



Despite its lability in solution, the bis( $\mu$ -sulfido) complex  $[\text{Cp}_2\text{Ti}(\mu\text{-S})_2\text{TiCp}_2]$  (**3**) may be isolated in a reasonably pure form and further characterised. Although the NMR tube experiments show that treatment of  $[\text{Cp}_2\text{Ti}(\text{N}^t\text{Bu})(\text{py})]$  (**1**) with 1 equivalent of either  $\text{H}_2\text{S}$  or  $[\text{Cp}_2\text{Ti}(\text{SH})_2]$  (**2**) affords **3**, it is the latter

method that is most convenient on a synthetic scale. Thus addition of a THF solution of **1** to a THF solution of **2** (1:1 molar ratio) afforded a dark red solution. Immediate removal of volatiles under reduced pressure followed by rapid precipitation of the product from a THF/hexane mixture afforded **3** as a red–brown pow-



Scheme 1.

der in good yield. The  $^1\text{H}$  NMR spectrum of this powder in  $\text{C}_6\text{D}_6$  showed a single resonance at  $\delta$  6.51 ppm and the  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR spectrum revealed a single resonance at  $\delta$  117.1 ppm. The IR spectrum (Nujol mull in the range 4000–400  $\text{cm}^{-1}$ ) showed no evidence for either an S–H or a Ti=S functional group [17], but was similar to the previously described IR spectra of  $[\text{Cp}_2\text{Ti}(\mu\text{-X})_2\text{TiCp}_2]$  (X = Cl, Br, I), for which Ti– $\mu\text{-X}$  absorptions were not observed down to 300  $\text{cm}^{-1}$  [18]. Unfortunately it was not possible to obtain a satisfactory mass spectrum of this material.

The reactions of  $[\text{Cp}_2\text{Ti}(\text{N}^i\text{Bu})(\text{py})]$  (**1**) with  $\text{H}_2\text{S}$ , MeSH and  $[\text{Cp}_2\text{Ti}(\text{SH})_2]$  (**2**) are the first reports of S–H bond activation by a Group 4 metal imido complex. Furthermore, the complex  $[\text{Cp}_2\text{Ti}(\mu\text{-S})_2\text{TiCp}_2]$  (**3**) represents the final ‘‘missing link’’ both in the Group 4 titano- and zirconocene bis( $\mu$ -chalcogenido) series  $[(\eta\text{-C}_5\text{R}_5)_2\text{M}(\mu\text{-E})_2\text{M}(\eta\text{-C}_5\text{R}_5)_2]$  (M = Ti or Zr; E = S or Se) and in the bis(titanocene)  $\mu$ -(poly)sulfido series  $[(\eta\text{-C}_5\text{H}_4\text{R})_2\text{Ti}(\mu\text{-S}_x)_2\text{Ti}(\eta\text{-C}_5\text{H}_4\text{R})_2]$  ( $x = 1, 2$  or  $3$ ), which have been the subject of considerable research activity [19–28]. The observation that treatment of solutions of **3** with  $\text{H}_2\text{S}$  affords  $[\text{Cp}_2\text{Ti}(\text{SH})_2]$  is consistent with the behaviour of the crystallographically characterised congener  $[\text{Cp}_2\text{Zr}(\mu\text{-S})_2\text{ZrCp}_2]$  [24,26]. The lability of **3** is also consistent with the reported instability of  $[\text{Cp}_2\text{Zr}(\mu\text{-S})_2\text{ZrCp}_2]$  in solution [25] and the decomposition of  $[(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Ti}(\mu\text{-S-S})_2\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Me})_2]$  at relatively mild elevated temperatures [22]. It is probably a combination of the thermal lability of **3** and its facile reactivity towards  $\text{H}_2\text{S}$  that has prevented its synthesis previously.

Unimetallic terminal chalcogenido derivatives  $[(\eta\text{-C}_5\text{R}_5)_2\text{M}(\text{E})(\text{L})]$  (M = Zr or Hf with E = O, S, Se or Te; M = Ti with E = O; L = py or substituted py) have been described recently [29–31]. No evidence for  $[\text{Cp}_2\text{Ti}(\text{S})(\text{py})]$  was found in the reactions where free pyridine was available. We are currently exploring the reactivity of  $[\text{Cp}_2\text{Ti}(\mu\text{-S})_2\text{TiCp}_2]$  (**3**) towards organic substrates, and the scope of early transition metal imido complexes in general as precursors to otherwise inaccessible materials.

### 3. Experimental section

Appropriate general experimental procedures used in these laboratories have been described in detail elsewhere [32,33].  $[\text{Cp}_2\text{Ti}(\text{N}^i\text{Bu})(\text{py})]$  was prepared by an analogous route to that previously described for  $[\text{Cp}_2\text{Ti}(\text{N}^i\text{Bu})(4\text{-NC}_5\text{H}_4\text{Bu})]$  [8] and full details will be described in a future contribution [12].  $\text{H}_2\text{S}$  and MeSH were used as received from the Aldrich Chemical Company. The NMR tube experiments were carried out using standard Wilmad 5 mm tubes equipped with Young's NMR/5 valves so that successive aliquots of

$\text{H}_2\text{S}$  or MeSH could be added and NMR spectra recorded of the mixtures at the various stages. Stoichiometric addition of  $\text{H}_2\text{S}$  and MeSH was achieved using a calibrated gas manifold.

#### 3.1. Synthesis of $[\text{Cp}_2\text{Ti}(\text{SH})_2]$ (**2**) from $[\text{Cp}_2\text{Ti}(\text{N}^i\text{Bu})(\text{py})]$ (**1**) and $\text{H}_2\text{S}$

$\text{H}_2\text{S}$  was slowly bubbled through a solution of  $[\text{Cp}_2\text{Ti}(\text{N}^i\text{Bu})(\text{py})]$  (**1**) (90 mg, 0.27 mmol) in dichloromethane (10  $\text{cm}^3$ ) for 2 min. The initially light red solution turned immediately very dark then became light red again. The volatiles were removed under reduced pressure to give a red solid which was identified as  $[\text{Cp}_2\text{Ti}(\text{SH})_2]$  (**2**). Yield 45 mg, 83%. Samples of **2** prepared this way are pure by  $^1\text{H}$  NMR spectroscopy. Spectroscopic data.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250 MHz, 293 K): 6.28 (s, 10 H, Cp), 3.38 (s, 2 H, SH) ppm (Lit. [13] ( $\text{CDCl}_3$ ): 6.28, 3.38 ppm).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 250 MHz, 293 K): 5.79 (s, 10 H, Cp), 3.72 (s, 2 H, SH) ppm.

#### 3.2. Synthesis of $[\text{Cp}_2\text{Ti}(\mu\text{-S})_2\text{TiCp}_2]$ (**3**) from $[\text{Cp}_2\text{Ti}(\text{N}^i\text{Bu})(\text{py})]$ (**1**) and $[\text{Cp}_2\text{Ti}(\text{SH})_2]$ (**2**)

To a degassed solution of  $[\text{Cp}_2\text{Ti}(\text{SH})_2]$  (**2**) (0.13 mmol, generated from **1** and  $\text{H}_2\text{S}$ ) in THF (10  $\text{cm}^3$ ) was added  $[\text{Cp}_2\text{Ti}(\text{N}^i\text{Bu})(\text{py})]$  (**1**) (42 mg, 0.13 mmol) in THF (15  $\text{cm}^3$ ) affording a very dark red solution. Volatiles were immediately removed under reduced pressure and the residue was redissolved in THF (10  $\text{cm}^3$ ). To this solution was added hexane (10  $\text{cm}^3$ ) and the red–brown solid formed was separated from the supernatant and washed with hexane ( $2 \times 5 \text{ cm}^3$ ) and dried in vacuo. Yield 45 mg, 82%. Analytical data.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 300 MHz, 293 K): 6.51 (s, Cp) ppm.  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 74.5 MHz, 293 K): 117.1 (Cp) ppm. IR (Nujol, CsBr windows): 1261 (m), 1092 (s), 1020 (s) and 801 (vs)  $\text{cm}^{-1}$ . Anal. Found: C, 55.1; H, 5.0.  $\text{C}_{20}\text{H}_{20}\text{Ti}_2\text{S}_4$  Calc.: C, 57.2; H, 4.8%.

#### 3.3. Synthesis of $[\text{Cp}_2\text{Ti}(\mu\text{-S})_2\text{TiCp}_2]$ (**3**) from $[\text{Cp}_2\text{Ti}(\text{N}^i\text{Bu})(\text{py})]$ (**1**) and $\text{H}_2\text{S}$

A solution of  $[\text{Cp}_2\text{Ti}(\text{N}^i\text{Bu})(\text{py})]$  (11 mg, 0.034 mmol) in  $\text{C}_6\text{D}_6$  (0.8  $\text{cm}^3$ ) in a 5 mm NMR tube was treated with ca. 1 equivalent of  $\text{H}_2\text{S}$ . The resultant NMR spectrum showed effectively quantitative formation of **3** together with resonances assignable to unreacted **1**, free py and  $^i\text{BuNH}_2$ .

#### 3.4. Synthesis of $[\text{Cp}_2\text{Ti}(\text{SH})_2]$ (**2**) from $[\text{Cp}_2\text{Ti}(\mu\text{-S})_2\text{TiCp}_2]$ (**3**) and $\text{H}_2\text{S}$

To a solution of **3** in  $\text{C}_6\text{D}_6$  in an NMR tube (generated in situ according to the above procedure) was added ca. 5 equivalents of  $\text{H}_2\text{S}$ . The NMR spectrum of

the reaction mixture revealed **2** as the only organometallic product.

### 3.5. Synthesis of $[\text{Cp}_2\text{Ti}(\text{SMe})_2]$ (**6**) from $[\text{Cp}_2\text{Ti}(\text{N}^i\text{Bu})(\text{py})]$ (**1**) and $\text{H}_2\text{S}$

A solution of **1** in  $\text{C}_6\text{D}_6$  ( $0.8 \text{ cm}^3$ ) in an NMR tube was treated with ca. 1 equivalent of MeSH. The NMR spectrum of the mixture showed resonances assignable to **1**, **6**, free py and  $^i\text{BuNH}_2$  together with a further set of resonances assignable to  $[\text{Cp}_2\text{Ti}(\text{NH}^i\text{Bu})(\text{SMe})]$  (**7**). The molar ratio of **1**:**6**:**7** was ca. 3:2:4 according to integration. Addition of an excess of MeSH to this mixture afforded **6** as the sole organometallic product, together with free py and  $^i\text{BuNH}_2$ . Analytical data.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 250 MHz, 293 K) for  $[\text{Cp}_2\text{Ti}(\text{SMe})_2]$  (**6**): 5.85 (s, 10 H, Cp), 2.84 (s, 6 H, SMe).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 250 MHz, 293 K) for  $[\text{Cp}_2\text{Ti}(\text{NH}^i\text{Bu})(\text{SMe})]$  (**7**): 5.83 (s, 10 H, Cp), 2.67 (s, 3 H, SMe), (1.29, 9 H,  $\text{N}^i\text{Bu}$ ) ppm (NH not identified).

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