

## Reactivity Studies on Tantalocene(sulfido)hydride $\text{Cp}'_2\text{Ta}(=\text{S})\text{H}$ ( $\text{Cp}' = \text{Bu}^t\text{C}_5\text{H}_4$ ): Cycloaddition on and Protonation of the $\text{Ta}=\text{S}$ Ligand

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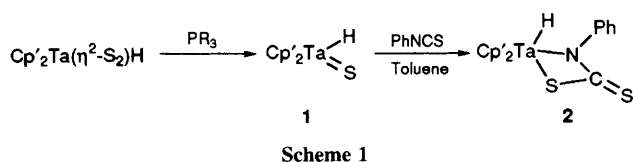
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Reactions of the tantalocene(sulfido)hydride  $\text{Cp}'_2\text{Ta}(=\text{S})\text{H}$  with PhNCS and HCl exhibit a surprisingly low metal-hydride reactivity; the  $\text{Ta}=\text{S}$  bond being involved either in a [2 + 2] cycloaddition or a protonation.

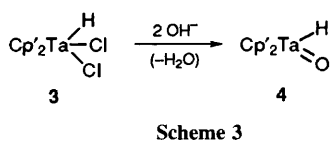
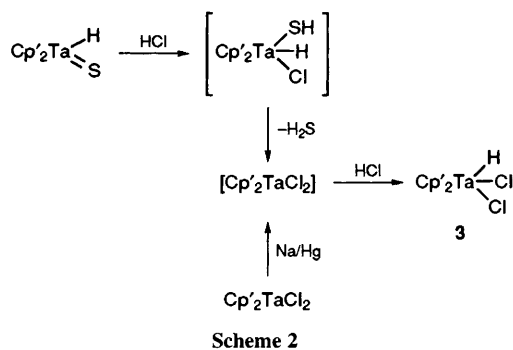
Interest in the chemistry of metallocenes containing doubly bonded chalcogene ligands<sup>1</sup> is particularly focused on oxo compounds.<sup>2-4</sup> The metal-sulfur double bond of group 4 metallocene sulfides may also exhibit exceptional reactivity.<sup>5</sup> A peculiar property of the higher group 5 metallocene sulfides ( $\text{M} = \text{Nb}, \text{Ta}$ ) is that they contain an additional hydride ligand.<sup>6</sup> A typical example is  $\text{Cp}'_2\text{Ta}(\eta^2\text{-S}_2)\text{H}$  ( $\text{Cp}' = \text{Bu}^t\text{C}_5\text{H}_4$ ), which readily undergoes a desulfurisation reaction in the presence of phosphine, resulting in the formation of the monosulfur complex **1**,  $\text{Cp}'_2\text{Ta}(=\text{S})\text{H}$  (Scheme 1). The combination of a nucleophilic sulfur ligand with a hydride ligand may be expected to form a difunctional metallocene. Characteristic of the  $\text{M}-\text{H}$  moiety ( $\text{M} = \text{Nb}, \text{Ta}$ ) are insertion reactions with heterocumulenes,<sup>7</sup> elemental sulfur<sup>8</sup> and activated alkynes.<sup>9</sup> We now report the first results on the reaction

of **1** with PhNCS and HCl, showing that the  $\text{Ta}=\text{S}$  bond may also be activated.

Complex **1** reacts with phenylisothiocyanate in boiling toluene to form a cream-coloured product. After chromatography and crystallisation from chloroform colourless crystals of **2** are obtained in 45% yield (Scheme 1). The spectroscopic<sup>†</sup> data are consistent with a product resulting from a cycloaddition of the ligand to the  $\text{Ta}=\text{S}$  double bond, only one isomer being formed. In the IR spectrum, the disappearance of the  $\text{Ta}=\text{S}$  absorption was concomitant with strong absorptions at 1483 and 1379  $\text{cm}^{-1}$ , characteristic of a conjugated  $\text{N}-\text{C}-\text{S}$  bond system. Another striking feature is the downfield shift of the  $\text{TaH}$  resonance in the  $^1\text{H}$  NMR spectrum from  $\delta$  2.79 in  $\text{Cp}'_2\text{Ta}(\text{S}_2)\text{H}$  to  $\delta$  7.91. A similar shift is observed for **1** and may be characteristic of  $\text{Ta}^{\text{V}}$  complexes containing electron-withdrawing ligands. There is no proof for the insertion into



<sup>†</sup> Spectroscopic data for **2**:  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  1.17 (s, 18H,  $\text{Bu}^t$ ), 5.31 (q, 2H,  $\text{C}_5\text{H}_4$ ), 5.54 (q, 2H,  $\text{C}_5\text{H}_4$ ), 6.00 (q, 2H,  $\text{C}_5\text{H}_4$ ), 6.40 (q, 2H,  $\text{C}_5\text{H}_4$ ), 6.94–7.19 (m, 5H,  $\text{C}_6\text{H}_5$ ), 7.91 (s, 1H,  $\text{TaH}$ ). IR(CsI):  $\nu/\text{cm}^{-1} = 1842$  ( $\nu_{\text{TaH}}$ ). FDMS ( $m/z$ ): 591.3 ( $\text{C}_{25}\text{H}_{32}\text{TaNS}_2$  requires 591.62).



the tantalum-hydride bond as observed in the reaction of heteroallenes with monohydride-tantalum(III) complexes.<sup>7</sup> An X-ray analysis (Fig. 1) confirms that **2** contains a planar *N,S*-coordinated dithiocarbamate.‡ However, there is only indirect evidence for the hydride: the orientation of the chelate is such that the N atom is close to the plane defined by the two ring centres and Nb. The remarkable selectivity of the chelate formation might have been initiated by a frontal attack of the C=N bond at the metal, followed by a [2 + 2] cycloaddition. Such a mechanism has been well documented for the insertion of alkynes into the M-L bond of bent metallocenes.<sup>10</sup> A lateral attack would have led to the orientation of S next to the hydride but is probably hindered by the Bu<sup>t</sup> substituents.

Another aspect of the reactivity of **1** is illustrated by its behaviour towards HCl (Scheme 2). The ABCD pattern of the aromatic protons in the <sup>1</sup>H NMR spectrum§ indicates that product **3** is in agreement with an unsymmetric distribution of the hydrido and the two chloro ligands. Thus, the formation of **3** seems to occur by an electrophilic attack of H<sup>+</sup> at sulfur, followed by a reductive elimination of H<sub>2</sub>S and then by an oxidative addition of HCl. The nature of **3** is supported by an independent experiment: the 16e complex Cp'2TaCl, prepared by reduction of Cp'2TaCl<sub>2</sub> with 1 equiv. of Na/Hg, also reacts with HCl to afford a compound with similar properties.

As the latter reaction provides an easy access to **3**, the reactivity of this new type of Ta<sup>V</sup> compounds was investigated by treatment of **3** with 10% aq. KOH. From this reaction the

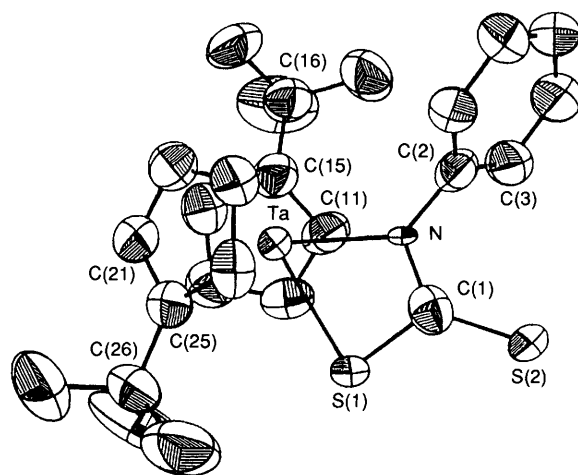


Fig. 1 ORTEP drawing (50% probability level) of (Bu<sup>t</sup>C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>-Ta(H)SC(S)NPh-CHCl<sub>3</sub> **2**. Solvent molecule is omitted. The position of the hydride follows from stereochemical considerations (see text). Selected bond lengths (Å) and angles (°): Ta-S(1) 2.567(3), Ta-N 2.203(8), S(1)-C(1) 1.73(1), S(2)-C(1) 1.68(1), N-C(1) 1.33(1); S(1)-Ta-N 62.4(3), Ta-S(1)-C(1) 82.3(4), Ta-N-C(1) 107.4(7), Ta-N-C(2) 131.6(6), C(1)-N-C(2) 120.4(8), S(1)-C(1)-N 107.9(7), S(1)-C(1)-S(2) 122.8(6), N-C(1)-S(2) 129.3(8).

oxo-hydrido-tantalocene **4**, another representative of doubly bonded main group ligand, was obtained in good yields (Scheme 3). IR, <sup>1</sup>H NMR and mass spectroscopy data¶ are close to those of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ta(=O)H, which has been characterised X-ray crystallographically.<sup>2</sup> Finally, it should be noted that compounds **3** and **4** as well as **1** and **2** exhibit <sup>1</sup>H NMR resonances that suggest a proton rather than hydride character for the TaH group. The reaction potential of this novel class of compounds is under investigation.

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‡ *Spectroscopic data for 3*: <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>): δ 1.38 (s, 18H, Bu<sup>t</sup>), 5.16 (q, 2H, C<sub>5</sub>H<sub>4</sub>), 5.59 (q, 2H, C<sub>5</sub>H<sub>4</sub>), 5.75 (q, 2H, C<sub>5</sub>H<sub>4</sub>), 6.25 (q, 2H, C<sub>5</sub>H<sub>4</sub>), 11.30 (s, 1H, TaH). IR (CsI): ν/cm<sup>-1</sup> = 1631 (ν<sub>TaH</sub>), 275 (ν<sub>TaCl</sub>). FDMS (*m/z*): 494.2 (C<sub>18</sub>H<sub>27</sub>Ta<sup>35</sup>Cl<sub>2</sub> requires 494.1).

§ *Crystal data for 2*: C<sub>26</sub>H<sub>34</sub>NS<sub>2</sub>Ta, *M* = 712.0, monoclinic space group *P2<sub>1</sub>/c* (No. 14), *a* = 12.121(2), *b* = 16.288(3), *c* = 15.458(4) Å, β = 110.83(2)°, *V* = 2852.3 Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.378 g cm<sup>-3</sup>, μ (Mo-Kα) = 39.589 cm<sup>-1</sup>. Intensity data were measured on an Enraf-Nonius CAD4 Diffractometer. The structure was solved and refined by conventional three-dimensional Patterson, difference Fourier and full-matrix least-squares methods. **2** crystallises with one solvent molecule (CHCl<sub>3</sub>) per formula unit. The hydrogen atoms (except the hydride and that of CHCl<sub>3</sub>) were included in calculated positions. The final *R* and *R<sub>w</sub>* factors are 0.046 and 0.052 for 3843 reflections with *I* ≥ 3σ(*I*). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ *Spectroscopic data for 4*: <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>): δ 1.31 (s, 18H, Bu<sup>t</sup>), 5.62 (q, 4H, C<sub>5</sub>H<sub>4</sub>), 5.97 (q, 2H, C<sub>5</sub>H<sub>4</sub>), 6.10 (q, 2H, C<sub>5</sub>H<sub>4</sub>), 6.97 (s, 1H, TaH). IR (CsI): ν/cm<sup>-1</sup> = 1819 (ν<sub>TaH</sub>), 850 (ν<sub>TaO</sub>). FDMS (*m/z*): 440.3 (C<sub>18</sub>H<sub>27</sub>TaO requires 440.15).