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Desulfurization and ring opening of thiirane induced by tantalocene trihydride complexes: synthesis, reactivity and X-ray structure of $Cp'_2Ta(=S)(S\text{-}^iPr)$ with $Cp' = \eta^5\text{-}C_5H_4^tBu$

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Abstract

The reaction of the tantalocene trihydride complexes Cp'_2TaH_3 **1** ($Cp' = \eta^5\text{-}C_5H_4^tBu$) or $Cp''CpTaH_3$ **1′** ($Cp'' = \eta^5\text{-}C_5H_2\text{-1,2-Me}_2\text{-4-}^tBu$) with propylene sulfide was found to proceed via an unprecedented sulfur transfer and regioselective ring opening reaction at once to yield sulfido-thiolato tantalocene complexes $Cp'_2Ta(=S)(S\text{-}^iPr)$ **2a** whose structure has been determined by X-ray crystallography or $Cp''CpTa(=S)(S\text{-}^iPr)$ **2′a**. Complex **1** reacts with ethylene sulfide to give $Cp'_2Ta(=S)(S–Et)$ **2b**. The reactivity of **2a** towards a variety of electrophilic moities has been investigated: protonation (with HBF_4) and alkylation (with MeI) reactions occur at the terminal sulfur ligand, leading to $[Cp'_2Ta(SH)(S\text{-}^iPr)]BF_4$ **4a**, $[Cp'_2Ta(SMe)(S\text{-}^iPr)]I$ **5a**; the reaction of **2b** with EtI was found to yield $[Cp'_2Ta(S–Et)_2]I$ **6b**. Complex **2a** (or **2′**) binds the unsaturated organometallic fragments $[W(CO)_5]$ and $[W(CO)_4]$; the new heterobimetallic complexes $Cp'_2Ta(S\text{-}^iPr)(\mu\text{-}S)W(CO)_5$ **7a** (or **7′a**) and $Cp'(\mu\text{-}S,S\text{-}^iPr)]W(CO)_4$ **8a** (or **8′a**) were formed. Inversion of configuration at the bridging μ-S atoms has been observed at low temperature for **8a** and has been studied by dynamic ^{1}H-NMR spectroscopy. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Tantalocene hydrides; Thiirane; Heterobimetallic complex; Crystal structure

1. Introduction

Transition metal complexes with unique structural features and unusual reactivities have been obtained by using chalcogen atoms as bridging ligands [1]. The sulfido ligand is one of the most versatile of them: it displays a wide range of bonding modes and electron-donating capability. A variety of metallocene complexes with mono-, di- or polysulfur ligands are prepared by reaction of organometallic derivatives with elemental sulfur [2]. Recent years have witnessed an increasing range of applications of thiiranes as a source of sulfur atoms in the synthetic route to transition-metal sulfido, thiolato or thioacyl complexes [3], sulfur bridged polymetalic complexes [4], sulfur insertion into a metal–hydrogen bond [5], coordinated thiirane complexes [6], reactivity onto the Mo(110) face [7], and notable developments in their stereospecific rhodium catalysed desulfurization [8] and catalytic transformation by tungsten carbonyl complexes [9].

In this respect, it was of interest to examine the reactivity of tantalocene trihydride complexes towards thiirane. We have observed that thiiranes are engaged in a facile and unprecedented addition with Cp'_2TaH_3 **1** ($Cp'=\eta^5\text{-}^tBuC_5H_4$), leading to a sulfido-alkanethiolato-tantalocene complex. The present communication reports the preparation of $Cp'_2Ta(=S)(S–CHR–Me)$ **2a** (R = Me) and **2b** (R=H) complexes, the crystal structure of **2a**, its reactivity towards electrophilic moieties

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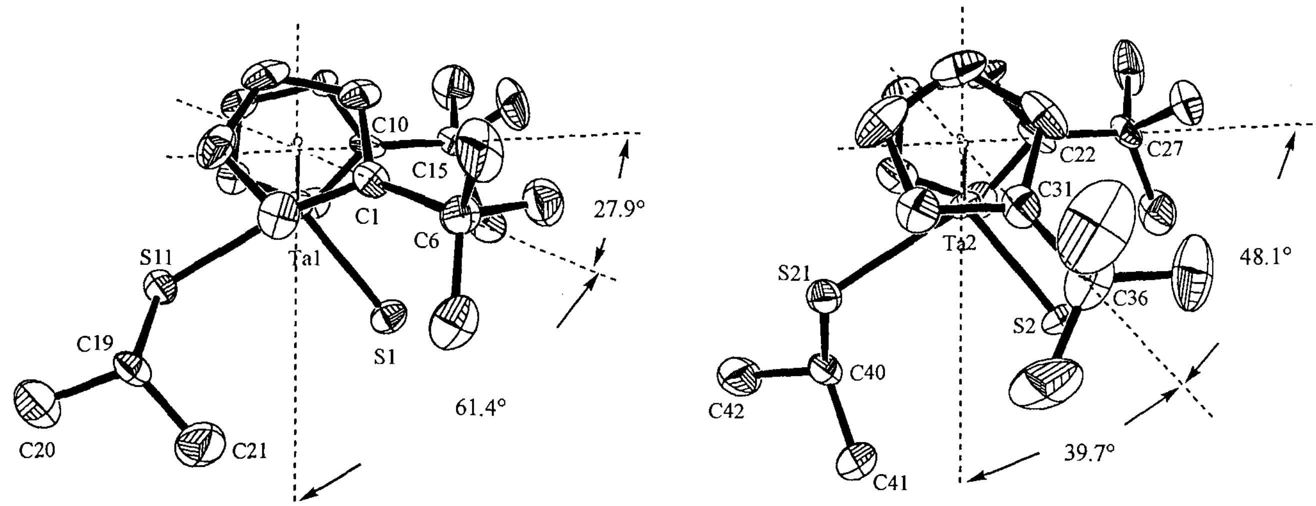


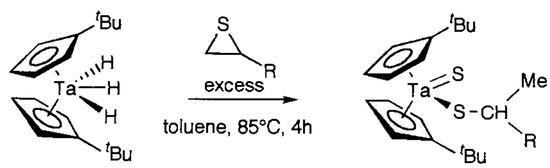
Fig. 1. ORTEP drawings of independent molecules in the crystal structure of **2a** (30% probability level).

as well as an aspect of its reactivity as a heterobimetallic precursor.

2. Results and discussion

2.1. Reaction tantalocene trihydides with thiiranes

Heating of Cp'_2TaH_3 **1** (one equivalent) with an excess of propylene sulfide or ethylene sulfide (five equivalents) in toluene, followed by silica gel chromatography (chloroform) resulted in the formation of complex **2a** or **2b**, respectively in good yield (ca. 60%) as the only isolable organometallic product (Eq. (1)).



1 **2a** (R=Me) **2b** (R=H) (1)

The analytical, IR ($\nu_{Ta=S} = 434$ cm^{-1}) and ^{1}H-NMR (presence of a deshielded $-CH$Me$_2$ signal) spectroscopic data are consistent with the formulation **2a** confirmed by an X-ray structure analysis.

There are two independent molecules of **2a** in the asymmetric unit of monoclinic $P2_1/n$ space group (Fig. 1). These two molecules differ in the conformations of ^{i}Pr groups with respect to the Cp′ rings and of the ^{t}Bu substituted rings. The dihedral angles S1/Ta1/S11//Ta1/S11/C19 and S2/Ta2/S21//Ta2/S21/C40 are equal to + 63.0 and − 51.9°, respectively.

Selected bond lengths and angles are gathered in Table 1. The single Ta–S(^{i}Pr) bond in the octacoordinated species **2a** (mean 2.48 Å) is 0.14 Å longer than the single Ta–S(CPh_3) bond in the hexacoordinated Cp*TaCl(S)(SCPh$_3$) complex [10] bearing a very bulky substituent on the thiolate ligand, while the formally double Ta=S bond in **2a** (mean 2.23 Å) is only 0.06 Å longer than the corresponding bond in hexacoordinated complex. This observation led us to think about the presence of additional bonding interactions between the tantalum and terminal sulfur atoms in **2a**. The Ta–S π bond $p\pi$(S) (p_y, p_z hybrid)-a$_1$(Cp$_2$Ta) [11] is located in the STaS plane (yz) bisecting those of Cp rings. The supplementary π interactions may involve the remainder $p\pi$ filled atomic orbital of sulfur perpendicular to this plane (p_x) and the high energy Cp–Ta antibonding molecular orbitals b$_1$ and a$_2$ (major contribution of Cp) together with their low energy bonding counterparts. Thus, some electron density is delocalized from sulfur atom into this fragment, leading to some triple nature of Ta=S bond. These hypotheses have been confirmed by EHMO calculations; the results of which may be obtained from the authors. At once, our description is consistent with the known electronic buffer nature of cyclopentadienyl ligands in transition metal complexes. If an electrophile attacks the terminal sulfur atom, it can withdraw the electron density from the rings

Table 1
Selected bond lengths (Å) and angles (°) for $(C_5H'_4Bu)_2Ta(=S)(S\text{-}^iPr)$ **2a**

Bond lengths (Å)			
Ta1–S1	2.235(4)	Ta2–S2	2.222(4)
Ta1–S11	2.492(4)	Ta2–S21	2.465(5)
Ta1–CP1	2.17	Ta2–CP2	2.16
Ta1–CP11	2.17	Ta2–CP21	2.16
Bond angles (°)			
CP1–Ta1–CP11	127.6	CP2–Ta2–CP21	127.8
S1–Ta1–S11	98.8(1)	S2–Ta2–S21	97.6(2)

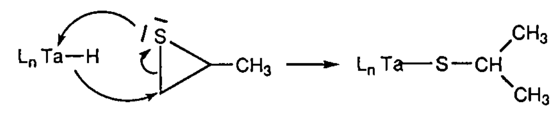
through the adequate 'Cp–M–S' molecular orbital. The metal–ligand double bond may remain little affected by coordination.

The formally double Ta=S bond length in dinuclear $Cp'_2Ta(H)(\mu\text{-}S)W(CO)_5$ is equal to 2.274(5) Å [12]; only 0.04–0.05 Å longer than the Ta=S bonds in **2a**. An increase of the bond length upon complexation is usually ascribed to its weakening. In the mentioned case it may be assigned to a transfer of supplementary π electron density mainly from metallocene rings toward the incoming metal affecting little the Ta=S bond. This is consistent with the resonances of Cp protons in **7a** which are deshielded with respect to the non-complexed **2a** (Section 3). Consequently, the 0.04–0.05 Å difference in multiple TaS bonds may be a measure of triple bond contribution. It has been recently reported by Cotton [13], that in some hexacoordinated complexes of Mo(IV) $Mo(P)_4S_2$ the formally triple Mo≡S bond (2.14 Å) predicted by ligand field theory is 0.1 Å shorter than the *pure* Mo=S double bonds (2.24 Å). The latter are in turn shorter by 0.2 Å than the single Mo–thiolate bonds (2.44 Å). Thus, assuming that the covalent radius of octacoordinated tantalum should be larger than that of hexacoordinated molybdenum, the metric parameters reported for **2a** argue for the partial triple bond contribution to the Ta=S bond.

The prochiral $Cp''CpTaH_3$ **1′** [14] ($Cp''=\eta^5\text{-}C_5H_2\text{-}1,2\text{-}Me_2\text{-}4\text{-}{}^tBu$) complex reacted in a similar manner with propylene sulfide, leading to the corresponding $Cp''CpTa(=S)(S\text{-}{}^iPr)$ **2′a** product. The presence of the chiral tantalum centre was evidenced by the proton NMR spectrum: at room temperature (r.t.), two singlets are observed for the two diastereotopic methyl groups ($\Delta\nu = 18$ Hz) of the substituted cyclopentadienyl ring and two doublets for the methyl protons ($\Delta\nu = 12$ Hz) of the thiolate ligand, displaying the stereostability of the chiral metallic atom.

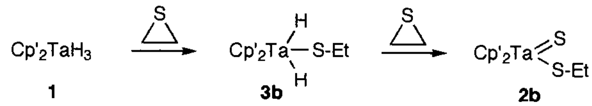
A sulfido thiolate complex $Cp_2Ta(=S)(S\text{–}Me)$ has been recently synthetised by photolysis of $Cp_2Ta(C_2H_2)(Me)$ or $Cp_2Ta(=S)(Me)$–thiirane mixture [15]. Its formation solely results from a desulfurization of thiirane. However, in the presence of tantalum trihydrides, thiirane exhibits a double reactivity consisting of the ring opening which is the source of the alkanethiolate ligand, and of the desulfurization, which leads to the formation of Ta=S chromophore.

The mechanism of the formation of **2** has been investigated in some detail, and it has been shown that the reaction takes place via initial ring opening. Consistent with this, our observations show that the heating of $Cp'_2Ta(=S)H$ with propylene sulfide in toluene for 4 h results, after work-up, in the isolation of unchanged hydride complex; on that account, no Ta=S to $Ta(\eta^2\text{-}S_2)$ transformation is evidenced in these relatively mild experimental conditions.



Scheme 1.

However, formation of **2b** follows the formation of the symmetrical thiolate complex **3b** (Eq. (2)) as observed by ^{1}H-NMR spectroscopy in the reaction of **1** with one equivalent of ethylene sulfide. We have identified this product as **3b** by comparison with an authentic sample, recently obtained by reaction of the cationic dihydride complex $[Cp'_2TaH_2]^+$ with one equivalent of sodium thioethanolate [16].



(2)

Thus, the formation of **2** appears to involve in a first step insertion of thiirane into the central transition metal–hydride bond. Moreover, the mechanism of the ring opening reaction is regioselective: as illustrated in Scheme 1, the hydride ligand attacks exclusively the more electrophilic and less hindered carbon atom of the thiirane and no formation of $S\text{-}{}^nPr$ isomer $Cp'_2Ta(=S)(S\text{–}CH_2CH_2CH_3)$ is observed.

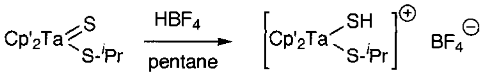
In the next step, insertion of a second molecule of thiirane could be expected but no dithiolate complex [17], like $Cp'_2Ta(SEt)_2H$, has been detected by NMR as intermediate.

This type of reactivity observed with alkene sulfides towards tantalocene trihydride complexes **1** does not occur either with trimethylene sulfide or with tetrahydrothiophene; under the same experimental conditions, complex **1** is recovered together with small amounts (ca. 5%) of the known tantalocene sulfido hydride $Cp'_2Ta(=S)H$ [2b].

2.2. Reaction with electrophiles

Metallocene complexes of the early transition metals bearing terminal oxo, imido or chalcogeno ligands are of continuing interest because of their rich and diverse chemistry ([2b], [15], [18]). The combination of the two different nucleophilic sulfur groups present in compounds **2** may be expected to form difunctional complexes; accordingly, they may serve to evaluate the reactivity of both sulfur ligands attached to the tantalum centre. We therefore set out to investigate the reactivity of complexes **2** towards a variety of electrophilic moities such as H^+ and R^+.

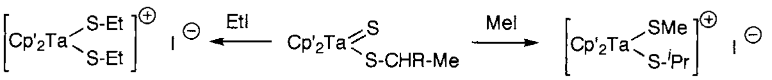
Addition of an excess of $HBF_4{\cdot}Et_2O$ to a pentane solution of **2a** gives a precipitate from which the red diamagnetic salt **4a** can be isolated. Analytical and spectroscopic data are consistent with the formulation shown in Eq. (3):



2a **4a** (3)

Protonation takes place directly at the terminal sulfur ligand, as indicated by the disappearance of $\nu_{Ta=S}$ absorption near 430 cm^{-1} as well as by a very weak absorption at 2564 cm^{-1}. The ^{1}H-NMR spectrum of **4a** exhibits a set of four deshielded (δ 6.34–6.65 ppm) resonances for the substituted rings according (i) to the electron deficient character of the metal centre (ii) to the prochiral environment around the tantalum atom. The ^{1}H resonance of the Ta–S*H* proton of **4a** has not been detected. However, the addition of D_2O results in a complete deprotonation reaction showing its strong acidity. Description of the structure **4a** as in Eq. (3) is supported by our recent results obtained in the Nb–O series ([18]i). The crystal structure of the $[Cp^*_2Nb(OH)(F)]BF_4$ shows a long Nb–O bond (1.847(8) Å) and the Nb–O*H* proton was also not detected in NMR.

The reaction of **2a** with an excess of iodomethane in toluene at r.t. affords an orange precipitate which was shown by elemental analyses and FD MS spectrometry to have the composition $[Cp'_2Ta(SMe)(S^iPr)]I$ **5a** (Eq. (4)). The structure of **5a** can be unequivocally assigned from its IR (absence of $\nu_{Ta=S}$ absorption near 430 cm^{-1}) and ^{1}H-NMR data: the presence of four noteworthy deshielded resonances (δ 6.81–7.01 ppm) for the Cp′ protons characteristic of the pronounced cationic feature of the metal centre.



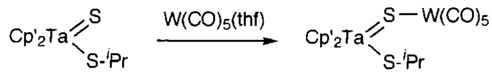
6b **2a** (R=Me) **2b** (R=H) **5a** (4)

The attack of the electrophilic moiety at the terminal sulfur ligand is confirmed by the formation of the symmetrical dithiolate complex **6b** obtained by alkylation of **2b** with iodoethane: the ^{1}H-NMR spectrum exhibits only two signals (δ 6.45 and 6.76 ppm) for the cyclopentadienyl protons characteristic of a C_{2v} symmetry. Outer-sphere coordination of the iodide ligand through sulfur atoms or its direct bonding to the metal can not be excluded because the ^{1}H-NMR of **6b** is easily recorded in C_6D_6.

2.3. Syntheses of heterobimetallic complexes

We recently embarked [12,19] on a project aimed at preparing of a series of heterobimetallic complexes containing a tantalocene moiety with various sulfur bridging ligands like sulfide, disulfide, or hydrosulfide. In this context it was of interest to check the reactivity of **2a** (and **2′a**) towards electrophilic metal carbonyls, e.g. $[W(CO)_5]$ and $[W(CO)_4]$.

The dinuclear species **7a** was obtained by stirring of a THF solution of **2a** with 20% excess of $W(CO)_5(THF)$ complex; the crude material was purified by chromatography (silica gel; toluene) to give pure **7a** as a deep-brown solid in ca. 65% yield (Eq. ((5))).

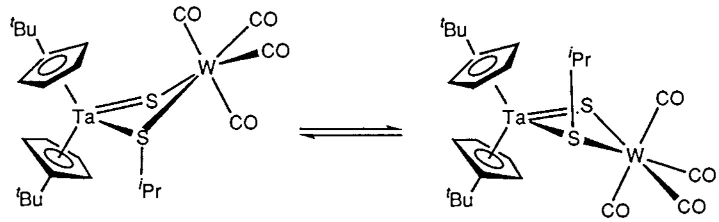


2a **7a** (5)

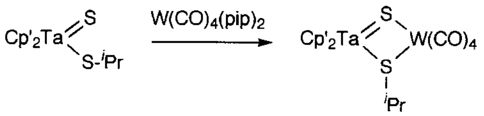
The composition of bimetallic **7a** has been confirmed by analytical and spectroscopic means. The IR spectrum of **7a** (in THF) exhibit the typical absorption pattern for the coordinated $W(CO)_5$ moiety; the IR band ascribed to the Ta=S vibration at 434 cm^{-1} in the spectrum (in CsI) of the free ligand **2a** is no longer observed in that of **7a** (several very weak bands are observed in the 400–360 cm^{-1} region), suggesting that the complexation occurs at the terminal sulfide with a significant weakening of the Ta=S bond. It apparently does not hold with the discussion of electronic structure of **2a** (vide supra). However, if one assumes that the electron density localized in the Ta=S bond is little affected (except that attributed to the triple bond) by complexation, the IR shift may be easily assigned to the mass effect of the heavy $W(CO)_5$ complexed fragment. The ^{1}H-NMR spectrum shows only one signal for the two *tertio*butyl proton groups, which indicates equivalent Cp′ ligands; as observed for $Cp'_2Ta(H)(\mu$-S)$W(CO)_5$ complex [12], such a pattern indicates a symmetrical position of the $W(CO)_5$ moiety in solution at r.t.

Starting from Cp″CpTa(=S)(S-^{i}Pr) **2′a** the bimetallic Cp″CpTa(S-^{i}Pr)(μ-S)$W(CO)_5$ **7′a** is obtained by a similar reaction. Its ^{1}H-NMR data are closely reminiscent of those for the precursor and display the stereostability of the chiral tantalum atom: non equivalence is observed for the methyl groups of the thiolate ligand ($\Delta\nu = 26$ Hz), the methyl groups ($\Delta\nu = 36$ Hz) and the hydrogen atoms ($\Delta\nu = 54$ Hz) of the cyclopentadienyl ligand.

From a topological viewpoint both sulfur atoms in **2a** (or **2′a**) may be considered as potential heterobimetallic connectors. With this aim, complex **2a** (or **2′a**) reacted with to a two-fold excess of $W(CO)_4(pip)_2$ in THF. The new bimetallic complexes **8a** (or **8′a**) have been isolated in 70% yields (Eq. (6)) as brown solids.



Scheme 2.



2a **8a** (6)

Analytical and spectroscopic data establish unambiguously the structure of these bimetallic compounds. The ambient temperature ^{1}H-NMR spectrum of **8a** in C_6D_6 solution shows a sharp singlet ($\delta = 1.21$ ppm; 18H) due to the ^{t}Bu groups. It indicates a rapid inversion at the μ-S atoms which is responsible for an averaging of the prochiral tantalum environment depicted on Scheme 2. The signals of the cyclopentadienyl protons and of the two methyl (^{i}Pr) groups appear as unresolved multiplets.

In order to check the inversion of configuration at sulfur atoms, complex **8a** was further examined by ^{1}H variable temperature NMR spectroscopy in a toluene-d_8 solution. On cooling, the signal due to the ^{t}Bu protons broadens, crosses over a coalescence point near -5°C, and splits into two singlets ($\Delta\nu = 20$ Hz at -35°C); the activation energy at 268 K is $\Delta G^{\ddagger} = 59 \pm 4$ kJ mol^{-1}.

On the other hand, the inversion of configuration at sulfur atoms does not occur at r.t. for complex **8′a** because only one diastereoisomer is observed (such an inversion should give rise to a diastereoisomeric form due to the presence of a chiral tantalum centre). The ^{1}H-NMR spectrum in C_6D_6 exhibits at ambient temperature two well resolved doublets for the two non-equivalent $-CH\mathit{Me}_2$ groups ($\Delta\nu = 78$ Hz), two sharp singlets for the methyl ring substituents ($\Delta\nu = 33$ Hz) and two doublets for the two diastereotopic cyclopentadienyl protons ($\Delta\nu = 56$ Hz); no coalescence is observed by heating up to 50°C.

In this case, steric requirements of the *iso*propyl-thiolato group and of the bulky trisubstituted cyclopentadienyl ligand hinder the inversion process. This suggests that one of the two stable enantiomers of complex **8′a** have a geometry illustrated in Fig. 2.

In summary, we have shown that tantalocene trihydrides are efficient reagents for desulfurization and ring opening of alkene sulfides leading in one pot reaction to the difunctional sulfurated complexes. We have investigated the mechanism of their formation and the reactivity of the Ta=S bond as illustrated by its conversion to the Ta–SH and Ta–SR linkages and its capability to bind electrophilic organometallic fragments. A proposed partial triple nature of the terminal Ta=S bond calls up the often forgotten higher energy molecular orbitals of bent metallocenes and agrees with a buffer behaviour of cyclopentadienyl rings.

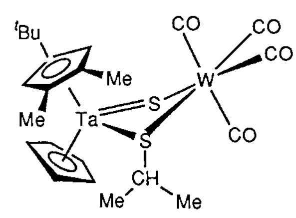
3. Experimental section

3.1. General

All procedures were performed under an atmosphere of purified argon. Solvents were distilled from sodium benzophenone ketyl. Column chromatography was carried out on silica gel (70–230 mesh). The following instruments were used in this work: Bruker AC 200 (RMN); Bruker IFS 66v spectrophotometer (IR); Finnigan MAT 311 (field desorption mass spectra); EA 1108 CHNS-O FISONS Instruments (Elemental analyses). The complexes Cp'_2TaH_3 **1** [20] and $Cp''CpTaH_3$ **1′** [14] were prepared by published procedures.

3.2. Preparations of complexes **2a** and **2′a**

Propylene sulfide (0.37 ml, 4.7 mmol) was added to a toluene solution of Cp'_2TaH_3 (0.67 g, 1.6 mmol); the mixture was heated for 7 h at 85°C in a closed flask. The brown–red solution was brought to dryness and complex **2a** separated by chromatography on silica gel. Elution with neat chloroform afforded a brown–red zone which contained 0.47 g (56%) of **2a**. Starting from a toluene solution of $Cp''CpTaH_3$ **1′**, complex **2′a** was obtained (52% yield) in a similar manner to the analogue **2a**.



8′a

Fig. 2. Geometry of one of the two enantiomers in the structure of **8′a.**

2a. Anal. Found: C, 47.33; H, 6.3. $C_{21}H_{33}TaS_2$ (530.1) Calc.: C, 47.54; H, 6.27%. FD-MS (from toluene): 530.2 (calc. 530.15 for $C_{21}H_{33}TaS_2$). ^{1}H-NMR (200 MHz, C_6D_6): 1.41 (s, 18H), 1.44 (d, 6.6 Hz, 6H), 3.17 (hep, 6.6 Hz, 1H), 4.94 (m, 2H), 5.33 (m, 2H), 5.80 (m, 2H), 6.07 (m, 2H) ppm. IR (CsI): ν(Ta=S): 434 cm^{-1}.

2′a. Anal. Found: C, 45.21; H, 5.99. $C_{19}H_{29}TaS_2$ (502.1) Calc.: C, 45.41; H, 5.82%. FD-MS (from toluene): 502.0 (calc. 502.12 for $C_{21}H_{33}TaS_2$). ^{1}H-NMR (200 MHz, C_6D_6): 1.22 (s, 9H), 1.40 (d, 6.7 Hz, 3H), 1.46 (d, 6.7 Hz, 3H), 1.90 (s, 3H), 1.99 (s, 3H), 3.11 (hep, 6.7 Hz, 1H), 5.15 (d, 2.6 Hz, 1H), 5.29 (d, 2.6 Hz, 1H), 5.82 (s, 5H) ppm. IR (CsI): ν(Ta=S): 425 cm^{-1}.

3.3. Preparation of complex **2b**

Ethylene sulfide (58 μl, 1 mmol) was added to a toluene solution of Cp'_2TaH_3 (90 mg, 0.21 mmol); the mixture was heated for 5 h at 55°C in a closed flask. The brown–red solution was brought to dryness and complex **2b** separated by chromatography on silica gel. Elution with neat chloroform afforded a brown–red zone which contained 70 mg (64%) of **2b**.

2b. Anal. Found: C, 46.00; H, 5.95. $C_{20}H_{31}TaS_2$ (530.1) Calc.: C, 46.51; H, 6.05%. FD-MS (from toluene): 530.2 (calc. 530.15 for $C_{21}H_{33}TaS_2$). ^{1}H-NMR (200 MHz, C_6D_6): 1.37 (t, 7.5 Hz, 3H), 1.38 (s, 18H), 2.87 (q, 7.5 Hz, 2H), 4.96 (m, 2H), 5.30 (m, 2H), 5.80 (m, 2H), 6.05 (m, 2H) ppm. IR (KBr): ν(Ta=S): 438 cm^{-1}.

3.4. Preparation of complex **4a**

To a solution of 110 mg (0.21 mmol) of **2a** in pentane was added 1.5 equivalents of HBF_4 in ether. The solution was filtered and the residue was washed with diethylether to give 90 mg (70% yield) of **4a**. The crude material was recrystallized from $CHCl_3$/ether.

4a. Anal. Found: C, 40.24; H, 5.43. $C_{21}H_{34}TaS_2BF_4$ (618.38) Calc.: C, 40.79; H, 5.54%. FD-MS (from $CHCl_3$): 531.2 (calc. 531.15 for $C_{21}H_{34}TaS_2$). ^{1}H-NMR (200 MHz, $CDCl_3$): 1.27 (d, 6.6 Hz, 6H), 1.39 (s, 18H), 3.92 (hep, 6.6 Hz, 1H), 6.34 (m, 2H), 6.42 (m, 2H), 6.56 (m, 2H), 6.65 (m, 2H) ppm. IR (KBr): ν(S–H): 2564 cm^{-1}.

3.5. Preparation of complex **5a**

A large excess of iodomethane (ca. 1 ml) was added to a solution of 100 mg (0.19 mmol) of **2a** in toluene. After stirring for 15 min at r.t. a red precipitate was formed; the solvent was removed in vacuo and the crude material was washed with pentane (2 × 5 ml). Recrystallization from CH_2Cl_2/pentane gave 95 mg of pure **5a** (ca. 75%).

5a. Anal. Found: C 38.86; H 5.38. $C_{22}H_{36}TaS_2I$ (662.4) Calc.: C, 39.29; H, 5.40%. FD-MS (from CH_2Cl_2): 545.2 (calc. 545.17 for $C_{22}H_{36}TaS_2$). ^{1}H-NMR (200 MHz, CD_3COCD_3): 1.41(s, 18H), 1.27 (d, 6.6 Hz, 6H), 4.26 (hep, 6.6 Hz, 1H), 3.30 (s, 3H), 4.94 (m, 2H), 5.33 (m, 2H), 5.80 (m, 2H), 6.07 (m, 2H) ppm.

3.6. Preparation of complex **6b**

A large excess of iodoethane was added to a solution of 80 mg (0.16 mmol) of **2b** in toluene. After 10 min at 50°C, the mixture turned red and the solvent was removed in vacuo. The dark red solid was recrystallized from toluene/pentane to give 55 mg (55% yield) of pure **6b.**

6b. Anal. Found: C 39.67; H 5.70. $C_{22}H_{36}TaS_2I$ (662.4) Calc.: C, 39.29; H, 5.40%. ^{1}H-NMR (200 MHz, C_6D_6): 1.01 (t, 7.3 Hz, 6H), 1.30 (s, 18H), 3.00 (q, 7.3 Hz, 4H), 6.45 (m, 4H), 6.76 (m, 4H) ppm.

3.7. Preparation of complexes **7a** and **7’a**

A solution of 100 mg (0.24 mmol) of $W(CO)_5$(THF) (prepared by irradiation of $W(CO)_6$) was added dropwise to a stirred solution of 122 mg (0.23 mmol) of $Cp'_2Ta(S)(S\text{-}^iPr)$ **2a** in 20 ml of THF. The resulting brown reaction mixture was stirred for 1 h and the solvent was then removed. The residual solid was chomatographed on silica gel (column 15 × 2.5 cm). with toluene: 80 mg (63%) of dark red **7a** were isolated.

7a. Anal. Found: C, 36.44; H, 3.87. $C_{26}H_{33}TaWS_2O_5$ (854.1) Calc.: C, 36.55; H, 3.89%. FD-MS (from toluene): 854.1 (calc. 854.07 for $C_{26}H_{33}TaWS_2O_5$). ^{1}H-NMR (200 MHz, C_6D_6): 1.03 (s, 18H), 1.28 (d, 6.6 Hz, 6H), 3.05 (hep, 6.6 Hz, 1H), 5.39 (m, 2H), 5.44 (m, 2H), 5.79 (m, 2H), 5.93 (m, 2H). IR (THF): ν(CO): 2061m, 1930vs, 1888s cm^{-1}.

7′a. Anal. Found: C, 34.96; H, 3.99. $C_{24}H_{29}TaWS_2O_5$ (826.4) Calc.: C, 34.88; H, 3.54%. ^{1}H-NMR (200 MHz, C_6D_6): 1.01 (s, 9H), 1.21 (d, 6.6 Hz, 3H), 1.34 (d, 6.6 Hz, 3H), 1.58 (s, 3H), 1.76 (s, 3H), 2.98 (hep, 6.6 Hz, 1H), 4.90 (d, 2.6 Hz, 1H), 5.17 (d, 2.6 Hz, 1H), 5.64 (s, 5H). IR (THF): ν(CO): 2061m, 1928vs, 1886s cm^{-1}.

3.8. Preparation of complexes **8a** and **8′a**

To a solution of 160 mg (0.32 mmol) of **2′a** in toluene, 0.3 g (0.64 mmol) of $W(CO)_4(pip)_2$ were added. After stirring for 1 h at 40°C, the dark red solution was brought to dryness and complex **8′a** separated by chromatography on silica gel. Elution with neat toluene afforded a yellow band of $W(CO)_4(pip)_2$ followed by a brown–red zone which contained 180 mg of **8′a** (70% yield). Starting from a toluene solution of $Cp''CpTa(S)(S^iPr)$ **2a**, complex **8a** was obtained in a manner similar to the analogue **8′a**.

Table 2
Crystallographic data for $(C_5H_4^tBu)_2Ta(=S)(S\text{-}^iPr)$ **2a**

Molecular formula	$C_{21}H_{33}S_2Ta$
Formula weight (g)	530.57
Crystal color and size (mm)	Red; 0.15, 0.1, 0.1
Crystal system	Monoclinic
Space group	$P2_1/n$ (no.14)
Cell dimensions	
a (Å)	11.637(2)
b (Å)	18.385(2)
c (Å)	20.767(3)
β (°)	96.47(2)
V (Å^3)	4414(1)
Z	8
$D_{calc.}$ (g cm^{-3})	1.596
F(000)	2112
Radiation (Å)	λ(Mo–K$_\alpha$) 0.71073
Linear abs. (μ cm^{-1})	51.047
T (°C)	18
Scan type	ω-2θ
Scan speed (deg min^{-1})	1.1–5.6
Scan width (°)	$\Delta\omega = 0.75 + 0.347 \tan\theta$
Reflections measured	$\pm h, k, l$ (12, 18, 20)
θ range (°)	2–25
No. of reflections measured	8915
Decay (%)	−3.1, corrected
Absorption correction (Ψ scan)	93.65–99.78
Cut off for obsd. data	$I \geq 2\sigma(I)$
No. of unique obsd. data (NO)	2932
No. of variables (NV)	433
R_f	0.036
wR_f	0.040
Weighting scheme	$1/\sigma(F_o)^2 = [\sigma(I)^2 + (0.04I)^2]^{-1/2}$
Goodness-of-fit	0.37
$\rho_{max-min}$ (e Å^{-3})	+1.05[a], −0.20

[a] Four highest peaks are 1.1–1.3 Å far from the Ta atoms.

8a. Anal. Found: C, 35.47; H, 4.65. $C_{25}H_{33}TaWS_2O_4$ (826.5) Calc.: C, 36.33; H, 4.02%. ^{1}H-NMR (200 MHz, C_6D_6, 20°C): 1.21 (s, 18H), 1.62 (br, 2H), 2.36 (hep, 6.5 Hz), 4.49 (br, 2H), 4.70 (m, 2H), 4.99 (br, 2H), 5.11 (br, 2H). IR (THF): ν(CO): 2006s, 1912m, 1883vs cm^{-1}.

8′a. Anal. Found: C, 34.23; H, 3.99. $C_{23}H_{29}TaWS_2O_4$ (798.4) Calc.: C, 34.60; H, 3.66%. ^{1}H-NMR (200 MHz, C_6D_6, 20°C): 1.25 (s, 9H), 1.31 (d, 3H), 1.34 (s, 3H), 1.51 (s, 3H), 1.70 (d, 3H), 2.24 (hep, 1H), 4.13 (d, 1H), 4.42 (d, 1H), 5.02 (s, 5H). ppm. IR (THF): ν(CO): 2003s, 1907m, 1877vs cm^{-1}.

3.9. X-ray analysis of $Cp'_2Ta(=S)(S\text{-}^iPr)$ 2a

A small red crystal of **2a** was grown from the acetone solution and mounted on a Enraf-Nonius CAD4 diffractometer. Unit cell was determined from 25 randomly selected reflections. The pertinent crystallographic data are given in Table 2. Intensity data were corrected for Lorentz, polarization and absorption effects. The structure was solved and refined by conventional Patterson, difference Fourier and full-matrix least-squares methods. All non-hydrogen atoms (Table

Table 3
Atomic coordinates of the non-hydrogen atoms for $(C_5H_4^tBu)_2Ta(=S)(S\text{-}^iPr)$ **2a**[a,b]

Atom	x	y	z	B(A2)
TA1	0.27725(5)	0.40607(3)	0.03996(3)	2.78(1)
TA2	0.85834(5)	0.40956(4)	0.30490(3)	3.50(1)
S1	0.1236(3)	0.3951(2)	0.0948(2)	3.84(9)
S11	0.3500(3)	0.5258(2)	0.0835(2)	3.83(9)
S2	0.8383(4)	0.3107(2)	0.3641(2)	4.7(1)
S21	0.7675(4)	0.4968(3)	0.3738(2)	5.5(1)
C1	0.342(1)	0.2903(7)	0.1011(7)	3.3(3)
C2	0.412(1)	0.3494(9)	0.1272(8)	4.6(4)
C3	0.478(1)	0.3755(9)	0.0787(8)	5.0(4)
C4	0.451(1)	0.3357(8)	0.0237(8)	4.6(4)
C5	0.365(1)	0.2846(8)	0.0359(7)	3.9(4)
C6	0.287(1)	0.2344(8)	0.1401(7)	4.2(4)
C7	0.260(1)	0.263(1)	0.2055(8)	6.0(5)
C8	0.373(2)	0.1720(8)	0.151(1)	6.9(5)
C9	0.176(1)	0.2038(9)	0.1036(8)	5.9(5)
C10	0.142(1)	0.3954(7)	−0.0643(6)	3.0(3)
C11	0.255(1)	0.3812(7)	−0.0768(6)	2.8(3)
C12	0.322(1)	0.4463(8)	−0.0645(7)	3.6(4)
C13	0.252(1)	0.4991(8)	−0.0452(6)	3.2(3)
C14	0.137(1)	0.4689(8)	−0.0452(6)	3.6(3)
C15	0.036(1)	0.3464(8)	−0.0832(7)	3.8(4)
C16	0.064(1)	0.2669(9)	−0.067(1)	6.8(5)
C17	−0.069(1)	0.370(1)	−0.0506(9)	6.1(5)
C18	0.011(2)	0.354(1)	−0.1571(8)	7.5(6)
C19	0.396(1)	0.5257(8)	0.1710(7)	4.0(4)
C20	0.455(2)	0.597(1)	0.1892(8)	7.2(5)
C21	0.295(2)	0.513(1)	0.2102(8)	7.6(6)
C22	0.774(1)	0.338(1)	0.2063(7)	4.9(4)
C23	0.825(1)	0.4011(9)	0.1864(7)	4.5(4)
C24	0.768(2)	0.463(1)	0.2040(8)	7.6(5)
C25	0.679(1)	0.439(1)	0.2389(8)	6.6(5)
C26	0.680(1)	0.362(1)	0.2406(8)	5.6(4)
C27	0.795(2)	0.2603(9)	0.1877(8)	5.4(4)
C28	0.732(2)	0.205(1)	0.224(1)	8.7(6)
C29	0.754(2)	0.255(1)	0.116(1)	10.4(7)
C30	0.923(1)	0.242(1)	0.197(1)	6.8(5)
C31	1.066(1)	0.4080(9)	0.3622(9)	5.5(4)
C32	1.019(1)	0.4764(9)	0.3694(9)	5.9(5)
C33	0.993(2)	0.511(1)	0.307(1)	9.0(6)
C34	1.022(2)	0.464(1)	0.262(1)	8.6(6)
C35	1.062(1)	0.399(1)	0.2923(9)	6.6(5)
C36	1.127(2)	0.363(1)	0.417(1)	8.2(6)
C37	1.071(2)	0.372(1)	0.4770(9)	13.1(9)
C38	1.134(2)	0.285(1)	0.395(1)	11.6(9)
C39	1.253(2)	0.394(2)	0.422(2)	16(1)
C40	0.629(1)	0.464(1)	0.3912(8)	5.6(5)
C41	0.642(2)	0.426(1)	0.4567(9)	8.2(6)
C42	0.541(2)	0.523(1)	0.391(1)	9.8(7)
CP1	0.4093	0.3271	0.0733	
CP11	0.2215	0.4381	−0.0592	
CP2	0.7453	0.4004	0.2152	
CP21	1.0323	0.4515	0.3186	

[a] CP are the geometrical centers of cyclopentadienyl rings.
[b] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3)*[$a2*B(1,1)+b2*B(2,2)+c2*B(3,3)+ab(\cos\gamma)*B(1,2)+ac(\cos\beta)*B(1,3)+bc(\cos\alpha)*B(2,3)$].

3) were refined with anisotropic thermal parameters. The hydrogen atoms were included in a riding model. All calculations were carried out with the MOLEN package [21].

4. Supporting information

H-atom coordinates, thermal parameters and full tables of bond lengths and angles (four pages).

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