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Preparation and Reactivity of Peralkylated Tantalocene Sulfur Complexes Having a Fulvenoid Substructure

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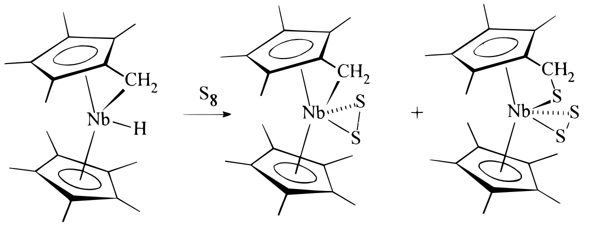
Summary: The equilibrium mixture of $Cp^*(\eta^6\text{-}C_5Me_4CH_2)TaH_2$ *and* $[Cp^*_2TaH]$ *reacts with elemental sulfur to give* $Cp^*_2Ta(\eta^2\text{-}S_2)H$ (***1***) *and* $Cp^*(\eta^6\text{-}C_5Me_4CH_2)Ta(\eta^2\text{-}S_2)$ (***2***). *Irradiation of* ***2*** *by sunlight in the presence of sulfur results in sulfur insertion into the Ta−methylene bond to give* $Cp^*(\eta^6\text{-}C_5Me_4CH_2S)Ta(\eta^2\text{-}S_2)$ (***4***). *The same reaction in the absence of sulfur produces* $Cp^*(\eta^6\text{-}C_5Me_4CH_2S)Ta({=}S)$ (***5***), *in which the* $Ta(\eta^2\text{-}S_2)$ *group is transformed into a Ta=S moiety accompanied by a migratory sulfur insertion into a Ta−C bond. As a byproduct in these reactions,* $Cp^*_2Ta({=}S)SH$ (***3***), *which is an isomerization product of the always present* ***1***, *is formed. These reactions provide a new insight into the sulfur chemistry of metallocenes having a fulvenoid substructure. All products are characterized by means of IR-,* ^1H-, *and* ^{13}C-*NMR spectra.*

Introduction

Recent studies have shown that the ring methyl groups in pentamethylcyclopentadienyl transition metal complexes can be activated for C−H insertion.[1] Of particular interest are permethylated metallocenes with fulvenoid substructures, e.g. complexes in which one Cp* (Cp* = C_5Me_5) ligand has been transformed into a η^4- or η^5,η^1-tetramethylfulvene[2,3] ligand. In these compounds the fulvene-like structure may coexist with a bent metallocene structure Cp^*_2M (M = Ti, Nb).[4] Although metallocenes of the early transition elements or their derivatives show a pronounced reactivity toward chalcogenes,[5] little is known about the related chemistry of their fulvene-like homologues.

In a recent paper we reported on the reaction of an equilibrium mixture containing two isomers of decamethylniobocene, Cp^*_2Nb and $Cp^*(\eta^6\text{-}C_5Me_4CH_2)NbH$, with sulfur. While Cp^*_2Nb gave $Cp^*_2Nb(\eta\text{-}S_2)L$ derivatives (L = H, SH), the products obtained from $Cp^*(\eta^6\text{-}C_5Me_4CH_2)NbH$ were in agreement with structures involving a tetramethylfulvene-derived ligand (eq 1).[6] However, low yields and purification problems prompted us to look for an alternative system in order to extend and generalize this kind of metallocene chemistry. As starting material, we choose $Cp^*(\eta^6\text{-}C_5Me_4CH_2)TaH_2$, which can be prepared by treatment of $Cp^*_2TaCl(THF)$ with $LiBEt_3H$ or by the reaction of $Cp^*_2TaCl_2$ with an excess of $LiCMe_3$.[7]



(1)

Experimental Section

All procedures were carried out under argon with argon-saturated, dry solvents. Elemental analyses were performed by the Mikroanalytisches Laboratorium, Universität Regensburg. IR spectra were obtained with a Perkin-Elmer 580B instrument, and field desorption mass spectra were run on a Finnigan MAT 95 instrument from toluene solutions. NMR spectra were recorded on a Bruker WM 400 instrument. $Cp^*_2TaCl_2$ was prepared as described elsewhere.[8]

Reaction of $Cp^*(\eta^6\text{-}C_5Me_4CH_2)TaH_2$ with Sulfur. $Cp^*(\eta^6\text{-}C_5Me_4CH_2)TaH_2$[7] was prepared from 1.64 g (3.14 mmol) of $Cp^*_2TaCl_2$ in 40 mL of THF to which 4.3 mL of *t*-BuLi (7.31 mmol, 1.7 M solution in pentane, Aldrich) was added dropwise.

[⊗] Abstract published in *Advance ACS Abstracts*, January 15, 1996.

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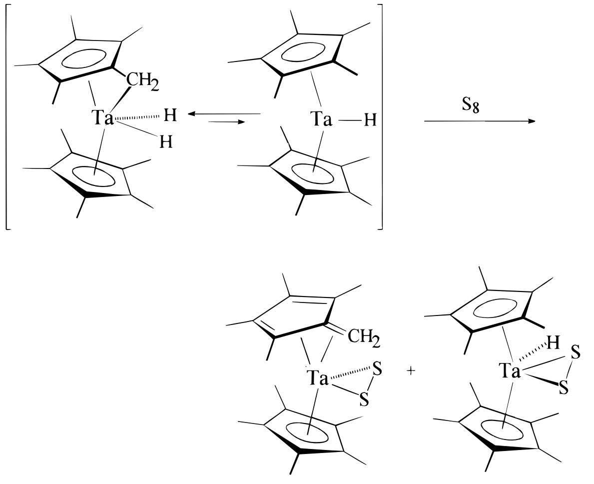
The suspension was stirred for 1 h to give a red solution to which 0.20 g (0.79 mmol) of S_8 was added. Then the mixture was stirred for 5 min at room temperature in the dark. The resulting orange solution was evaporated to dryness, and the residual solid was chromatographed on silica gel (column 25 × 2 cm). With toluene a yellow band containing **1** and **2** in a ratio of about 1:2 was eluted. The total yield is 50%. Low-pressure chromatography on five connected Merck-Lobar columns (24 × 1 cm; Lichroprep Si 60 (40−63 μm)) gave a broad yellow band upon elution with toluene, which contained at the top complex **2** and at the end spectroscopically pure **1**. Both compounds were recrystallized from toluene at −20 °C to give microcrystalline powders. Anal. Calcd for $C_{20}H_{31}TaS_2$ (**1**): C, 46.51; H, 6.05; mol wt, 516.5. Found: C, 45.68; H, 6.10; mol wt, 516.1 (FD-MS). IR (KBr): ν_{S-S} 526 w cm^{-1}. Anal. Calcd for $C_{20}H_{29}TaS_2$ (**2**): C, 46.69; H, 5.68; mol wt, 514.5. Found: C, 45.11; H, 5.66; mol wt, 514.0 (FD-MS). IR (KBr): $\nu_{=C-H}$ 3046 w cm^{-1}, ν_{S-S} 526 w cm^{-1}.

Preparation of Cp*(η^5,η^1-$C_5Me_4CH_2S$)TaS_2 (4). To a solution of 150 mg (0.29 mmol) of **1** and **2** (ratio 1:2) in 20 mL of THF was added 20 mg (0.08 mmol) of S_8. The reaction mixture was exposed to sunlight for 4 h, during which time the color changed from yellow to red. Then the solvent was removed under vacuum and chromatographed on silica gel (column 15 × 2 cm). With toluene were eluted two red bands containing **3** and **4** in 20% and 62% yield, respectively. Recrystallization of **3** and **4** from toluene at −20 °C gave red microcrystals. Anal. Calcd for $C_{20}H_{31}TaS_2$ (**3**): C, 46.51; H, 6.05; mol wt, 516.5. Found: C, 45.68; H, 6.10; mol wt, 516.1 (FD-MS). IR (KBr): ν_{S-H} 2538 vw cm^{-1}, $\nu_{Ta=S}$ 434 s cm^{-1}. Anal. Calcd for $C_{20}H_{29}TaS_3$ (**4**): C, 43.95; H, 5.35; mol wt, 546.6. Found: C, 43.17; H, 5.61; mol wt, 546.1 (FD-MS). IR (KBr): ν_{S-S} 528 cm^{-1}.

Preparation of Cp*(η^5,η^1-$C_5Me_4CH_2S$)TaS (5). A 200 mg (0.39 mmol) amount of a mixture of **1** and **2** (ratio 1:2) was dissolved in 20 mL of THF and irradiated by sunlight for 4 h. The resulting red solution was evaporated to dryness and then chromatographed on silica gel (column 15 × 2 cm). A pale yellow band (discarded) was eluted with toluene, and a red band containing **3** and **5** was eluted with toluene/THF (10:1). The concentrated solution was rechromatographed on a Merck-Lobar column (24 × 1 cm; Lichroprep Si 60 (40−63 μm)). With toluene **3** and **5** were eluted as two red bands in 28% and 59% yield, respectively. Both compounds were recrystallized from toluene at −20 °C. Anal. Calcd for $C_{20}H_{29}TaS_2$ (**5**): C, 46.69; H, 5.68; mol wt, 514.5. Found: C, 46.87; H, 5.76; mol wt, 514.0 (FD-MS). IR (KBr): $\nu_{Ta=S}$ 428 s cm^{-1}.

Results and Discussion

It has already been established that Cp*(η^6-C_5Me_4-CH_2)TaH_2 exists in an equilibrium with [Cp*$_2$TaH] via hydrogen migration from metal to the ring methylene and *vice versa*.[7,9] Therefore, treatment of this mixture with elemental sulfur gives a mixture of **1** and **2** (eq 2) along with H_2S. While the ratio **1**:**2** is about 1:1 in toluene, it is ≈1:2 in THF. This may be explained by the kinetic stabilization of [Cp*$_2$TaH] by coordinating THF.[7] Separation of **1** and **2** can be achieved by low-pressure chromatography but with considerable loss of material. Although it was impossible to obtain a crystalline material of analytical purity, FD mass spectra along with ^{1}H and ^{13}C NMR data provide sufficient support for a clear structural description. They also prove that **2** contains two hydrogens less than **1**.



2 **1**

(2)

The IR and ^{1}H-NMR spectroscopic data of **1** (Table 1) are in close analogy with those recently published for Cp′$_2$TaS$_2$H (Cp′ = *t*-BuCp) bearing a terminal disulfide along with a hydride ligand.[10] In agreement with the π-character of the Cp* ligand, there is one resonance in the ^{1}H NMR spectrum for the Cp* methyl groups and one resonance each in the ^{13}C NMR spectrum. The Ta−H resonance is observed at 2.85 ppm. The formation of **1** may be explained by oxidative addition of sulfur onto [Cp*$_2$TaH] and subsequent fragmentation to give the TaS_2 unit, while during formation of **2** evolution of H_2S may be expected.

The IR spectrum of **2** exhibits a weak but characteristic ν_{S-S} absorption at 526 cm^{-1} which is typical of a S_2^{2-} ligand.[11] The NMR spectra of **2** (Table 1) are in agreement with a Cp* ligand of fulvenoid character along with an intact Cp* ligand. The intense ^{1}H resonance at 1.89 ppm ($CDCl_3$) can be assigned to the ring methyl groups of the intact ligand, while the diastereotopic ring methyl groups of the other ring system show four singlets. One of the CH_3 resonances is considerably shielded, probably as a consequence of a skew arrangement of the ligand, bringing one CH_3 group in close proximity to the metal. An AX system may be ascribed to the diastereotopic CH_2 group. The ^{13}C NMR spectrum shows two intense resonances which belong to the equivalent aliphatic and ipso carbons of the obviously intact Cp* ligand. Additionally, four aliphatic resonances are found between 11 and 12 ppm, while the ring carbons may be assigned to five resonances between 105 and 130 ppm. Finally a resonance for the CH_2 carbon is situated at 60.02 ppm.

The bonding in **2** may be described by the two resonance structures **A** and **B** (Figure 1). Structure **A** resembles the classical Cp*$_2$Ta structure with the exception of one additional Ta−C σ-bond to the cyclopentadienyl methylene group. Structure **B** contains a η^6-fulvene ligand, as already observed for Cp*(η^6-C_5Me_4-CH_2)TiMe,[12] Cp*(η^6-$C_5Me_4CH_2$)WH,[13] and Cp*(η^6-C_5-

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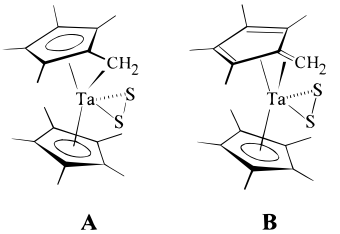
Table 1. NMR Spectroscopic Data (δ) for Complexes 1−5

		^{1}H				^{13}C		
no.	solvent	$\mathrm{C}\boldsymbol{H}_3$	$\mathrm{C}\boldsymbol{H}_2$	$\mathrm{Ta}\boldsymbol{H}$	$\mathrm{S}\boldsymbol{H}$	$\mathrm{C}\boldsymbol{C}\mathrm{H}_3$	$\boldsymbol{C}\mathrm{CH}_3$	$\mathrm{C}\boldsymbol{C}\mathrm{H}_2$
1	C_6D_6	1.76 (s, 30H)		2.85 (1H)				
	$CDCl_3$					11.67 (10C)	109.63 (10C)	
2	C_6D_6	1.50 (s, 3H), 1.60 (s, 3H), 1.68 (s, 3H), 1.71 (s, 15H), 1.84(s, 3H)	2.39 (d, 1H, J_{H-H} = 3.6 Hz), 3.01 (d, 1H, J_{H-H} = 3.6 Hz)					
	$CDCl_3$	1.30 (s, 3H), 1.89 (s, 15H), 1.91 (s, 3H), 1.98 (s, 3H), 2.08 (s, 3H)	2.42 (d, 1H, J_{H-H} = 3.7 Hz), 2.79 (d, 1H, J_{H-H} = 3.7 Hz)			10.98 (1C), 11.12 (1C), 11.23 (5C), 11.76 (1C), 12.08 (1C)	105.88 (1C), 109.26 (1C), 110.30 (1C), 110.69 (5C), 114.77 (1C), 130.06 (1C)	60.02 (1C)
3	C_6D_6	1.88 (s, 30H)			-0.28 (s, 1H)			
	$CDCl_3$					12.54 (10C)	118.61 (10C)	
4	C_6D_6	1.37 (s, 3H), 1.69 (s, 15H), 1.76 (s, 6H), 1.86 (s, 3H)	3.40 (d, 1H, J_{H-H} = 10.8 Hz), 3.69 (d, 1H, J_{H-H} = 10.8 Hz)					
	$CDCl_3$	1.62 (s, 3H), 1.84 (s, 15H), 1.95 (s, 3H), 1.99 (s, 3H), 2.19 (s, 3H)	3.38 (d, 1H, J_{H-H} = 10.8 Hz), 3.83 (d, 1H, J_{H-H} = 10.8 Hz)			9.47 (1C), 10.76 (1C), 11.19 (5C), 11.42 (1C), 12.72 (1C)	98.41 (1C), 99.75 (1C), 107.64 (1C), 111.25 (1C), 114.62 (5C), 124.27 (1C)	18.26 (1C)
5	C_6D_6	1.48 (s, 3H), 1.52 (s, 3H), 1.87 (s, 15H), 1.94 (s, 3H), 2.77 (s, 3H)	3.83 (d, 1H, J_{H-H} = 11.2 Hz), 4.06 (d, 1H, J_{H-H} = 11.2 Hz)					
	$CDCl_3$	1.93 (s, 3H), 1.99 (s, 3H), 2.00 (s, 3H), 2.02 (s, 15H), 2.67 (s, 3H)	4.04 (d, 1H, J_{H-H} = 11.2 Hz), 4.17 (d, 1H, J_{H-H} = 11.2 Hz)			9.48 (1C), 10.67 (1C), 11.92 (5C), 12.79 (1C), 14.46 (1C)	99.74 (1C), 109.50 (1C), 114.61 (1C), 118.83 (5C), 119.26 (1C), 122.47 (1C)	21.17 (1C)



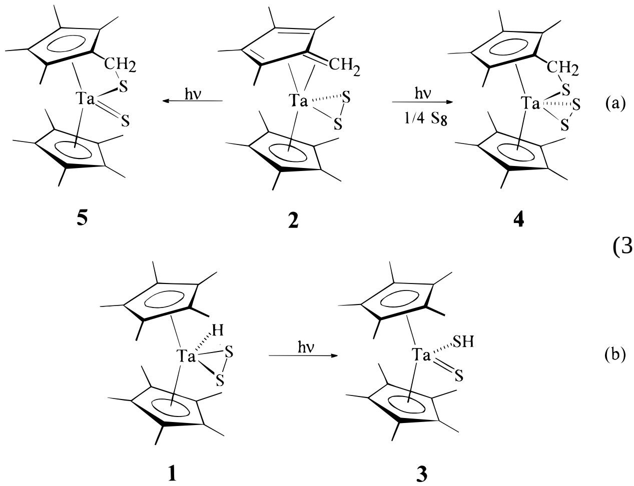
A **B**

2

Figure 1.

$Me_4CH_2)TiH$.[4b] ^{1}H-NMR data suggest structure **B** to be the better representation: the diastereotopic hydrogens of the methylene bridge are coupled to each other with $^2J_{H-H}$ = 3.6 Hz, which is in close agreement with values expected for geminal hydrogen atoms attached to sp^2-hybridized carbon. Typical for such hydrogens are 0−3 Hz in contrast to 12−15 Hz for geminal hydrogens attached to sp^3-hybridized carbon.[14] This view is supported by an olefinic C−H stretching frequency at 3046 cm^{-1} in the IR spectrum[15] which is absent in the case of **4** and **5** (see below). Correspondingly, $^2J_{H-H}$ coupling constants of 10.8 and 11.2 Hz for the methylene groups are observed for **4** and **5** which are in the range of sp^3 hydrogens.

Because of the difficulties to separate **1** and **2** on a preparative scale, the mixture directly obtained from the starting materials (eq 2) was used for further studies. Irradiation by sunlight in the presence of 2 equiv of sulfur leads to the formation of **3** and **4** (eq 3).



5 **2** **4**

1 **3**

(3)

Whereas the formation of **3** may be described as an isomerization reaction of **1**,[16] analytical and spectroscopic data indicate an insertion of sulfur into the Ta-methylene bond of **2** to give **4**.

If the same reaction is carried out in the absence of sulfur, complex **5** is formed as the main product along

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[14] Emsley, J. W.; Feeney, J.; Sutclife, L. H. *High Resolution Nuclear Magnetic Resonance Spectroscopy*; Pergamon Press: New York, 1966; p 710.

[15] Absorptions at 3040 cm^{-1} have been observed for Cp*(C_5Me_4-CH_2)TiMe (see ref 12) and at 3055 cm^{-1} for ($C_5Me_3(CH_2)_2$)Ta(H)$_2$-(PMe_3)$_2$ (see ref 1d).

[16] Similar isomerization reactions have been reported for Cp*$_2$-Nb(=S)SH (Brunner, H.; Gehart, G.; Meier, W.; Wachter, J.; Nuber, B. *J. Organomet. Chem.* **1993**, *454*, 117) and Cp*$_2$Ta(Se)SeH (Shin, J. H.; Parkin, G. *Organometallics* **1995**, *14*, 1104).

with **3** (eq 3a). Analytical data confirm **5** to be an isomer of **2** formed by S−S bond fission and migratory insertion of one sulfur into the Ta−methylene bond. Accordingly, the ν_{S-S} absorption typical of **2** (and **4**) disappeared with the corresponding appearance of a strong $\nu_{Ta=S}$ absorption at 428 cm^{-1} for **5**. It is interesting that this sulfur migration is much more selective than that observed in the transformation of $(C_5H_5)_2Ta(\eta^2\text{-}S_2)CH_3$ into $(C_5H_5)_2Ta(=)SCH_3$.[17]

While irradiation of **1** and **2** leads to well-defined compounds, no reaction is observed during thermolysis up to 80 °C. Temperatures above 80 °C lead to decomposition of **1** and **2**. If a solution of **4** in toluene is heated up to 100 °C with an excess of phosphites, one S atom is abstracted to give **5**. However, attempts to synthesize $Cp^*(\eta^6\text{-}C_5Me_4CH_2)Ta{=}S$ by analogous abstraction of one S atom from **2** were not successful and led only to decomposition of **2**.

The NMR spectra of **4** and **5** are in agreement with a tetramethyl methylene sulfido cyclopentadienyl ligand along with an intact Cp* ligand (Table 1). Thus, ^1H NMR spectra show one intense resonance for the five equivalent methyl groups, four singlets (from 2.7 to 1.3 ppm) for the diastereotopic ring methyl groups, and an AB system for the CH_2 protons. Two intense resonances in the ^{13}C NMR spectra belong to the equivalent aliphatic and ipso carbons of the intact Cp* ligand. Aliphatic resonances are those between 9 and 15 ppm, while the ring carbons of the fulvenoid system may be assigned to resonances between 98 and 125 ppm. The chemical shifts of the CH_2 carbons are in agreement with a $-SCH_2-$ group.

Conclusions

In the reaction of $Cp^*(\eta^6\text{-}C_5Me_4CH_2)TaH_2$ with sulfur we have found a convenient synthesis for the novel tantalocene disulfide **2**. Reactivity studies reveal an unprecedented migratory sulfur transfer from the TaS_2 unit to the organic ligand. More generally, the sulfur chemistry of metallocenes has been extended to complexes with fulvenoid substructures.

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