Comparative studies in the $Cp_2M(\eta^2\text{-}S_2)H$ series ($Cp = t\text{-}BuC_5H_4$, C_5Me_4Et; M = Nb, Ta) on the reactivity of hydride and disulfide ligands

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Abstract

Reactions of $Cp'_2Ta(S_2)H$ (**1**; $Cp' = t\text{-}BuC_5H_4$) and $Cp^x_2Nb(S_2)H$ (**2**; $Cp^x = C_5Me_4Et$) with S_8, I_2, and CH_3I are investigated. Sulfur insertion into the M–H bond of **1** results in the formation of $Cp'_3Ta_3S_{12}$ and $Cp'_4Ta_4S_{13}$, where structures are known by analogy, and $Cp'_6Ta_8S_{17}$, which is characterised spectroscopically. Complex **2** gives in the analogous reaction $Cp^x_3Nb_3S_{12}$ as the only product. This compound desulfurises in boiling decane to give $Cp^x_3Nb_3S_7$ (**8**). An X-ray diffraction analysis of **8** revealed an unusual M_3S_7 core containing four monosulfide and one trisulfide ligand. The polysulfide ligand is arranged in such a way that its inner sulfur atom is at the top of the molecule in a noncoordinating fashion. Whereas reaction of **1** or **2** with I_2 gives spectroscopically characterised $Cp'_2Ta(S_2)I$ and $Cp^x_2Nb(S_2)I$ by an H/I exchange, only the reaction of **1** with CH_3I leads to well defined products. At 0°C $[Cp'_2Ta(S_2CH_3)H]I$ is formed as an intermediate product which converts into $Cp'_2Ta(=S)I$ at higher temperatures. The attack of CH_3I at the disulfide ligand gives rise to the formation of a chiral sulfur site as inferred from ^1H NMR data.

Keywords: Metallocenes; Hydride ligand; Disulfide ligand; Reactivity; X-ray structure

1. Introduction

Side-on coordinated S_2^{2-} ligands represent the simplest coordination type among the many examples of disulfide ligands [1]. They preferentially occur in multinuclear transition metal complexes and only relatively few examples are known for mononuclear complexes. Of particular interest are metallocene disulfides, e.g. $(C_5Me_5)_2VS_2$ [2] and $(C_5H_5)_2MoS_2$ [3]. In these compounds a significant portion of the coordination sphere of the metal is sterically encumbered by the bent Cp ligands whereas the S_2^{2-} ligands are exposed and may be responsible for a distinct reactivity pattern [4].

The metallocene disulfides of Nb and Ta bear an additional 1 e$^-$ ligand [5]. Introduction of peralkylated Cp ligands along with the presence of a hydride ligand [6] makes this type of metallocenes an interesting and easily accessible class of compounds. $Cp_2M(\eta^2\text{-}S_2)H$ complexes may be expected to offer several reaction

possibilities: i) insertion reactions into the metal–hydrogen bond, ii) attack of electrophiles at the electron rich S_2^{2-} ligand, iii) breaking and formation of new S–S bonds. Such processes are proposed to play a role in the reaction of Cp_2MH_3 with S_8 where different combinations of Cp ligands with Nb or Ta afforded products of differing nuclearity [6,7]. For example, formation of $Cp'_4Nb_2S_9$ from Cp'_2NbH_3 [8] and a complex mixture of products in the reaction of $(C_5Me_5)_2TaH_3$ [9] suggest an electronic and steric influence of the Cp ligands coupled with differences of the metal reactivity. In this paper we report on studies of the comparative reactivities of $Cp'_2Ta(S_2)H$ (**1**) and $Cp^x_2Nb(S_2)H$ (**2**) towards S_8, I_2, and CH_3I.

2. Results and discussion

2.1. Sulfur insertion into the M–H bonds of 1 and 2

Reaction of **1** with elemental sulfur does not occur at room temperature, but in boiling toluene the

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Table 1
IR (KBr, CsI (cm^{-1})) and ^{1}H-NMR spectroscopic data (δ values in ppm, i-TMS) of compounds 3–5 and 8–12

	IR		^{1}H-NMR							
	ν(S–S)	ν(Ta=S)	C$_5$H$_4$	Ta–H	SCH_3	CCH_3	CH_2CH$_3$	CH$_2$CH_3	CpCH_3	
3	515w		^{m}6.12(1), ^{m}5.79(1), ^{m}5.63(2), ^{m}5.55(1), ^{m}5.47(1), ^{m}5.39(1), ^{m}5.31(5), ^{m}5.29(2), ^{m}4.97(1), ^{m}4.75(1)			^{s}1.31(9), ^{s}1.30(9), ^{s}1.21(9)				a
4	520m		^{t}6.11(2), ^{q}6.05(2), ^{t}5.78(2), ^{q}5.68(2), ^{q}5.38(2), ^{m}5.34(2), ^{m}5.32(2), ^{t}5.19(2)			^{s}1.37(9), ^{s}1.30(18), ^{s}1.26(9)				a
5	514s		6.82–4.75 ^{b}			1.41–1.29 ^{b}				
8	465w						^{q}2.47(4) ^{d}, ^{q}2.37(2) ^{d}	^{t}1.14(6) ^{d}, ^{t}1.10(3) ^{d}	^{s}2.11(12), ^{s}2.10(12), ^{s}2.03(6), ^{s}2.02(6)	c
9	535m		^{q}6.14(2), ^{q}5.47(2), ^{q}5.31(2), ^{q}4.87(2)			^{s}1.14(18)				e
10	544m						^{m}2.16(4)	^{t}0.72(6) ^{d}	^{s}1.84(6), ^{s}1.79(6), ^{s}1.75(6), ^{s}1.70(6)	f
11	515m		^{q}7.01(1), ^{q}6.64(1), ^{q}6.24(1), ^{q}6.06(1), ^{q}5.05(1), ^{q}5.01(1), ^{q}4.48(1), ^{q}4.41(1)	^{s}4.33(1)	^{s}2.72(3)	^{s}1.39(9), ^{s}1.30(9)				a
12		434s	^{q}6.54(2), ^{q}6.44(2), ^{q}5.86(2), ^{q}5.61(2)			^{s}1.41(18)				a

^{a} CDCl$_3$, 400 MHz. ^{b} See Fig. 1. ^{c} CDCl$_3$, 250 MHz. ^{d} ^3J(H–H) 7 Hz. ^{e} C$_6$D$_6$, 400 MHz. ^{f} C$_6$D$_6$, 250 MHz.

polynuclear compounds 3–5 are formed (Eq. 1). More directly, but in lower yields, 4 and 5 are obtained by the reaction of excess sulfur with Cp$_2'$TaH$_3$ in boiling toluene [9]. From analytical and mass spectroscopic data of 3–5 the loss is indicated of at least one cyclopentadienyl ligand per Ta.

The ^{1}H NMR spectrum of 3 (Table 1) resembles that of Cp$_3'$Nb$_3$S$_{12}$ [10] for it exhibits similar resonances for the t-butyl and the aromatic protons. We believe it to be isostructural with the Nb analogue being built up by five different mono-, di-, and trisulfide ligands arranged in an asymmetrical manner.

The ^{1}H NMR data of 4 are consistent with a symmetry plane through the molecule. A plane of symmetry is also found crystallographically for (C$_5$H$_5$)$_4$Ta$_4$S$_{13}$ [11], prepared from the reaction of (C$_5$H$_5$)TaCl$_4$ with (Me$_3$Si)$_2$S. A similar geometry has also been identified for [Mo$_4$(NO)$_4$(S)$_3$(S$_2$)$_5$]$^{4-}$ [12] which is isoelectronic with 4. The molecular structure of 5 merits attention because the molecule contains more metal centres than organic ligands and because its ^{1}H NMR spectrum (Fig. 1, Table 1) exhibits six distinct resonances for the t-Bu groups indicating the absence of any symmetry. Unfortunately single crystals cannot yet be obtained. It
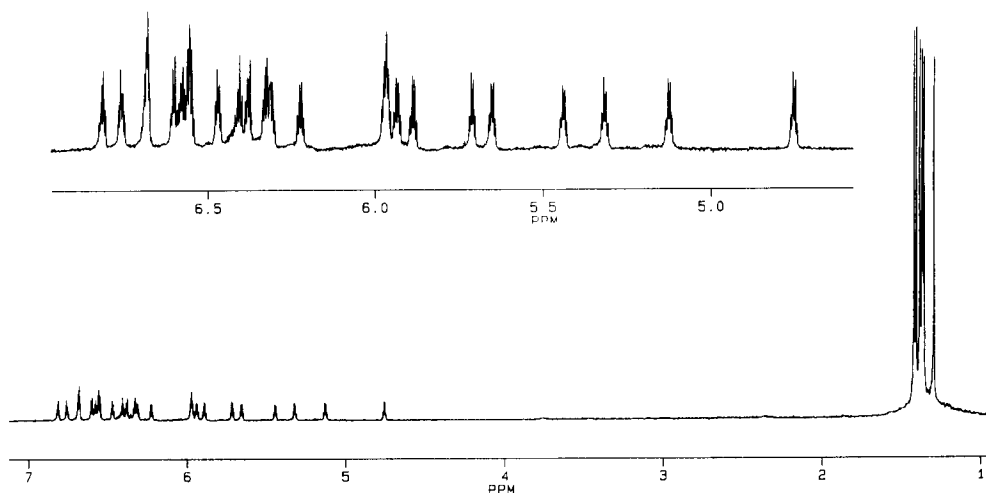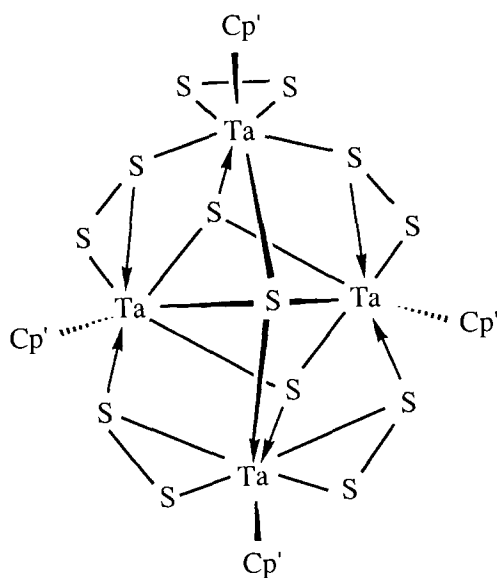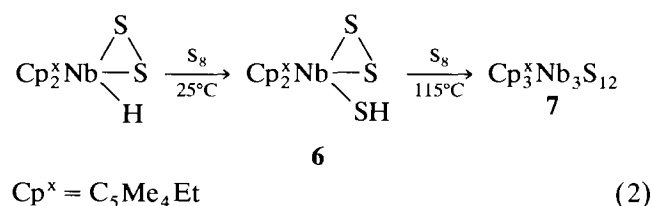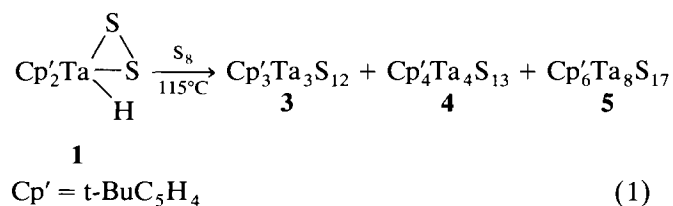

Fig. 1. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of Cp$_6'$Ta$_8$S$_{17}$ (5).

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Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\mathring{A}^2 \times 10^3$) for $Cp_3^x Nb_3 S_7$ (8)

atom	x	y	z	U_{eq} [a]
Nb(1)	6920(1)	4955(1)	2527(1)	27(1)
S(1)	5126(2)	3613(2)	1633(2)	77(1)
S(2)	8284(2)	4698(2)	3706(1)	38(1)
S(3)	6801(7)	3953(5)	4700(3)	40(3)
C(1)	6540(6)	6612(6)	1881(5)	33(3)
C(2)	7892(6)	7137(6)	1876(5)	33(3)
C(3)	8291(6)	7251(6)	2789(5)	37(3)
C(4)	7223(7)	6833(7)	3348(5)	39(4)
C(5)	6130(7)	6437(6)	2788(5)	36(3)
C(6)	5733(7)	6464(6)	1085(5)	41(4)
C(7)	8747(7)	7646(6)	1078(5)	49(4)
C(8)	9684(7)	7883(7)	3074(5)	55(4)
C(9)	7230(8)	6901(8)	4356(5)	63(5)
C(10)	4789(7)	6019(7)	3113(5)	50(4)
C(11)	5498(7)	7582(7)	977(5)	58(5)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalised U_{ij} tensor.

Table 3
Selected bond lengths ($\mathring{A}$) and angles (°) for $Cp_3^x Nb_3 S_7$ (8)

Nb(1)–S(1)	2.366(3)	Nb(1b)–Nb(1)–S(2)	51.4(1)
Nb(1)–S(2)	2.533(3)	Nb(1a)–Nb(1)–Nb(1b)	60.0(1)
Nb(1)–Nb(1a)	3.163(2)	S(1)–Nb(1)–S(2a)	78.4(1)
S(2)–S(3)	2.146(6)	S(2)–Nb(1)–S(2a)	77.1(1)
		Nb(1)–S(1)–Nb(1a)	84.1(1)
Nb(1a)–Nb(1)–S(1)	47.9(1)	Nb(1)–S(2)–S(3)	94.1(2)
Nb(1a)–Nb(1)–S(2)	89.9(1)	Nb(1)–S(2)–Nb(1b)	77.3(1)
Nb(1b)–Nb(1)–S(1)	94.7(1)	S(3)–S(2)–Nb(1b)	113.7(2)

is striking that in spite of the high sulfur content and lack of symmetry only one ν_{S-S} absorption is present in the IR spectrum. This observation may indicate that disulfide ligands do not seem to play an important role [10].

$$ \underset{1}{\underset{H}{\overset{S}{\underset{|}{Cp_2'Ta\overset{/\backslash}{-}S}}}} \xrightarrow[115°C]{S_8} \underset{3}{Cp_3'Ta_3S_{12}} + \underset{4}{Cp_4'Ta_4S_{13}} + \underset{5}{Cp_6'Ta_8S_{17}} $$

$$ Cp' = t\text{-}BuC_5H_4 \tag{1} $$

$$ \underset{H}{\underset{|}{Cp_2^x Nb\overset{/\backslash}{\underset{\backslash}{-}}S}} \xrightarrow[25°C]{S_8} \underset{6}{\underset{SH}{\underset{|}{Cp_2^x Nb\overset{/\backslash}{\underset{\backslash}{-}}S}}} \xrightarrow[115°C]{S_8} \underset{7}{Cp_3^x Nb_3 S_{12}} $$

$$ Cp^x = C_5 Me_4 Et \tag{2} $$

Reaction of 2 with excess sulfur starts with insertion of sulfur into the Nb–H bond. The resulting SH complex 6 is relatively stable and it reacts only at higher temperatures to give the polynuclear compound $Cp_3^x Nb_3 S_{12}$ (7) (Eq. 2) [7]. Compared to the insertion of sulfur into the Ta–H bond this reaction is much more selective. We now observed that 7 loses sulfur in boiling decane to give green $Cp_3^x Nb_3 S_7$ (8), whose composition was determined by mass spectrometry and elemental analyses. Addition of PBu_3 as a sulfur abstracting reagent does not result in the elimination of further sulfur or in the formation of compounds of higher nuclearity. Therefore we believe 8 to be the

most thermodynamically stable polynuclear CpNb sulfide under the reaction conditions tested thus far. An analogous thermolysis of $Cp_3' Nb_3 S_{12}$ [10] is less selective and gives a complex mixture of inseparable compounds. Previously we have reported on the formation of $Cp_3^x Nb_3 S_7$ by irradiation of $Cp^* Nb(CO)_4$ in the presence of sulfur [8]. For this compound a structure has been proposed on the basis of the usual $[M_3 S_7]^{n+}$ ($n = 1$: M = V [13]; $n = 4$: M = Mo, W [14]) core geometry in which the M–M edges of the central $M_3 S$ tetrahedron are bridged by six sulfur ligands. The seventh sulfur ligand is coordinated to all metal centres and thus serves as a μ_3-bridge.

The IR spectrum of 8 exhibits a weak absorption at 465 cm^{-1} which may be characteristic of an S–S vibration [1]. The ^{1}H NMR spectrum of 8 (Table 1) consists of two sets of resonances for the methyl- and the ethyl-Cp protons each in a 2:1 ratio, indicating the presence of two equivalent Cp rings.

An X-ray diffraction analysis (Tables 2, 3) shows the core of 8 to consist of an equilateral Nb_3 triangle (Fig. 2, 3). Whereas the lower half of the molecule consists of three S^{2-} bridges the upper half contains one S^{2-} and one S_2^{2-} bridge. The middle sulfur S(3) of the latter is in an uncoordinated mode at the top of the
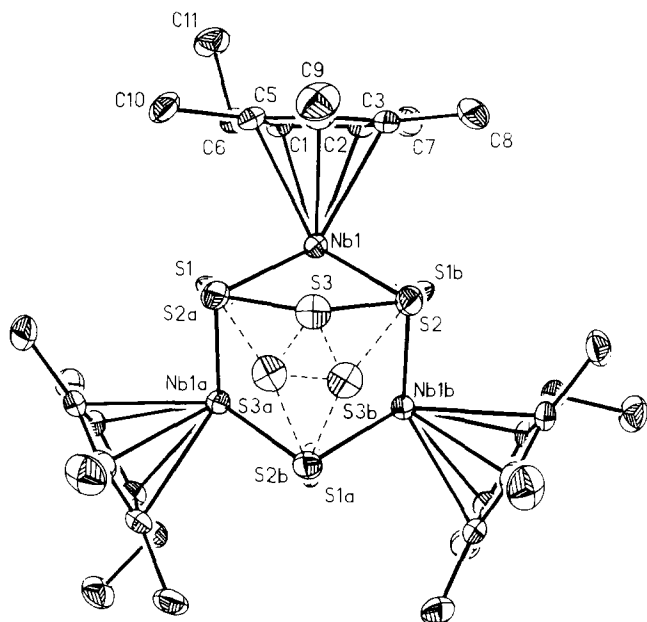
Fig. 2. Molecular structure of $Cp_3^x Nb_3 S_7$ (**8**) (ORTEP drawing) with the view along the C_3 axis. At the top of the molecule the disordered sulfur S(3) is indicated by dashed lines. The occupancy of S(3), S(3a), and S(3b) is 1/3 each.

molecule. The structure is disordered in such a way that positions S(3), S(3a), and S(3b) are of 33% occupancy each leading to trigonal symmetry in the crystal. Therefore, the Nb–Nb distances cannot be determined exactly but it must be noted that they are relatively short (3.163(2) Å) compared to those in other polynuclear CpNb sulfides (> 3.4 Å) [10]. The Nb–S(1) and
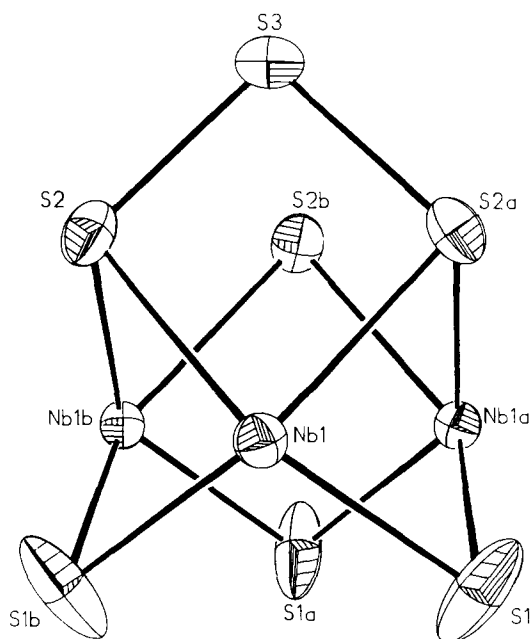

Fig. 3. Side view of the $Nb_3 S_7$ core of **8** without the disordered S atoms S(3a) and S(3b).

Nb–S(2) distances range from 2.366(3) to 2.533(3) Å, within the range generally observed for Nb–S distances.

During thermolysis of **7** the μ_3-S^{2-} ligand is removed and the S_2^{2-} ligands are transferred into S^{2-} ligands. Surprisingly, the S_3^{2-} ligand remains intact and only its coordination mode changes (Eq. 3). The diamagnetic nature of **8** requires the postulation of a Nb–Nb bond between two Nb^{IV} centres. The remaining Nb^V site may be stabilised by Nb–S–d_π–p_π interactions [15]. Thus, **8** represents the first example in the series of trinuclear CpNb sulfides in which bonding interactions between the metals have been established.

$$(3)$$

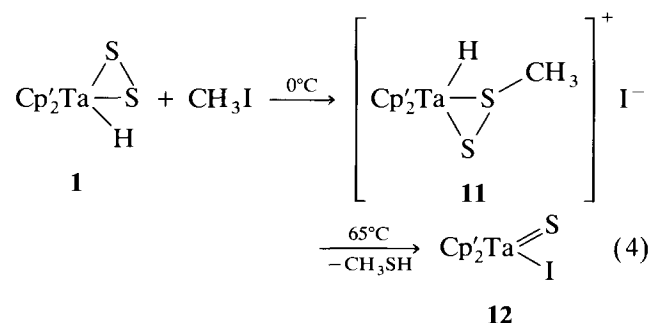7   8
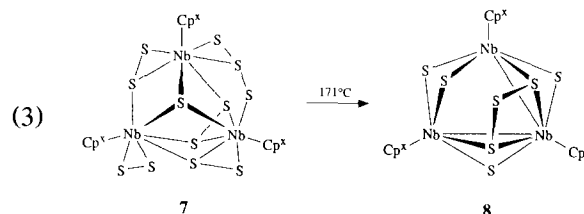
2.2. Reaction with electrophiles

Complexes **1** and **2** readily react at ambient temperature with I_2 to give brown $Cp'_2 Ta(S_2)I$ (**9**) and green-brown $Cp_2^x Nb(S_2)I$ (**10**) in good yields. Synthesis and workup have to be carried out in chlorine-free solvents in order to avoid an I/Cl exchange. The IR spectra of **9** and **10** (Table 1) are nearly unchanged when compared with those of **1** and **2** with the exception that the weak ν_{Ta-H} absorption of **1** has disappeared. In the ^1H NMR spectrum of **9** the disappearance of the Ta–H resonance is observed as well as a slight deshielding effect of the aromatic protons when compared to **1** (Table 1). The ^1H NMR spectrum of **10** contains four resonances of equal intensities for the ring methyl-Cp groups.

9   10
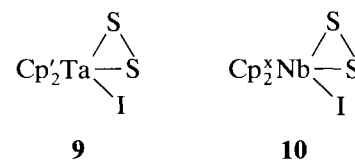
The reaction of **1** with excess CH_3I in toluene at 0°C gives a green precipitate **11** which was shown by elemental analyses and FD mass spectroscopy to have the composition $[Cp'_2 Ta(S_2 CH_3)H]I$ (**11**). Solutions of **11** in $CHCl_3$ give upon heating the brown complex **12**, analysed as $Cp'_2 Ta(S)I$ (Eq. 4). The structures of **11** and **12** can be unequivocally assigned from their IR and ^1H NMR data (Table 1). Whereas an IR absorption at 515 cm^{-1} of **11** may be interpreted as ν_{S-S} frequency, a strong absorption in the spectrum of **12** at 434 cm^{-1} may be attributed to a Ta=S bond. Other examples with Nb–S or Ta–S double bonds involve $Cp_2^x Nb(=S)SH$

[7] and $Cp'_2Ta(=S)H$ [6] in which $\nu_{M=S}$ frequencies in the same range have been observed.

Pronounced differences also exist in the ^1H NMR spectra of **11** and **12**. A complex spectrum is observed for **11** which shows eight signals for the cyclopentadienyl protons and two signals for the t-butyl groups. There is also a resonance for the Ta–H moiety at 4.33 ppm which may be a consequence of an electron withdrawing η^2-$S_2CH_3^-$ ligand, and which is absent in the spectrum of **12**. In contrast, the spectrum of **12** consists only of four signals for the aromatic and of one signal for the aliphatic protons. On the basis of these spectra we suggest that attack of the electrophile at the disulfide ligand creates a chiral centre, most likely at the central sulfur site. Nucleophilic attack of the iodide counteranion at Ta causes elimination of CH_3SH and transformation of the Ta–S single bond into a double bond.

$$Cp'_2Ta\begin{smallmatrix}S\\|\ \ \ \ \ \ \\ -S\\ \diagdown\\ H\end{smallmatrix} + CH_3I \xrightarrow{0°C} \left[Cp'_2Ta-S\begin{smallmatrix}H\\ /\\ \diagup CH_3\\ \diagdown /\\ S\end{smallmatrix} \right]^+ I^-$$

1   **11**

$$\xrightarrow[-CH_3SH]{65°C} Cp'_2Ta\begin{smallmatrix}S\\ \diagdown\\ I\end{smallmatrix} \qquad (4)$$

12

The reaction of **2** with CH_3I proceeded only at elevated temperatures and produced a complex array of products. Therefore, it may be argued on the basis of steric reasons that peralkylation of the Cp ligands renders alkylation of the disulfide ligand more difficult.

2.3. Conclusions

In principle, similar results in the reaction of **1** and **2** with S_8 have been observed although there are no mononuclear Ta intermediate products. The different multinuclear character of the products may also be a consequence of slight differences in the electronic and steric control by the Cp ligands and the metal. It is of interest that the tendency to form higher aggregates seems to be more pronounced in the Ta series. In addition, thermolysis of **7** under forced conditions gives complex **8** which as a particular feature reveals Nb–Nb bonds. The reactions of **1** and **2** with I_2 extend the examples of H/Hal exchange reactions for metallocene hydrides [16]. Electrophilic attack at the S_2^{2-} ligand in **1** and **2** gives reasonable results only in the case of the sterically less hindered Cp ligand.

3. Experimental details

All procedures were carried out under N_2 with dry solvents. Elemental analyses were performed by the

Mikroanalytisches Laboratorium, Universität Regensburg. IR spectra were obtained with a Beckman 4240 spectrophotometer and a Perkin-Elmer 580 B instrument. All molecular weights were determined by field desorption mass spectra on a Finnigan MAT 95 instrument. NMR spectra were recorded on Bruker WM 250 and 400 instruments. Complexes **1** [6] and **2** [1] were prepared by literature procedures.

3.1. Reaction of 1 with S_8

To the solution of 950 mg (1.95 mmol) of **1** in 70 ml of toluene, 187 mg (0.73 mmol) of sulfur was added and the resulting mixture was refluxed for 5 h. After evaporation of the solvent the resulting dark residue was chromatographed on SiO_2 (column 30×3 cm). With toluene pale yellow and orange bands were eluted, which were both discarded. The following bands contain brown-yellow $Cp'_3Ta_3S_{12}$ (**3**), orange $Cp'_4Ta_4S_{13}$ (**4**), and red $Cp'_6Ta_8S_{17}$ (**5**) in 7.1%, 53%, and 7.8% yield, respectively. All compounds gave microcrystalline material upon recrystallisation from CH_2Cl_2 or toluene at $-20°C$. Elemental analyses **3** Found: C, 25.89; H, 3.11. $C_{27}H_{39}Ta_3S_{12}$ (1289.8 for ^{32}S) Calc.: C, 26.38; H, 3.09%. Mol. weight (from toluene) 1290.5. **4** Found: C, 26.38; H, 3.09; S, 25.77. $C_{36}H_{52}Ta_4S_{13}$ (1623.8 for ^{32}S) Calc.: C, 26.60; H, 3.20; S, 25.65%. Mol. weight (from toluene) 1624.0. **5** Found: C, 24.43; H, 2.69. $C_{54}H_{78}Ta_8S_{17}$ (2717.7 for ^{32}S) Calc.: C, 23.85; H, 2.89%. Mol. weight (from toluene) 2720.6.

3.2. Thermolysis of $Cp_3^xNb_3S_{12}$

A solution of 150 mg (0.14 mmol) of $Cp_3^xNb_3S_{12}$ in 50 ml of n-decane was refluxed for 15 h. After vacuum distillation of the solvent the solid residue was chromatographed on SiO_2 (column 20×3 cm). A green band was eluted with toluene/pentane 3:1, containing $Cp_3^xNb_3S_7$ (**8**) in 13% yield. Recrystallisation from toluene/ether/pentane 4:1:1 at $-20°C$ gave dark green crystals. Elemental analyses **8** Found: C, 41.68; H, 5.31. $C_{33}H_{51}Nb_3S_7$ (951.0) Calc.: C, 41.68; H, 5.36%. Mol. weight (from toluene) 950.5.

3.3. Preparation of $Cp'_2Ta(S_2)I$ and $Cp_2^xNb(S_2)I$

To a solution of **1** or **2** in toluene a solution of 1 equiv. of I_2 in toluene was added dropwise. After removal of the solvent under reduced pressure the residue was chromatographed on silanised SiO_2 (column 12×3 cm). The products were eluted with toluene as brown bands in yields of 79% (**9**) and 50% (**10**). Crystals were obtained by recrystallisation in toluene, but they gave a correct analysis only in the case of **10**. Elemental analyses **9** Found: C, 34.20; H, 4.39. $C_{18}H_{26}TaS_2I$ (614.4) Calc.: C, 35.18; H, 4.27%. Mol. weight (from toluene) 614.2. **10** Found: C, 46.04; H,

6.02. $C_{22}H_{34}NbS_2I$ (582.5) Calc.: C, 45.36; H, 5.88%. Mol. weight (from toluene) 582.1.

3.4. Reactions of 1 with CH_3I

3.4.1. Preparation of $[Cp_2'Ta(\eta^2\text{-}S_2CH_3)H]I$

A mixture of 320 mg (2.25 mmol) of CH_3I, 280 mg (0.57 mmol) of 1, and 50 ml of toluene was stirred for 60 min at 0°C. After stirring at room temperature for further 3 h, a dark green suspension was obtained. After evaporation of the solvent the residue was recrystallised from $CHCl_3$/pentane to give green crystals of 11 in 86% yield.

3.4.2. Preparation of $Cp_2'Ta(=S)I$

A mixture of 600 mg (1.23 mmol) of 1, 524 mg (3.69 mmol) of CH_3I, and 40 ml of chloroform was stirred for 4 h at room temperature. At this stage analysis by ^1H NMR spectrometry showed the presence of both 11 and 12. Then the mixture was refluxed for 1.5 h and after removal of the solvent chromatographed on SiO_2. A bright brown band was eluted with toluene which contained 12 in 56% yield. From recrystallisation in toluene/pentane golden plates were isolated.

Elemental analyses 11 Found: C, 36.90; H, 4.81. $C_{19}H_{30}TaS_2I$ (630.4) Calc.: C, 36.20; H, 4.80%. Mol. weight (from $CHCl_3$) 503.4 (calc. 503.1 for $C_{19}H_{30}TaS_2$). 12 Found: C, 37.34; H, 4.22. $C_{18}H_{26}TaSI$ (582.3) Calc.: C, 37.13; H, 4.50%. Mol. weight (from toluene) 582.2.

3.5. Crystallographic data of 8

Black-green hexagonal prism (0.25 × 0.25 × 0.4 mm^3), hexagonal $C3i/1$, $P\text{-}3$ (147); cell: a 12.091(7), c 14.907(7) Å; V 1887.3 $Å^3$, $Z = 2$; empirical absorption correction: 5 reflections $6.7 < 2\Theta < 40.6°$. Trans. factor (min/max) 0.84/1.00, μ 1.25 mm^{-1}. $F(000)$ 968, d(calc) = 1.67 g/cm^{-3}; Syntex R3. Mo $K\alpha$ radiation, graphite monochromator, 2826 unique observed reflections; 2030 independent reflections ($I > 2.5\sigma(I)$). Structure solution by Patterson and Fourier methods. $R = 0.061$, $R_w = 0.053$; residual electron density (max/min) 2.3/−2.0 $e/Å^3$, shift/esd (max) 0.07, GOOF = 3.26.

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