

Chemical evidence for the existence of peralkylated niobocene in a fulvenoid form by its reaction with sulfur

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Abstract

Completely reduced $\text{Cp}_2^*\text{NbCl}_2$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) solutions (two equivalents of Na–Hg) which were previously supposed to contain two isomers **A** and **B** of decamethylniobocene react with sulfur to give products **1**–**4**. Their ^1H and ^{13}C NMR spectroscopy investigations allow for the first time a clear assignment of the structures of **A** and **B**. As **1** and **2** are identical with the previously reported $\text{Cp}_2^*\text{Nb}(\eta\text{-S}_2)\text{L}$ derivatives ($\text{L} = \text{H}$ (**1**), SH (**2**)) a bent niobocene structure follows for isomer **A**. Products **3** and **4** are in agreement with structures involving a $\eta^1:\eta^5$ -tetramethylfulvene ligand which in the case of **4** is slightly modified by sulfur insertion into the $\text{CH}_2\text{-Nb}$ bond. Thus the structure of isomer **B** may be derived from bent niobocene by a hydride migration from one CH_3 group to Nb.

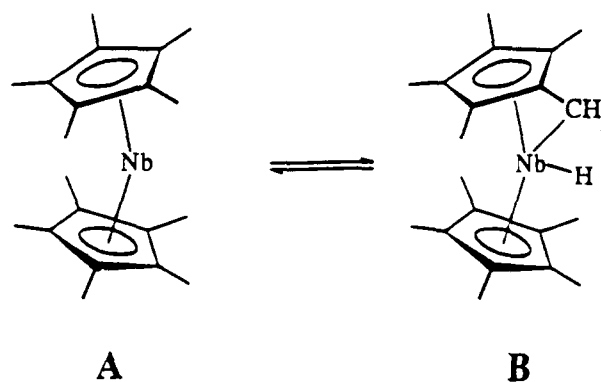
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1. Introduction

Activation of the C–H bonds of ring methyl groups in pentamethylcyclopentadienyl transition metal complexes is a field of growing interest [1]. A particular role play permethylated metallocenes in which one Cp^* ($\text{Cp}^* = \text{C}_5\text{Me}_5$) ligand has been transformed into η^4 [2] or $\eta^1:\eta^5$ [3] coordinated tetramethylfulvene ligands. The coordination mode is dependent on the metal centre. Only one example (Cp_2^*Ti) is known thus far in which a bent metallocene structure has been established in coexistence with a fulvene-like structure [4].

In a recent paper we have reported the $2e^-$ reduction of $(\text{C}_5\text{Me}_4\text{R})_2\text{NbCl}_2$ ($\text{R} = \text{Me}$ or Et) to give two paramagnetic species for which, in analogy to the Cp_2^*Ti system, two niobocene isomers **A** and **B** have been proposed [5]. As their structures were assigned only on the basis of electron paramagnetic resonance (EPR) spectra, chemical support would be desirable. In this paper we provide chemical evidence for this formulation by trapping both forms in their reaction with sulfur

as diamagnetic compounds which now allow detailed NMR spectroscopy investigations.



2. Experimental section

Experimental techniques and synthesis of $\text{Cp}_2^*\text{NbCl}_2$ have been described in Ref. [5]. The ^1H NMR spectra were taken at 400.13 MHz and the ^{13}C NMR at 100.61 MHz on a Bruker ARX 400 instrument (CDCl_3 ; tetramethylsilane; 294 K), the EPR spectra on a Bruker ESP 300 spectrometer.

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2.1. Preparation of 1–4

280 mg (0.65 mmol) of $\text{Cp}_2^* \text{NbCl}_2$ were dissolved in 50 ml of tetrahydrofuran (THF) and stirred over Na–Hg (60 mg (2.60 mmol) Na in 10 ml of Hg). After 1 h the orange–brown solution was separated from the amalgam by decantation. At this stage EPR spectra were taken to determine the ratio of isomer **A** to isomer **B**.

To the reduced solution, 133 mg (0.52 mmol) of S_8 were added and stirred for 1 h at room temperature. The brown–green mixture was then filtered and evaporated to dryness. After dissolving in toluene the solution was chromatographed on SiO_2 (activity II–III; column, 12 \times 3 cm). With toluene an orange band was eluted containing **1** and **3** in ratios corresponding to the initial ratio of **A** to **B**. The total yield is about 23%. A second red band was eluted with toluene:ether 10:1. Subsequent chromatography on SiO_2 (column, 15 \times 3 cm) gave upon elution with toluene a red band of **2** (yield, 8%) and with toluene:ether 50:1 a dark-red band containing **4** with a 7% yield (about 2 l of solvent were necessary for the separation!).

The spectroscopic and analytical data of **1** and **2** are identical with those of $\text{Cp}_2^* \text{Nb}(\text{S}_2)\text{H}$ and $\text{Cp}_2^* \text{Nb}(\text{S}_2)\text{SH}$ [5].

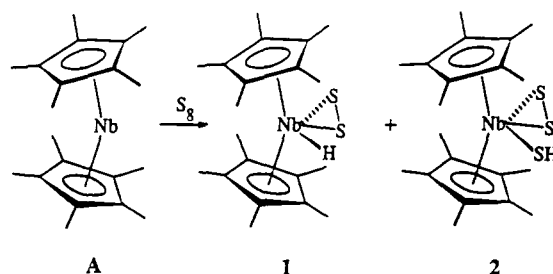
3: Anal. Found: C, 55.87; H, 7.09, $\text{C}_{20}\text{H}_{29}\text{NbS}_2$ (426.5) Calc.: C, 56.31; H, 6.85%. FD mass spectroscopy (MS) (from toluene): 426. ^1H NMR: 1.08 (s, 3), 1.81 (s, 15), 1.86 (s, 3), 1.97 (s, 3), 1.99 (s, 3), 2.62 (d, $^2J_{\text{HH}} = 2.5$ Hz, 1H), 2.99 (d, $^2J_{\text{HH}} = 2.5$ Hz, 1H) ppm. ^{13}C NMR: 10.74 (CH_3 , 1C), 11.06 (CH_3 , 1C), 11.25 (CH_3 , 5C), 11.98 (CH_3 , 1C), 12.00 (CH_3 , 1C), 65.15 (CH_2 , 1C), 109.9 (C_5R_5 , 1C), 110.9 (C_5R_5 , 1C), 111.8 (C_5R_5 , 5C), 113.3 (C_5R_5 , 1C), 116.8 (C_5R_5 , 1C), 130.2 (C_5R_5 , 1C) ppm.

4: Anal. Found: C, 52.03; H, 6.36 $\text{C}_{20}\text{H}_{29}\text{NbS}_3$ (458.6) Calc.: C, 52.38; H, 6.34%. FD MS (from toluene): 458.3 ^1H NMR: 1.46 (s, 3), 1.78 (s, 15), 1.79 (s, 3), 1.94 (s, 3), 2.10 (s, 3), 3.37 (d, $^2J_{\text{HH}} = 10.7$ Hz, 1H), 3.69 (d, $^2J_{\text{HH}} = 10.7$ Hz, 1H) ppm. ^{13}C NMR: 9.38 (CH_3 , 1C), 10.87 (CH_3 , 1C), 11.13 (CH_3 , 5C), 11.81 (CH_3 , 1C), 12.61 (CH_3 , 1C), 18.44 (CH_2 , 1C), ppm; for the ring carbons see text.

3. Results and discussion

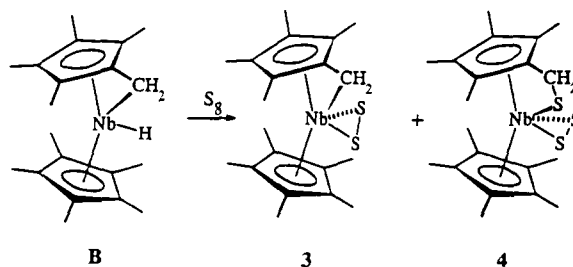
Reduction of $\text{Cp}_2^* \text{NbCl}_2$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) with two equivalents of Na–Hg gives an orange–brown solution always containing both species **A** and **B** in different ratios for different experiments. Unfortunately, we were unable to produce solutions containing only one isomer. The ratio of **A** to **B** is certainly influenced by external factors which, however, have not yet been found [5]. EPR spectra of the THF solutions were taken before the reaction with sulfur was carried out.

If the reduced solution containing preferentially isomer **A** is treated with 0.5 equivalents of S_8 , two orange compounds **1** and **2** are separated with moderate yields by column chromatography:



Analytical and mass spectroscopy data support formulae $\text{Cp}_2^* \text{NbS}_2\text{H}$ (**1**) and $\text{Cp}_2^* \text{NbS}_3\text{H}$ (**2**). The IR and ^1H NMR spectroscopy data are in good agreement with those recently published for complexes bearing a side-on disulfide along with a hydride (**1**) or a sulfhydryde ligand (**2**). Both compounds have been previously characterized by single-crystal molecular structures [6]. Typical of these compounds are one resonance in the ^1H NMR spectra for the Cp^* methyl groups (**1**, 1.82; **2**, 1.78 ppm) and one resonance each in the ^{13}C NMR spectra for the methyl and ring carbon atoms (**1**, 11.59 (CH_3), 110.6 (C_5Me_5); **2**, 11.76 (CH_3), 115.4 ppm (C_5Me_5)), thus confirming the π character of both Cp^* ligands. The formation of **1** may be explained by nucleophilic attack of isomer **A** at sulfur and rapid fragmentation of the S_8 ring [7], finally resulting in the oxidative addition of an S_2 fragment to Nb. No larger metal-lathiocycles [8] were formed. As niobocene(IV) sulfides tend to be rather unstable [6,9], hydrogen transfer probably from the solvent gives more stable Nb(V) complexes. Complex **2** may be an insertion product of sulfur into the Nb–H bond of **1** [10].

If the reduced solution contains predominantly isomer **B**, then a complex mixture is obtained in its reaction with sulfur. It still contains **1** and **2** but also the new diamagnetic products **3** and **4**:



Whereas **1** and **3** behave very similarly **2** and **4** were separated by column chromatography with considerable

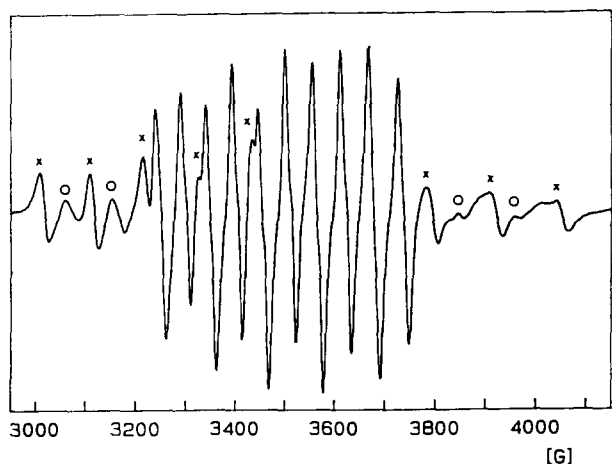


Fig. 1. EPR spectrum of the niobocene isomer **B** leading to ratios of **1** to **3** as shown in Figs. 2 and 3. (x, $\text{Cp}_2^*\text{NbCl}_2$; o, isomer **A**) Coupling constants are given in [5].

loss of material. Elemental analyses of **3** and **4** are in the same range as those of **1** and **2**, but their FD mass spectra exhibit molecular peaks which are two units lower than those of **1** and **2**. Comparable with **1** and **2**, **3** and **4** also show $\nu_{\text{S-S}}$ absorptions in the IR spectra at 528 and 531 cm^{-1} respectively.

^1H NMR and ^{13}C NMR spectra of **3** and **4** show each compound to contain a Cp^* ligand of a fulveneoid character together with an intact Cp^* ligand. The following description is based on a typical experiment for which the EPR spectrum of the reduced solution (Fig. 1) and the corresponding ^1H NMR spectrum of **3** (Fig. 2) are shown. The latter still contains about 35% **1** as determined by integration of the signals of the intact Cp^* ligands at 1.82 ppm (**1**) and 1.81 ppm (**3**). Four singlets at 1.08, 1.86, 1.97 and 1.99 ppm may be assigned to diastereotopic ring methyl groups. One of the CH_3 resonances is considerably shielded, probably as a consequence of a skew arrangement of the ligand,

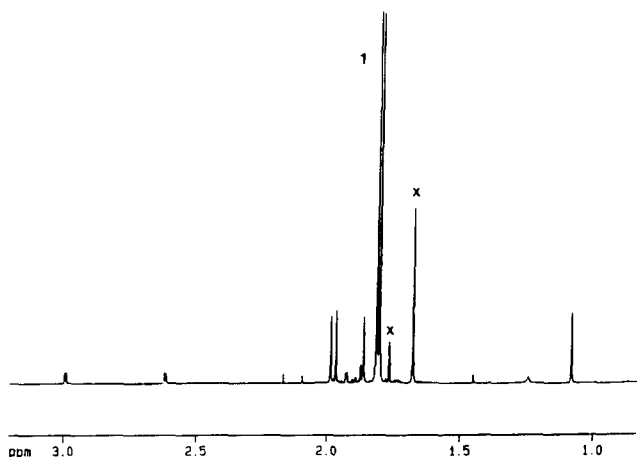


Fig. 2. ^1H NMR (400.13 MHz; CDCl_3) spectrum of **3** still containing about 35% of **1**; x, impurities.

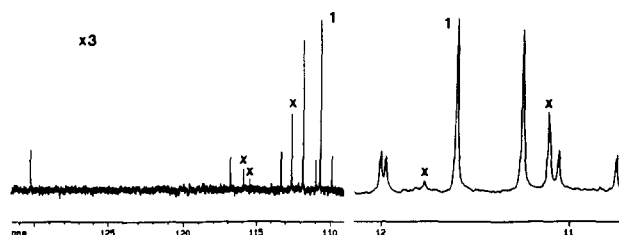


Fig. 3. ^{13}C NMR (100.61 MHz; CDCl_3) spectrum of **3** together with about 35% of **1** where the CH_2 resonance at 65.15 ppm is omitted: x, impurities.

bringing one CH_3 group in proximity to the metal. The AX system at 2.62 and 2.99 ppm indicates a diastereotopic CH_2 group. In this context it may be noted that in the case of an η^4 fulvene ligand the spectrum should be of less complexity.

The ^{13}C NMR spectrum of **3** (Fig. 3) may clearly be interpreted after subtracting the resonances for **1** and after H–C correlation. The intensive resonances at 11.25 and 11.8 ppm belong to equivalent carbon atoms of the obviously intact and still aromatic Cp^* ligand. Aliphatic resonances are those at 10.74, 11.06, 11.98 and 12.00 ppm, while the ring carbon atoms may be assigned to resonances at 109.9, 110.9, 113.3, 116.8 and 130.2 ppm. Finally, a resonance at 65.15 ppm correlates with both protons of the ^1H AX system. This value is in between those found in polar (fulvene) $\text{Cr}(\text{CO})_3$ complexes [11] and that found in the only structurally characterized example for an $\eta^1:\eta^5$ tetramethylfulvene complex [12].

Similar NMR patterns are observed for **4** which still contains some **2**. The ^1H NMR spectrum exhibits four signals of equal intensities between 1.46 and 2.10 ppm and a dominating signal at 1.78 ppm which is superposed by the singlet characteristic of **2**. The CH_2 group gives rise to an AX system at 3.37 and 3.69 ppm. The ^{13}C NMR spectrum exhibits four resonances between 9.38 and 12.24 ppm besides an intense signal at 11.13 ppm. Another intense signal at 115.9 ppm may be assigned to the intact Cp^* ligand whereas, from six resonances between 94.97 and 125.2 ppm, one has to be eliminated as arising from a byproduct. The only significant difference between the spectra of **3** and **4** concerns the resonance at 18.44 ppm. It may be ascribed by means of a DEPT experiment to a CH_2 group and the value of δ is in agreement with an $-\text{SCH}_2-$ group.

In conclusion, this work provides for the first time chemical evidence of two different peralkylated niobocene isomers. In spite of the difficulties in a selective $2e^-$ reduction of $\text{Cp}_2^*\text{NbCl}_2$ it follows unequivocally from the NMR spectra of **3** and **4** that, besides the “classical” bent metallocene structure **A**, another form **B** exists in which one highly symmetrical Cp^* ligand is transformed into an $\eta^1:\eta^5$ fulvene ligand. As one possible pathway which leads to isomer **B**

an intramolecular hydride migration from a ring CH_3 to Nb is very likely. The following reaction of **B** with S_8 may proceed with loss of H_2S and fragmentation of sulfur down to S_2 units. A side reaction involves insertion of sulfur into the Nb–*exo*-C bond of the fulvene ligand, thus leading to small amounts of **4**.

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