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Synthesis and molecular structure of $[Fe_3(\mu_2\text{-}H)(\mu_3\text{-}Te)(CO)_9][Cp_2^{\#}Nb(CO)_2]$ ($Cp^{\#} = C_5Me_5$, C_5Me_4Et)

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Abstract

Reaction of $[Cp_2^{\#}Nb(Te_2H)]$ ($1^{\#}$) ($Cp^{\#} = Cp^*$ (C_5Me_5) or Cp^x (C_5Me_4Et)) with $[Fe_2(CO)_9]$ in boiling toluene gives $[Fe_3(\mu_2\text{-}H)(\mu_3\text{-}Te)(CO)_9][Cp_2^{\#}Nb(CO)_2]$ (**2**) ($Cp^{\#} = Cp^*$) and (**3**) ($Cp^{\#} = Cp^x$) in 33 and 39% yield, respectively. The crystal structure of **3** contains the already known $[Fe_3HTe(CO)_9]^-$ anion and a $[Cp_2^xNb(CO)_2]^+$ cation in a 1:1 ratio. The latter belongs to the class of bent metallocenes in which the $Nb(CO)_2$ plain bisects the cation. For the first time, localization of the hydrogen in the solid state as a μ_2-bridge in the cluster anion has been established. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Iron; Telluride cluster; Niobocene carbonyl

1. Introduction

There is current interest in the synthesis of metal telluride clusters and the investigation of their properties [1]. Recent developments include the stepwise condensation of molecular telluride complexes to solid state compounds [2,3]. In this regard, we have reported on the novel tellurium transfer reagent $[Cp_2^{\#}Nb(Te_2H)]$ ($1^{\#}$) ($Cp^{\#} = Cp^*$ (C_5Me_5) or Cp^x (C_5Me_4Et)) [4], which gives in its reaction with $[Co_2(CO)_8]$ compounds with different cobalt telluride cluster anions and niobocene dicarbonyl cations [5]. Thermally labile intermediate products, assembling all building blocks together in a neutral complex, have also been characterized. In order to extend the use of $1^{\#}$ on the synthesis of other metal telluride clusters, we decided to study the formation of iron tellurides via the reaction of $1^{\#}$ with $[Fe_2(CO)_9]$.

2. Results

The reaction of $[Fe_2(CO)_9]$ with $1^{\#}$ has been carried out with a twofold excess of iron carbonyl under different temperature conditions and in different solvents. In THF at room temperature (r.t.), a violet product forms always, being contaminated with a varying amount of a red compound. A separation into distinct compounds was not possible because of the sensitivity of the solutions. Thus, no analytical data and no clear spectroscopic information are available. The IR spectra absorptions between 2036 and 1905 cm^{-1} may be attributed to terminal CO ligands. Provided that the system $1^{\#}/[Fe_2(CO)_9]$ behaves analogously to that of $1^{\#}/[Co_2(CO)_8]$ [5], one may assume that the formation of labile neutral cluster compounds in which $Fe_x(CO)_y$, Te, and $Cp_2^{\#}Nb$ building blocks are connected together. As a third product $[Fe_3(CO)_9Te_2]$ forms in 15% yield, which has been identified by comparison of IR and ^{125}Te-NMR spectroscopic data with those of the already well known cluster [6].

In boiling toluene, the red–brown compounds **2** and **3**, respectively, were formed. They have been identified in the case of **3** by means of X-ray crystallography as 1:1 salts consisting of the $[Fe_3HTe(CO)_9]^-$ anion and a $[Cp_2^xNb(CO)_2]^+$ cation. In agreement with this finding, FD mass spectra of **2** and **3** show the corresponding peaks for the niobocene dicarbonyl cations, whereas the negative species has been found in a FAB experiment with a negative source. However, C, H analyses are always too low, probably because of the initial Te precipitation during recrystallization.

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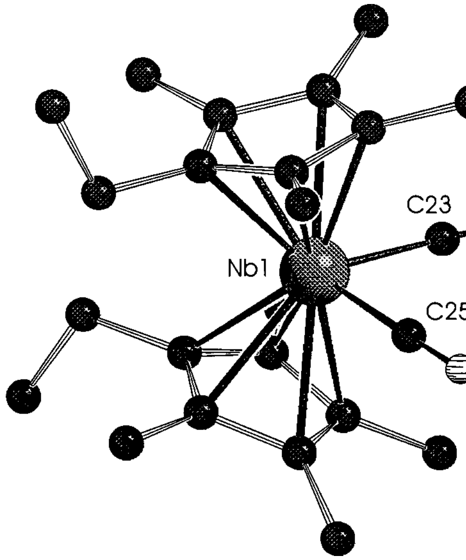

Fig. 1. Molecular structure of the $[(C_5Me_4Et)_2Nb(CO)_2]^+$ cation in **3**.

Table 1
Selected bond lengths (Å) and angles (°) for $[(C_5Me_4Et)_2Nb(CO)_2][HFe_3Te(CO)_9]$ (**3**)

Bond lengths	
Nb(1)–C(23)	2.038(6)
Nb(1)–C(25)	2.066(5)
Nb(1)–$C(1–5)_{mean}$	2.418(1)
Nb(1)–$C(12–16)_{mean}$	2.413(1)
Te(1)–Fe(1)	2.4931(7)
Te(1)–Fe(2)	2.4852(7)
Te(1)–Fe(3)	2.5029(7)
Fe(1)–Fe(2)	2.6415(9)
Fe(1)–Fe(3)	2.7026(10)
Fe(2)–Fe(3)	2.6355(9)
Fe(1)–H(45)	1.63(5)
Fe(3)–H(45)	1.43(5)
Fe(1)–C(27)	1.750(6)
Fe(1)–C(29)	1.746(7)
Fe(1)–C(31)	1.783(6)
Fe(2)–C(33)	1.761(6)
Fe(2)–C(35)	1.754(7)
Fe(2)–C(37)	1.741(5)
Fe(3)–C(39)	1.779(5)
Fe(3)–C(41)	1.755(6)
Fe(3)–C(43)	1.760(8)
Bond angles	
C(23)–Nb(1)–C(25)	85.3(2)
Fe(2)–Te(1)–Fe(1)	64.09(2)
Fe(2)–Te(1)–Fe(3)	63.79(2)
Fe(1)–Te(1)–Fe(3)	65.50(2)
Te(1)–Fe(1)–Fe(2)	57.81(2)
Te(1)–Fe(1)–Fe(3)	57.43(2)
Fe(2)–Fe(1)–Fe(3)	59.08(3)
Te(1)–Fe(2)–Fe(3)	58.43(2)
Te(1)–Fe(2)–Fe(1)	58.10(2)
Fe(3)–Fe(2)–Fe(1)	61.61(3)
Te(1)–Fe(3)–Fe(2)	57.78(2)
Te(1)–Fe(3)–Fe(1)	57.08(2)
Fe(2)–Fe(3)–Fe(1)	59.30(3)

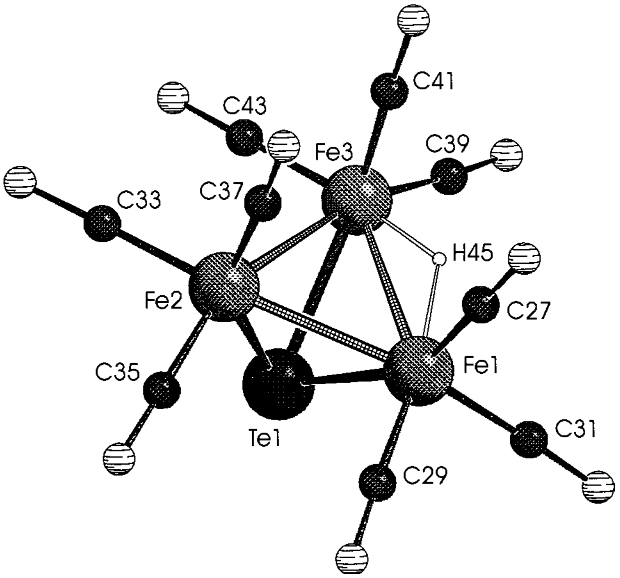

Fig. 2. Molecular structure of the $[Fe_3HTe(CO)_9]^-$ anion in **3**.

IR spectra (KBr) of **2** and **3** show five absorptions typical of terminal CO ligands between 2038 and 1902 cm^{-1}. The observed pattern does not exactly match that observed for $Cs[Fe_3HTe(CO)_9]$ [7], the additional band at 2018 cm^{-1} may be ascribed to one of the two expected ν(CO) vibrations of the $[Cp^{\#}_2Nb(CO)_2]^+$ cation, whereas the second band seems to be superposed. The ^1H-NMR spectra of **2** and **3** contain signal sets typical for the $Cp^{\#}$ ligands of the peralkylated niobocene part, along with a highfield resonance at −21.96 ppm, common to both compounds, which has been previously attributed to a bridging hydrido ligand rather than to a tellurium bonded proton [7,8].

The crystal structure of **3** consists of ion pairs of separate $[Cp^{x}_2Nb(CO)_2]^+$ and $[Fe_3HTe(CO)_9]^-$ ions without close contacts. The skeleton of the niobocene derived cation (Fig. 1) is related to that in $[Cp^{x}_2NbCl_2]$ [9] and $[Cp^{x}_2NbF_2]PF_6$ [9]. The mean distance Nb–CO is 2.0523 (6) Å (Table 1), the angle OC–Nb–CO is 85.3 (2)°. Angles in the same range have been found in the isoelectronic compounds $[Cp^{*}_2M(CO)_2]$ (M = Ti, Zr, Hf) [10] and in the Group 5 metal analogue $[C_5H_5V(CO)_2][Co(CO)_4]$ [11]. Niobocene dicarbonyl complexes are still rare. $[(C_5H_5)_2Nb(CO)_2]PF_6$ has been characterized spectroscopically only [12].

The structure of the cluster anion (Fig. 2) is similar to that in $Cs[Fe_3HTe(CO)_9]$ [7] and closely related to the $[Fe_3Te(CO)_9]^{2-}$ cluster dianion [8]. A triangle of iron atoms is capped by the tellurium atom, Fe1–Fe3 being 0.06 Å longer than the two other Fe–Fe bonds. As already predicted in a previous study [7], this longer Fe–Fe bond is bridged by a hydrogen atom. This μ_2-H bridge is of slightly asymmetric nature.

In conclusion the reaction of $[Cp^{\#}_2NbTe_2H]$ ($\mathbf{1}^{\#}$) with $[Fe_2(CO)_9]$ in boiling toluene produces the salts **2** and **3**, respectively, which may be regarded as the final products of a cross-transfer of Te and CO ligands from one metal center to the other. Compounds incorporating all building blocks in a covalent niobocene–irontelluride cluster are obviously too labile. It may further be speculated that the source of hydrogen for the μ_2-H bridge in the $[Fe_3HTe(CO)_9]^-$ anion is the η^2-Te_2H ligand in **1**$^{\#}$.

3. Experimental

Experimental and spectroscopic techniques are reported in Ref. [9], the preparation of $Cp_2^{\#}NbTe_2H$ (**1**$^{\#}$) is given in Ref. [4].

3.1. Synthesis of $[Fe_3(\mu_2\text{-}H)(\mu_3\text{-}Te)(CO)_9][Cp_2^{\#}Nb(CO)_2]$

The solution of 0.60 mmol of $[Cp_2^{\#}NbTe_2H]$ (**1**$^{\#}$) and 410 mg (1.10 mmol) of $[Fe_2(CO)_9]$ in 100 ml of toluene was refluxed for 15 h. After cooling to r.t. and evaporation of the solvent, the residue was dissolved in 12 ml of toluene–acetone 1:1. Chromatography on SiO_2 (column 15 cm, ∅ 3 cm) gave upon elution with toluene, a trace amount of a short red band (unidentified) and then with toluene–acetone 1:1, a red–brown band containing 190 mg (0.20 mmol, 33%) of $[Fe_3H(CO)_9Te][Cp_2^*Nb(CO)_2]$ (**2**) and 230 mg (0.23 mmol, 39%) of $[Fe_3H(CO)_9Te][Cp_2^xNb(CO)_2]$ (**3**). Complexes **2** and **3** were recrystallized from CH_2Cl_2–Et_2O 3:1.

Complex **2**: Anal. Calc.: C, 38.48; H, 3.23. Found: $C_{31}H_{31}Fe_3NbO_{11}Te$ (967.6), C, 37.16; H, 3.20%. ^{1}H-NMR (CD_2Cl_2): -21.96 (s, 1), 1.96 (s, 30) ppm. IR (KBr): ν_{CO} 2038m, 2018s, 2000vs, 1977vs, 1962sh, 1935s, 1922m, 1902m cm^{-1}. Complex **3**: Anal. Calc.: C, 39.81; H, 3.54. Found: $C_{33}H_{35}Fe_3NbO_{11}Te$ (995.7), C, 37.08; H, 3.74%. ^{1}H-NMR (CD_2Cl_2): -21.96 (s, 1), 1.11 (t, 6; $^3J_{HH} = 7.1$ Hz), 1.94 (s, 12), 1.95 (s, 12), 2.21 (q, 4; $^3J_{HH} = 7.1$ Hz) ppm. IR (KBr): ν_{CO} 2038m, 2018s, 2000vs, 1980vs, 1962vs cm^{-1}. FAB-MS (NI-LSIMS, NBA–acetone) 548.9 (Anal. Calc. 548.7 for $C_9HO_9Fe_3Te$).

3.2. Crystallographic data for **3**

Dark needles ($0.24 \times 0.14 \times 0.12$ mm^3), monoclinic $P2_1/n$; cell: a, 9.1262(5), b, 21.5887(10), c, 19.9069(12) Å; β, 100.680(6)°; V, 3854.2 Å^3, $Z = 4$; absorption correction: numerical from crystal shape (X-RED, Stoe, 1996). Transmission factor (min/max) 0.6829/0.7784, μ, 2.192 mm^{-1}. $F(000)$ 1968, $d_{calc} = 1.716$ g cm^{-3}; Stoe-IPDS. Mo–K_α-radiation, graphite monochromator, 21 377 collected reflections; 6833 unique reflections $[I > 2.0\sigma(I)]$. Structure solution by means of direct methods and Fourier synthesis. $R = 0.0687$, $R_w = 0.0504$; residual electron density (max/min) $0.644/-0.249$ e Å^{-3}, goodness-of-fit = 0.698. The μ_2-H atom H(45) was found in the difference fourier synthesis as the first peak, which was not a residual electron density of one of the heavy atoms.

4. Supplementary material

Crystallographic data of **3** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-136899. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccsc.cam.ac.uk).

Acknowledgements

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