

Rotational versus Migration Isomerism in $[(t\text{BuC}_5\text{H}_4)_2\text{NbH}(\mu_3\text{-Te})(\mu_4\text{-Te})\text{Fe}_2(\text{CO})_6] \cdot \text{Cr}(\text{CO})_5$, a Sterically Crowded Polymetallic Telluride Complex

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Summary: The reaction of $[\text{Cp}'_2\text{Nb}(\text{Te}_2)\text{H}]$ (**1**) ($\text{Cp}' = t\text{BuC}_5\text{H}_4$) with $[\text{Fe}_2(\text{CO})_9]$ gives $[\{\text{Cp}'_2\text{NbH}(\text{Te})_2\}\text{Fe}_2(\text{CO})_6]$ (**2**). Compound **2** reacts with $[\text{Cr}(\text{CO})_5\text{THF}]$ to give $[\{\text{Cp}'_2\text{NbH}(\text{Te})_2\text{Fe}_2(\text{CO})_6\} \cdot \text{Cr}(\text{CO})_5]$ (**3**) in nearly quantitative yield. The crystal structure of **3** reveals that the $\text{Fe}_2(\text{CO})_6$ unit in this complex (and consequently in **2**) is inserted in a perpendicular manner into the original NbTe_2 moiety of **1**, while the incoming $\text{Cr}(\text{CO})_5$ fragment is attached at the central Te atom and in vicinity (*vic*) to the Nb-H moiety. ^1H NMR investigations of solutions of **3** at -80°C show that only the sterically crowded *vic-3* has been separated by recrystallization. At -60°C a rapid exchange is observed for the ring protons, which may be explained by rotation of the Cp' rings around the $\text{Cp}'\text{-Nb}$ axes. Above 0°C an additional set of C_5H_4 , $t\text{Bu}$, and NbH resonances appears, which may be assigned to migration of the $\text{Cr}(\text{CO})_5$ fragment from the central to the lateral Te atom. The resulting *opp-3* is in a 55:45 equilibrium with *vic-3* at 20°C .

Introduction

Transition metal telluride clusters are of great interest because of their wide structural diversity and their considerable reactivity potential.¹ Different strategies for the synthesis of such compounds have been developed, and special attention has been devoted to compounds bearing CO groups as co-ligands.² We have recently realized the synthesis of substituted niobocene ditelluride hydrides of general formula $[\text{Cp}_2\text{NbTe}_2\text{H}]$, in which hydrogen is bonded either to Te ($\text{Cp} = \text{C}_5\text{Me}_5$)^{3a} or to Nb ($\text{Cp} = \text{Cp}'$).^{3b,c} These compounds are convenient tellurium transfer reagents toward reactive transition metal fragments.^{3b,c} In particular the cross transfer of Te^{2-} and CO ligands from one metal center to another is of importance in the formation of metal telluride clusters.^{3c,4} In this paper we describe the reaction of $[(t\text{BuC}_5\text{H}_4)_2\text{Nb}(\text{Te}_2)\text{H}]$ (**1**)^{3b,c} with $[\text{Fe}_2(\text{CO})_9]$ and the subsequent reaction of the product obtained with $[\text{Cr}(\text{CO})_5(\text{THF})]$. The resulting sterically crowded di- and

Table 1. Crystallographic Data for the Complex $3 \cdot \text{C}_7\text{H}_8$

formula	$\text{C}_{29}\text{H}_{27}\text{CrFe}_2\text{NbO}_{11}\text{Te}_2 \cdot \text{C}_7\text{H}_8$
fw	1155.46
space group	<i>P</i> 1
cryst syst	triclinic
<i>a</i> /Å	11.940(1)
<i>b</i> /Å	12.170(1)
<i>c</i> /Å	16.283(1)
α /deg	81.2(0)
β /deg	72.6(0)
γ /deg	62.6(0)
<i>V</i> /Å ³	2005.2(4)
<i>Z</i>	2
<i>TK</i>	173(2)
<i>D</i> _{calcd} /g cm ⁻³	1.912
λ /Å	0.71073
μ /mm ⁻¹	2.733
abs corr	numerical
transmn max/min	0.8872/0.7563
$\theta_{\text{min}}, \theta_{\text{max}}$ /deg	1.88, 25.8
no. of reflns measd (total)	17 821
no. of reflns measd (unique)	7172 (<i>R</i> _{int} = 0.031)
no. of variables	478
<i>R</i> 1, <i>wR</i> 2 (all data)	0.040, 0.058
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2 σ (<i>I</i>))	0.0258, 0.0559
GOF on <i>F</i> ²	0.894
residual electron/e Å ⁻³	0.800 to -0.395

trimetallic telluride complexes have been subjected to spectroscopic and structural investigations.

Experimental Section

All procedures were carried out under nitrogen using Schlenk techniques and dry solvents. Elemental analyses were performed by the Mikroanalytisches Laboratorium, Universität Regensburg. IR spectra were obtained with a Mattson Genesis Series FTIR instrument; field desorption mass spectra were obtained with a Finnigan MAT 95 instrument from $\text{CH}_2\text{-Cl}_2$ solutions. NMR spectra were recorded on a Bruker ARX 400 instrument. $[\text{Cp}'_2\text{Nb}(\text{Te})_2\text{H}]$ (**1**) was prepared from $[\text{Cp}'_2\text{-NbH}_3]$ and elemental tellurium.^{3b,c}

Crystal Structure Determination of $3 \cdot \text{C}_7\text{H}_8$. A red-brown needle of dimensions $0.10 \times 0.09 \times 0.06$ mm was used for data collection on a Stoe-IPDS diffractometer (Mo $K\alpha$ radiation, graphite monochromator). Crystallographic details are given in Table 1. The structure was solved by direct methods and refined by full-matrix least-squares (SHELXL97 program) with all reflections. All nonhydrogen atoms were refined with anisotropic displacement parameters, the H atoms were calculated geometrically, and a riding model was used during the refinement process.

Synthesis of $[\{\text{Cp}'_2\text{Nb}(\text{Te})_2\text{H}\}\text{Fe}_2(\text{CO})_6]$ (2**).** A mixture of $[\text{Cp}'_2\text{Nb}(\text{Te})_2\text{H}]$ (**1**) (330 mg, 0.56 mmol), $[\text{Fe}_2(\text{CO})_9]$ (410 mg, 1.13 mmol), and toluene (140 mL) was stirred for 20 h at 110°C . During this time the color changed from red-orange to dark brown and a metallic mirror was deposited on the wall of the flask. After the solvent was removed under reduced pressure, the copper-like colored residue was suspended in 2:1 toluene/

(1) (a) Kolis, J. W. *Coord. Chem. Rev.* **1990**, *105*, 195. (b) Roof, L. C.; Kolis, J. W. *Chem. Rev.* **1993**, *93*, 1037.

(2) Henkel, G.; Weissgräber, S. In *Metal Clusters in Chemistry*; Braunstein, P., Oro, L. A., Raithby, P. R., Eds.; Wiley-VCH: New York, 1999; Vol. 1, p 163.

(3) (a) Blacque, O.; Brunner, H.; Kubicki, M. M.; Nuber, B.; Stubenhofer, B.; Wachter, J.; Wrackmeyer, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 351. (b) Wanninger, R. Ph.D. Thesis, Universität Regensburg, 2000. (c) Brunner, H.; Catey, H.; Evrard, D.; Kubicki, M. M.; Vigier, E.; Wachter, J.; Wanninger, R.; Zabel, M. *Eur. J. Inorg. Chem.*, in press.

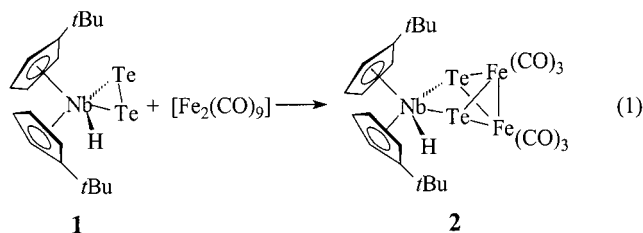
(4) (a) Brunner, H.; Lucas, D.; Monzon, T.; Mugnier, Y.; Nuber, B.; Stubenhofer, B.; Stückl, A. C.; Wachter, J.; Wanninger, R.; Zabel, M. *Chem. Eur. J.* **2000**, *6*, 493. (b) Brunner, H.; Wachter, J.; Wanninger, R.; Zabel, M. *Eur. J. Inorg. Chem.* **2001**, 1151. (c) Brunner, H.; Stückl, A. C.; Wachter, J.; Wanninger, R.; Zabel, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 2463.

acetone (15 mL) and transferred to the top of a column with SiO₂ (15 cm, Ø 3 cm). A broad dark brown band was eluted with 2:1 toluene/acetone. After removal of the solvent, the residue was suspended in toluene (10 mL) and filtered. Whereas the filtrate was discarded, the residue was dissolved in acetone (70 mL). Dark brown **2** (230 mg, 47%) was obtained after evaporation of the solvent. Complex **2** was recrystallized from toluene at -24 °C to give fine needles. IR (KBr; νCO): 2035(s), 1985(s), 1935(s), 1915(s,sh) cm⁻¹. ¹H NMR (CD₂Cl₂): δ 6.25 (2H), 5.40, (2H), 5.16 (2H), 5.02 (m, 2H, C₅H₄), 1.27 (s, 18H, *t*Bu), -0.96 (s, 1H, NbH). Anal. Calcd for C₂₄H₂₇Fe₂NbO₆-Te₂ (871.27): C 33.08, H 3.12. Found: C 32.51, H 3.12. FDMS (CH₂Cl₂): 870.0 (M⁺).

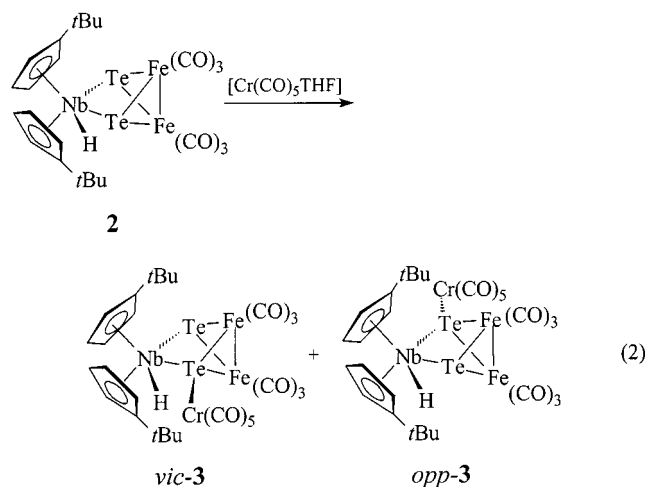
Synthesis of [Cp'₂Nb(Te)₂HFe₂(CO)₆]·Cr(CO)₅ (3**).** The combined solutions of [Cr(CO)₅(THF)] (from [Cr(CO)₆] (140 mg, 0.64 mmol) in THF (100 mL)) and **2** (270 mg, 0.31 mmol) in THF (20 mL) were stirred in the dark for 3 h at room temperature. The solvent was removed under reduced pressure. The residue was dissolved in 1:3 acetone/toluene (10 mL) and quickly filtered over SiO₂. **3** was obtained in nearly quantitative yield after evaporation of the solvent. Recrystallization from 1:5 acetone/toluene at -24 °C gave red-brown prisms of *vic*-**3**. The mother liquor was kept cold, and after evaporation of the solvent the residue consisted predominantly of *opp*-**3**. IR (KBr; νCO): 2058(s), 2034(s), 1996(s), 1953(s), 1908(s) cm⁻¹. ¹H NMR of *vic*-**3** (CD₂Cl₂, -80 °C): δ 6.84 (1H), 6.57 (1H), 6.36 (1H), 5.95 (1H), 5.80 (1H), 4.58 (1H), 4.38 (m, 1H, C₅H₄), 1.17 (9H), 1.13 (s, 9H, *t*Bu), -0.99 (s, 1H, NbH). ¹H NMR of *opp*-**3** (CD₂Cl₂, -80 °C): δ 6.41 (2H), 6.15 (2H), 5.38 (2H), 4.40 (m, 2H, C₅H₄), 2.36 (s, 18H, *t*Bu), -0.28 (s, 1H, NbH). Anal. Calcd for C₂₉H₂₇CrFe₂NbO₁₁Te₂·C₇H₈ (1155.46): C 37.42, H 3.05. Found: C 37.05, H 3.04. FDMS (CH₂Cl₂): 1062.9 (M⁺, 40), 871.0 ([M - Cr(CO)₅]⁺, 100).

Results and Discussion

The reaction of [Cp'₂Nb(Te)₂H] (**1**) with 2 equiv of [Fe₂(CO)₉] in boiling toluene gave the dark brown bimetallic complex [Cp'₂Nb(Te)₂H]Fe₂(CO)₆ (**2**) in 47% yield (eq 1). Complex **2** was characterized by FDMS, IR, and ¹H NMR spectroscopy, while a single-crystal X-ray diffraction analysis was handicapped by insufficient crystal quality. However, the heavy atom core of the molecule was found to correspond to that of **3**, which is the Cr(CO)₅ adduct of **2** (see below). Accordingly, **2** may be considered as an insertion product of the Fe₂(CO)₆ unit of [Fe₂(CO)₉] into the Te-Te bond of **1**. It may be noted that the reaction of [(C₅Me₅)₂Nb(Te₂H)] with [Fe₂(CO)₉] under analogous conditions produces the cluster-salt [(C₅Me₅)₂Nb(CO)₂][Fe₃(μ₂-H)(μ₃-Te)(CO)₉] as the only stable product.⁵ A labile intermediate in the latter reaction may have a structure analogous to **2**. The different behavior is ascribed to the steric influence of the peralkylated Cp ring rather than to electronic effects.^{4c}



The IR spectrum of **2** exhibits three strong absorptions around 2000 cm⁻¹ characteristic of CO ligands. The ¹H NMR spectrum at 21 °C contains four multiplets for the C₅H₄ protons, a singlet at δ 1.27 for the *t*Bu group, and a relatively broad resonance at δ -0.96. The latter signal is assigned to the hydride fixed at Nb, being deshielded with respect to that in the precursor complex **1**. The ²J_{Te-H} coupling, which is 86.7 Hz in **1**, has disappeared. At -80 °C the C₅H₄ resonances are considerably broadened, indicating that a dynamic process may be blocked at still lower temperatures (see below).



The reaction of **2** with 1 equiv of [Cr(CO)₅(THF)] at room temperature gave in nearly quantitative yield the Cr(CO)₅ monoadduct **3** (eq 2). According to the coplanar arrangement of the H and Te atoms in the plane bisecting the niobocene unit, one may anticipate the incoming Cr(CO)₅ fragment in vicinity (*vic*) or opposition (*opp*) to the Nb-H moiety. Recrystallization of the product from toluene/acetone at -24 °C gave red-brown needles. Low-temperature ¹H NMR studies (see below) reveal this material to consist of only one stereoisomer, to which *vic*-**3** configuration is assigned by means of single-crystal diffraction analysis. The composition is confirmed by FD mass spectroscopy and elemental analysis. The IR spectrum (KBr) of *vic*-**3** exhibits five strong CO absorptions between 2058 and 1908 cm⁻¹ as the sum of the absorption patterns of **2** and those of the attached Cr(CO)₅ fragment.

According to the crystal structure analysis, the structure of *vic*-**3** reveals a bent niobocene unit with the *t*Bu groups in lateral positions (Figure 1). The torsional angle C(6)-Cp(1)_{center}/C(15)-Cp(2)_{center} is 140°. Both Te atoms lie in the plane that bisects the niobocene unit, and they connect the Nb center with the Fe centers of the Fe₂(CO)₆ moiety, which is perpendicularly oriented to the plane defined by the Nb and Te atoms. Approximately in the same plane and coordinated to Te(1) lies the Cr(CO)₅ group. Although the H atom fixed at the Nb atom could not be localized, its position may be deduced from the observation that Te(1) lies -0.95 Å outside the plane defined by the centers of both Cp' rings and Nb, compared to +2.12 Å for Te(2). The distances of Fe(1) and Fe(2) to this plane are +0.95 and +0.89 Å, respectively. This means that the hydrido ligand is located in vicinity to Te(1) and Cr(1) and also

(5) Brunner, H.; Wachter, J.; Wanninger, R.; Zabel, M. *J. Organomet. Chem.* **2000**, *603*, 135.

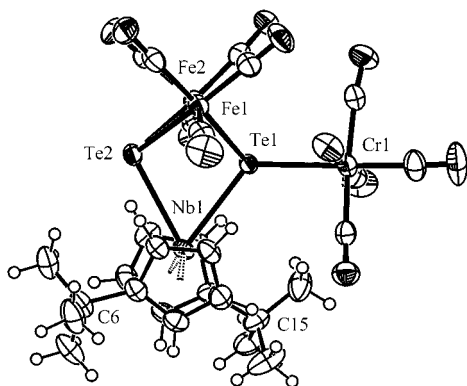


Figure 1. Molecular structure of *vic-3* viewed down along the axis of the centers of the Cp' rings. ORTEP drawing (40% probability).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Complex 3-C₇H₈^a

Te(1)–Nb(1)	2.928(1)
Te(1)–Fe(1)	2.563(1)
Te(1)–Fe(2)	2.554(1)
Te(1)–Cr(1)	2.706(1)
Te(2)–Nb(1)	2.947(1)
Te(2)–Fe(1)	2.571(1)
Te(2)–Fe(2)	2.577(1)
Fe(1)–Fe(2)	2.624(1)
Te(1)···Te(2)	3.158(1)
Nb(1)–Te(1)–Fe(1)	100.8(1)
Nb(1)–Te(1)–Fe(2)	100.1(1)
Nb(1)–Te(1)–Cr(1)	125.9(1)
Fe(1)–Te(1)–Fe(2)	61.7(1)
Fe(1)–Te(1)–Cr(1)	118.9(1)
Fe(2)–Te(1)–Cr(1)	129.7(1)
Nb(1)–Te(2)–Fe(1)	100.1(1)
Nb(1)–Te(2)–Fe(2)	99.3(1)
Fe(1)–Te(2)–Fe(2)	61.3(1)
Te(1)–Nb(1)–Te(2)	65.0(1)
Te(1)–Fe(1)–Te(2)	75.9(1)
Te(1)–Fe(1)–Fe(2)	59.0(1)
Te(2)–Fe(1)–Fe(2)	59.5(1)
Cp(1)–Nb(1)–Cp(2)	135.9(1)

^a Cp(1) represents the centroid of the C(1)–C(5) ring; Cp(2) represents the centroid of the C(10)–C(14) ring.

in the plane defined by these atoms and Nb and Te(2). The presence of a metal-bonded hydrogen also follows from the ¹H NMR spectra discussed below.

Alternatively, the molecular structure of *vic-3* may be described as the formal insertion product of a two-electron Cp'₂NbH fragment into the Te–Te bond of [Fe₂(CO)₆(μ-Te₂)].⁶ Related clusters are [{Fe(CO)₃PPh₃}(μ₃-Te)₂Fe₂(CO)₆]⁷ and [{Fe(CO)₃I}(μ₃-Te)₂Fe₂(CO)₆][–].⁸ The bond parameters of the Fe₂Te₂ core of *vic-3* (Table 2) are similar to those in other compounds with the same structural unit.⁹ This concerns Fe–Fe, Fe–Te, and Te–Te distances. The latter is 3.158(1) Å in *vic-3*, which is

considerably longer than the Te–Te bond in [Fe₂(CO)₆-Te₂],¹⁰ and it is also longer than that of side-on coordinated Te₂ ligands.¹¹ On the other hand this range still allows interactions between opposite Te ligands in M₂-Te₂ rings.¹² However, from simple electron bookkeeping it is evident that all metal centers achieve 18 electrons, when Te(1) is considered as a μ₄-six-electron donor and Te(2) as a μ₃-four-electron donor.

For an ¹H NMR spectroscopic study crystals of *vic-3* were dissolved in CD₂Cl₂ at –80 °C. The observed pattern consists of a set of seven multiplets (the eighth one being superposed by the solvent signal) between δ 6.84 and 4.38 (C₅H₄), two singlets at δ 1.17 and 1.13 (*t*Bu), and one singlet at δ –0.99 (NbH). This is in agreement with the solid-state structure (Figure 1). It also means that the rotation around the Cp'–Nb bonds is blocked by steric interactions between the *t*Bu groups and the bulky Cr(CO)₅ unit. Raising the temperature to –60 °C reveals a dynamic process ($k = 41 \text{ s}^{-1}$, $\Delta G^\ddagger_{203} = 10.2 \pm 0.5 \text{ kcal mol}^{-1}$). The multiplets are completely broadened at –60 °C, whereas four multiplets (C₅H₄) and one singlet each for *t*Bu and NbH are observed at 0 °C (Figure 2). This process is reversible.

It may be noted that rotation around the Cp'–M axis in "simple" bent metallocene derivatives such as [Cp'₂-Nb(Te₂)H]^{3b,c} or [Cp'₂MoTe₂]¹³ usually is too fast to be observed. Complex **2** seems to be between both extremes, for its C₅H₄ multiplets show beginning coalescence at –80 °C and a splitting into distinct signals upon further cooling could not be achieved. The existence of chiral ground-state geometries in bent group(IV) metallocenes of general formula [(RC₅H₄)₂MX₂] has been established only recently for Cp ligands bearing bulky substituents R.¹⁴ In these cases hindered Cp–M rotation may be detected by pairwise coalescence of the diastereotopic RC₅H₄ resonances in dynamic ¹H NMR spectroscopy.

Further warming of the solution of *vic-3* to 21 °C gives rise to the appearance of an additional set of signals consisting of four multiplets for the *t*BuC₅H₄ hydrogens and singlets at δ 1.36 (*t*Bu) and –0.28 (NbH) (Figure 2d). The equilibrium ratio between this new isomer, which is assigned *opp-3*, and *vic-3* is 55:45. Interestingly, the same isomer ratio has been found for the crude material before recrystallization. When cooling the "equilibrium mixture" down to –80 °C the signal set characteristic for the low-temperature limit spectra of *vic-3* duplicates as described above, whereas the resonances belonging to *opp-3* remain invariant (Figure 2e). If one extends the possibility of a blocked rotation

(10) Bachmann, R. E.; Whitmire, K. H. *J. Organomet. Chem.* **1994**, *479*, 31.

(11) Te–Te distances in η²-Te₂ complexes: (a) [Cp*₂Ti(Te₂)] (2.703–(2) Å); Fischer, J. M.; Piers, W. E.; MacGillivray, L. R.; Zaworotko, M. J. *Inorg. Chem.* **1994**, *34*, 2499. (b) [Cp*₂Zr(Te₂)CO] (2.688(1) Å); Howard, W. A.; Parkin, G.; Rheingold, A. L. *Polyhedron* **1994**, *14*, 25. Shin, J. H.; Hascall, T.; Parkin, G. *Organometallics* **1999**, *18*, 6. (c) [W(PMe₃)(CN*t*Bu)₄(Te₂)] (2.680(2) Å); Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 9822. (d) [triphosNi(Te₂)] (2.668(1) Å); Di Vaira, M.; Peruzzini, M.; Stoppioni, P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 916. (e) [Cp'₂Nb(Te₂)H-Cr(CO)₅] (2.695(1) Å).^{3b,c}

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(13) Shin, J.-H.; Savage, W.; Murphy, V. J.; Bonanno, J. B.; Churchill, D. G.; Parkin, G. *J. Chem. Soc., Dalton Trans.* **2001**, 1732.

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(8) Roof, L. C.; Smith, D. M.; Drake, G. W.; Pennington, W. T.; Kolis, J. W. *Inorg. Chem.* **1995**, *34*, 337.

(9) Recent examples for compounds with an Fe₂Te₂ core: (a) [Fe₂(CO)₆(Te₂CH₂)]: Mathur, P.; Reddy, V. D.; Bohra, R. *J. Organomet. Chem.* **1991**, *401*, 339. (b) [Fe₅(CO)₁₄Te₄]^{2–}: Roof, L. C.; Pennington, W. T.; Kolis, J. W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 913. (c) [Fe₂(CO)₆(TeCH₃)₂]: Bachmann, R. E.; Whitmire, K. H. *Organometallics* **1993**, *12*, 1988. (d) [Fe₈(CO)₂₄Te₆]^{2–}: Shieh, M.; Chen, P.-F.; Peng, S.-M.; Lee, G.-H. *Inorg. Chem.* **1993**, *32*, 3389. (e) [Fe₄(CO)₁₄Te₂]^{2–}: Das, B. K.; Kanatzidis, M. G. *J. Organomet. Chem.* **1996**, *513*, 1.

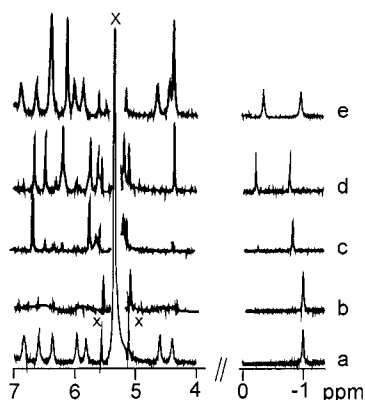
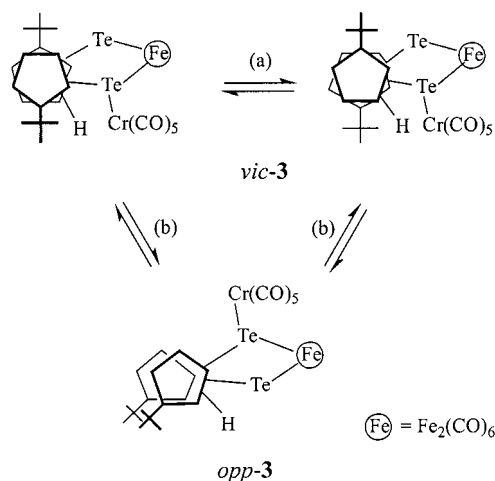


Figure 2. Variable-temperature ^1H NMR spectra (400 MHz, CD_2Cl_2) of **3** (x = solvent, sidebands; \circ = impurities). C_5H_4 and NbH signals (top) and $t\text{Bu}$ resonances (bottom) of *vic*-**3** dissolved at -80°C (a), -60°C (b), 0°C (c), and 21°C (d); spectrum e contains the “equilibrium mixture” d measured at -80°C .

around the $\text{Cp}'\text{-Nb}$ bonds to *opp*-**3**, an eclipsed conformation of both $t\text{Bu}$ groups in this stereoisomer seems to be likely, which would lead to a pairwise coincidence of the diastereotopic ring protons.

It was not possible to isolate *opp*-**3** in pure form, but the mother liquor predominantly contains *opp*-**3** when kept cold during workup. This has been verified by an ^1H NMR spectrum at -80°C . If this solution is warmed to room temperature the equilibrium ratio *opp*/*vic* of 55:45 is again observed. Further heating results in the loss of the $\text{Cr}(\text{CO})_5$ group and re-formation of **2**.

Scheme 1



On the basis of these results it is evident that the rapid dynamic process observed for *vic*-**3** may be explained by rotation around the $\text{Cp}'\text{-Nb}$ axes, leading to an enantiomerization within the niobocene moiety (Scheme 1a). For the second dynamic process, which takes place above 0°C , one may assume a migration of the $\text{Cr}(\text{CO})_5$ fragment to the lateral Te atom (Scheme 1b). In the resulting *opp*-**3** steric interactions between the Cp' ligands and the $\text{Cr}(\text{CO})_5$ fragment should become still more important than in *vic*-**3**. As a consequence, the $t\text{Bu}$ groups of both Cp' rings are forced into an eclipsed conformation, making them equivalent. The observation that both stereoisomers of **3** re-form **2** during chromatography or after heating may be a hint for facile dissociation of the $\text{Cr}(\text{CO})_5$ fragment.

In conclusion, the reaction of **1** with $[\text{Fe}_2(\text{CO})_9]$ and the subsequent addition of a $\text{Cr}(\text{CO})_5$ fragment give rise to the formation of a sterically crowded trimetallic telluride complex in which two different kinds of isomerization processes take place. Compounds **2** and **3** are the first examples for an insertion of a dimetal unit into a niobocene ditelluride bond. Thus, the reaction is an important step in metal telluride cluster formation from niobocene ditelluride hydrides and binary transition metal carbonyls.³⁻⁵

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Supporting Information Available: This material is available free of charge via the Internet at <http://pubs.acs.org>. OM020066Y