*Organometallics* **1994,** *13,* 134–140

# Preparative, Structural, and Electrochemical Investigations on Peralkylated Niobocene Dichlorides and Difluorides[†]

Henri Brunner, Günther Gehart, Walter Meier, and Joachim Wachter*

*Institut für Anorganische Chemie der Universität Regensburg, D-93040 Regensburg, Germany*

Astrid Riedel

*Institut für Biophysik und Physikalische Biochemie der Universität Regensburg, D-93040 Regensburg, Germany*

Soumia Elkrami and Yves Mugnier

*Laboratoire de Synthèse et d'Electrosynthèse Organométalliques, associé au CNRS (URA 1685), Université de Bourgogne, F-21100 Dijon, France*

Bernd Nuber

*Institut für Anorganische Chemie der Universität Heidelberg, D-69120 Heidelberg, Germany*

*Received July 6, 1993*[⊗]

$Cp^{\dagger}_2NbCl_2$ ($Cp^{\dagger}$ = $\eta^5$-$C_5Me_4Et$) (**1b**) was synthesized from $NbCl_5$ and a slight excess of $Cp^{\dagger}Li$ and $NaBH_4$. Its electrochemical (2 $e^-$, $E_{1/2} = -1.6$ V) and chemical reduction (2 equiv of Na/Hg) was studied showing that peralkylation of the Cp ligand facilitates two-electron reduction compared to less substituted $Cp_2NbHal_2$ derivatives. The reduced solutions of $Cp^*_2NbCl_2$ ($Cp^*$ = $C_5Me_5$) (**1a**) and of **1b** were shown by means of EPR spectroscopy to contain two new paramagnetic species **1A,B** for which bent niobocene ($A_{Nb}$ = 100 G) and fulvene-like structures ($A_{Nb}$ = 55 G) are proposed. The high reduction potential of these species led in their reaction with $HPF_6$ to the first stable difluoroniobocene derivative, $[Cp^{\dagger}_2NbF_2]PF_6$ (**2**), in good yield. The molecular structures of **2** and a cocrystallizate of **2** and $[Cp^{\dagger}_2NbCl_2]PF_6$ (**3**), analyzing as $[Cp^{\dagger}_2NbCl(Cl,F)]PF_6$ (**4**), were studied by X-ray diffraction techniques. Comparison with the structure of **1b** shows a marked decrease of the angle Hal–Nb–Hal from 102.3(4)° (**2**) to 85.2(1)° (**1b**). Electrochemical 1 $e^-$ reduction of **2** gave rise to the formation of $Cp^{\dagger}_2NbF_2$, which exhibits a much lower potential ($E_{1/2} = -2.38$ V) than other niobocene dihalides. Reaction of **2** with $Li_2S_2$ gave $Cp^{\dagger}_2Nb(\eta$-$S_2)F$, whereas **3** was reduced by $Li_2S_2$ to give **1b**.

## Introduction

Niobocene dihalides $Cp_2NbHal_2$ represent a class of widely investigated organometallic compounds exhibiting interesting electronic and structural properties.[1,2] Their potential in synthesis is based on the ability to undergo metathetical reactions and to form lower Nb oxidation states by chemical[3] or electrochemical reduction.[4] Such compounds are of actual interest because of their application in catalysis[1,5] and the activation of small molecules.[6] The stability of the paramagnetic and coordinatively unsaturated $Cp_2NbHal_2$ compounds was ascribed to a balance between electronic (general preference for higher Nb oxidation states) and steric factors (three ligands in addition to both Cp's would result in a crowded coordination sphere).[1] Therefore, it is rather surprising that only little is known on more substituted Cp derivatives although the influence of e.g. multiple alkylation has been investigated in many other organometallic compounds. One reason may be the lack of a convenient synthesis for peralkylated niobocene halides. The method developed for $Cp^*_2NbCl_2$ (**1a**) by Bercaw et al.[7] has to pass through $Cp^*_2NbBH_4$, a compound known for a laborious preparation.[8] We now wish to report on a rational synthesis of $Cp^{\dagger}_2NbCl_2$ (**1b**) as well as the evaluation of its reduction chemistry in comparison to lower substituted niobocene derivatives. The nature of the generated Nb(II) species will be discussed, including an example for application in the synthesis of new niobocene fluoride derivatives.

## Experimental Section

**Syntheses.** All procedures were carried out under argon (as far as handling of $NbCl_5$ was concerned) or nitrogen with $N_2$-

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[†] Abbreviations employed throughout the text: Cp = any substituted cyclopentadienyl ligand; Cp′ = *tert*-butyl-, Cp* = pentamethyl-, and $Cp^{\dagger}$ = ethyltetramethylcyclopentadienyl.

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1993.

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**Table 1. Crystal Data and Data Collection Parameters for $Cp^{\dagger}_2NbCl_2$ (1b), $[Cp^{\dagger}_2NbF_2]PF_6$ (2), and $[Cp^{\dagger}_2NbCl(Cl,F)]PF_6$ (4)**

| | **1b** | **2** | **4** |
|---|---|---|---|
| mol formula | $NbCl_2C_{22}H_{34}$ | $NbF_8PC_{22}H_{34}$ | $NbCl_{1.67}F_{6.33}PC_{22}H_{34}$ |
| fw | 462.3 | 574.4 | 601.83 |
| cryst syst | monoclinic | monoclinic | monoclinic |
| space group | $C2_h^2$, $P2_1/m$ (No. 11) | $C2_h^5$, $P2_1/c$ (No. 14) | $C2_h^5$, $P2_1/c$ (No. 14) |
| cell dimens | | | |
| *a*, Å | 8.248(2) | 13.35(1) | 10.898(5) |
| *b*, Å | 17.939(5) | 11.72(1) | 8.667(4) |
| *c*, Å | 8.452(3) | 15.88(2) | 27.56(1) |
| *β*, deg | 118.99(2) | 100.14(7) | 101.17(4) |
| *V*, $Å^3$ | 1093.9 | 2445.8 | 2553.8 |
| *Z* | 2 | 4 | 4 |
| *T*, K | 296 | 296 | 296 |
| $d_{calc}$, $g \cdot cm^{-3}$ | 1.40 | 1.56 | 1.56 |
| linear abs, *μ*, $cm^{-1}$ | 7.8 | 6.0 | 7.3 |
| *F*(000) | 482 | 1176 | 1224 |
| radiation, Å | λ(Mo Kα) = 0.710 73 | λ(Mo Kα) = 0.710 73 | λ(Mo Kα) = 0.710 73 |
| scan type | *ω* | *ω*–*δ* | *ω* |
| rflns measd | *h*, 0–12; *k*, 0–26; *l*, –12 to 12 | *h*, –14 to 14; *k*, 0–12; *l*, 0–16 | *h*, 0–16; *k*, 0–13; *l*, –39 to 39 |
| 2*θ* range, deg | 3–60 | 3–44 | 3–60 |
| no. of rflns measd | 3474 | 3710 | 8149 |
| abs cor; range of transmissn | empirical, 7 rflns; $9.0 < 2\theta < 42.0$ | empirical, 4 rflns; $5.0 < 2\theta < 21.0$ | empirical, 8 rflns; $7.6 < 2\theta < 46.2$ |
| no. of unique obsd data | 2771, $I > 2.5\sigma(I)$ | 1416, $I > 2.5\sigma(I)$ | 4998, $I > 2.5\sigma(I)$ |
| no. of params (NV) | 109 | 180 | 291 |
| *R*(*F*) | 0.059 | 0.068 | 0.054 |
| $R_w(F)$ | 0.059 | 0.057 | 0.049 |
| GOF | 4.19 | 2.05 | 3.10 |
| *ρ*, residual, $e \cdot Å^{-3}$ | 1.07 | 0.56 | 0.71 |

**Table 2. Atomic Coordinates (×$10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2$ × $10^3$) for $(C_5Me_4Et)_2NbCl_2$ (1b)**

| atom | *x* | *y* | *z* | $U_{eq}$[a] |
|---|---|---|---|---|
| Nb | 2374(1) | 2500 | 8378(1) | 28(1) |
| Cl1 | –928(3) | 2500 | 6083(3) | 59(1) |
| Cl2 | 1243(3) | 2500 | 10589(3) | 54(1) |
| C1 | 2037(12) | 3822(5) | 8250(13) | 33(2) |
| C2 | 2324(14) | 3617(5) | 6765(11) | 30(2) |
| C3 | 4220(13) | 3339(5) | 7541(12) | 37(2) |
| C4 | 5077(13) | 3368(5) | 9477(13) | 35(2) |
| C5 | 3595(18) | 3677(8) | 9885(18) | 47(4) |
| C6 | 366(17) | 4222(7) | 8075(16) | 67(3) |
| C7 | 1134(16) | 3728(6) | 4760(14) | 61(3) |
| C8 | 5193(16) | 3202(6) | 6508(15) | 61(3) |
| C9 | 7009(17) | 3251(7) | 10767(16) | 66(3) |
| C10 | 4037(16) | 3880(6) | 11776(14) | 57(3) |
| C11 | 4775(20) | 4724(7) | 12222(17) | 71(3) |
| C21 | 2142(15) | 1148(6) | 9060(16) | 32(2) |
| C22 | 1615(16) | 1184(6) | 7137(17) | 38(3) |
| C23 | 3123(21) | 1436(7) | 7000(17) | 36(3) |
| C24 | 4655(17) | 1519(7) | 8728(17) | 35(3) |
| C25 | 4047(17) | 1359(6) | 10032(15) | 16(2) |
| C26 | 901(21) | 825(9) | 9710(19) | 65(4) |
| C27 | –245(25) | 908(10) | 5577(22) | 80(5) |
| C28 | 3410(28) | 1412(11) | 5266(24) | 94(6) |
| C29 | 6689(25) | 1555(10) | 9362(23) | 81(5) |
| C30 | 5103(18) | 1319(7) | 12079(16) | 43(3) |
| C31 | 5792(21) | 522(8) | 12626(18) | 54(4) |

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

**Table 3. Atomic Coordinates (×$10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2$ × $10^3$) for $[(C_5Me_4Et)_2NbF_2]PF_6$ (2)**

| atom | *x* | *y* | *z* | $U_{eq}$[a] |
|---|---|---|---|---|
| Nb | 2274(1) | 2185(1) | 357(1) | 35(1) |
| F1 | 2398(6) | 2806(9) | 1489(4) | 68(4) |
| F2 | 1650(7) | 743(8) | 472(6) | 72(4) |
| C1 | 3570(12) | 1460(14) | –424(9) | 45(5) |
| C2 | 3547(12) | 690(14) | 239(9) | 39(4) |
| C3 | 3902(11) | 1325(14) | 971(9) | 42(5) |
| C4 | 4095(12) | 2466(13) | 817(9) | 44(5) |
| C5 | 3913(11) | 2580(13) | –105(8) | 40(5) |
| C6 | 3434(12) | 1132(13) | –1374(8) | 50(5) |
| C7 | 3302(12) | –528(13) | 167(9) | 63(5) |
| C8 | 4044(12) | 829(13) | 1880(8) | 62(6) |
| C9 | 4529(12) | 3425(14) | 1410(9) | 68(6) |
| C10 | 4284(11) | 3577(13) | –577(9) | 49(5) |
| C11 | 5394(12) | 3349(15) | –672(10) | 83(7) |
| C21 | 821(11) | 2334(15) | –799(9) | 48(5) |
| C22 | 434(11) | 2611(13) | –8(9) | 40(5) |
| C23 | 900(11) | 3608(13) | 297(9) | 36(4) |
| C24 | 1595(11) | 4003(12) | –196(9) | 32(4) |
| C25 | 1494(11) | 3242(12) | –923(9) | 34(4) |
| C26 | 503(12) | 1340(14) | –1389(9) | 71(6) |
| C27 | –351(11) | 1881(13) | 259(9) | 61(6) |
| C28 | 692(11) | 4209(13) | 1088(8) | 52(5) |
| C29 | 2141(11) | 5123(13) | –96(9) | 54(5) |
| C30 | 1824(12) | 3566(14) | –1773(9) | 58(5) |
| C31 | 954(12) | 4165(14) | –2360(9) | 61(5) |
| P1 | 2477(5) | 7765(8) | 7575(4) | 90(3) |
| F11 | 3184(12) | 7802(18) | 8411(8) | 214(11) |
| F12 | 1854(11) | 8728(16) | 7929(10) | 181(11) |
| F13 | 1781(12) | 7764(18) | 6723(8) | 200(11) |
| F14 | 3093(18) | 6848(19) | 7248(13) | 284(16) |
| F15 | 1761(19) | 6936(17) | 7900(11) | 242(15) |
| F16 | 3080(16) | 8699(21) | 7254(12) | 247(15) |

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

saturated, dry solvents. $Li_2S_2$ was prepared from $S_8$ and $LiEt_3BH$ in THF as a 0.5 M solution.[9]

Elemental analyses were performed by the Mikroanalytisches Laboratorium, Universität Regensburg. IR spectra were obtained with a Beckman 4240 spectrophotometer. Field desorption mass spectra were run on a Finnigan MAT 95 instrument. NMR spectra were recorded on Bruker WM 250 and WM 400 instruments, and EPR spectra were taken at the X-band with Bruker ER 200 and ESP 300 spectrometers.

**Electrochemical Equipment and Cells.** Voltammetric analyses were carried out in a standard three-electrode cell with a Tacussel UAP4 unit. The reference electrode was a saturated calomel electrode separated from the solution by a sintered glass disk. The auxiliary electrode was a Pt wire. For all voltammetric measurements the working electrode was a Pt disk electrode (surface area: 3.1 $mm^2$) which was initially polished with alumina of decreasing particle size (down to 0.05 mm). For the polarograms, a three-electrode Tacussel Tipol polarograph was used. The dropping Hg electrode characteristics were $m = 3\ mg \cdot s^{-1}$ and

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**Table 4. Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$ × 10$^3$) for [(C$_5$Me$_4$Et)$_2$NbCl(Cl,F)]PF$_6$ (4)**

| atom | *x* | *y* | *z* | $U_{eq}$[a] |
|---|---|---|---|---|
| Nb | 2015(1) | 3155(1) | 5940(1) | 35(1) |
| Cl1 | 1567(2) | 5802(1) | 5832(1) | 70(1) |
| Cl2 | 106(2) | 2282(2) | 5562(1) | 73(1) |
| C1 | 2010(6) | 4101(6) | 6782(2) | 65(2) |
| C2 | 3091(5) | 3207(7) | 6800(2) | 59(2) |
| C3 | 2691(4) | 1665(5) | 6702(2) | 47(2) |
| C4 | 1392(4) | 1637(5) | 6602(2) | 45(2) |
| C5 | 957(5) | 3163(6) | 6641(2) | 54(2) |
| C6 | 2021(8) | 5746(6) | 6955(2) | 121(4) |
| C7 | 4421(6) | 3711(9) | 7024(2) | 108(3) |
| C8 | 3478(6) | 236(7) | 6832(2) | 89(3) |
| C9 | 585(6) | 223(6) | 6515(2) | 90(3) |
| C10 | –402(6) | 3621(8) | 6600(2) | 100(3)(5) |
| C11 | 2672(4) | 3633(5) | 5142(2) | 43(1) |
| C12 | 2365(4) | 2054(5) | 5143(2) | 50(2) |
| C13 | 3175(5) | 1332(5) | 5532(2) | 49(2) |
| C14 | 4062(4) | 2457(5) | 5762(2) | 43(1) |
| C15 | 3714(4) | 3884(5) | 5522(2) | 39(1) |
| C16 | 2054(5) | 4783(6) | 4765(2) | 65(2) |
| C17 | 1389(6) | 1270(7) | 4756(2) | 84(3) |
| C18 | 3247(6) | –399(5) | 5610(2) | 78(3) |
| C19 | 5341(4) | 2132(6) | 6066(2) | 63(2) |
| C20 | 4431(5) | 5353(5) | 5623(2) | 60(2) |
| C21 | –817(7) | 3369(10) | 7088(2) | 157(5) |
| C22 | 6218(5) | 1691(7) | 5722(2) | 83(3) |
| P1 | 2930(2) | 2613(2) | 8350(1) | 59(1) |
| F11 | 2359(5) | 2175(5) | 7814(1) | 146(3) |
| F12 | 4304(4) | 2500(6) | 8263(2) | 160(3) |
| F13 | 3544(5) | 3030(4) | 8898(1) | 131(2) |
| F14 | 1589(4) | 2662(6) | 8461(2) | 147(3) |
| F15 | 3019(3) | 869(4) | 8508(1) | 99(2) |
| F16 | 2888(6) | 4335(4) | 8204(2) | 173(3) |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

$E$ = 0.5 s. For controlled-potential electrolysis, a mercury pool was used as cathode and a Pt plate as anode, the latter being separated from the solution by a sintered glass disk. High-scale electrolyses were carried out in a cell with three compartments being separated with fritted glasses of medium porosity. In all cases, the electrolyte was a 0.2 M solution of $n$-Bu$_4$NPF$_6$ in THF or CH$_2$Cl$_2$. The electrolyses were performed with an Amel 552 potentiostat coupled to an Amel 721 electronic integrator.

**Preparation of Cp$^{\dagger}_2$NbCl$_2$ (1b).** A suspension of 2.32 g (14.83 mmol) of LiCp$^{\dagger}$ and 0.35 g (9.27 mmol) of NaBH$_4$ in 80 mL of dimethoxyethane was cooled to –78 °C. Under argon 1.67 g (6.18 mmol) of NbCl$_5$ was added with efficient stirring. The resulting light-brown mixture was allowed to warm to 25 °C and then refluxed for 15 h. The following workup was carried out under nitrogen. After evaporation of the solvent the resulting green oil was washed with pentane to remove the oily components and blue Cp$^{\dagger}_2$Nb$_2$($\mu$-B$_2$H$_6$)Cl$_2$[8] and then dried. The green solid was sublimed at 200 °C (0.1 Pa, 50% yield). Additional **1b** (10% yield) was obtained by chromatographic workup (SiO$_2$, column 20 × 3 cm; 10:1 toluene/ether as eluent) of the pentane extracts. Analytically pure samples were obtained by recrystallization from CH$_2$Cl$_2$ as green needles. Anal. Calcd for C$_{22}$H$_{34}$Cl$_2$Nb: C, 57.16; H, 7.41; mol wt, 462.3. Found: C, 57.20; H, 7.18; mol wt, 461.5 (FD-MS from CH$_2$Cl$_2$).

**Preparation of [Cp$^{\dagger}_2$NbF$_2$]PF$_6$ (2).** A 300-mg amount (0.65 mmol) of **1b** was dissolved in 50 mL of THF and stirred over Na/Hg containing 2.60 mmol of Na in 10 mL of Hg for 1 h. After separation of the orange-brown solution from the amalgam, 1 mL of HPF$_6$ (75% in H$_2$O, 15-fold excess) was added. Spontaneous evolution of H$_2$ and a significant color change from orange-brown to red-brown was observed. After stirring of the mixture for 1 h, the solvent was removed under vacuum to give a dark oil. Washing with ether gave an orange-yellow solid, which was dissolved in CH$_2$Cl$_2$. After filtration and evaporation of the solvent **2** was obtained in 62% yield. Recrystallization from 5:1 CH$_2$Cl$_2$/toluene at -25°C gave orange crystals. Anal. Calcd for C$_{22}$H$_{34}$F$_8$PNb (**2**): C, 46.00; H, 5.97; mol wt, 574.4. Found: C, 45.63; H, 5.95; mol wt, 429.4 (FD-MS from CH$_2$Cl$_2$; calcd 429.4 for C$_{22}$H$_{34}$F$_2$Nb). $^1$H-NMR (CDCl$_3$): $\delta$ 1.05 (t, 6), 2.10, 2.17 (s, 24), 2.69 (q, 4). $^{31}$P-NMR (CDCl$_3$): $\delta$ –145.74 (sep, $J_{P-F}$ = 712 Hz); $^{19}$F–NMR: $\delta$ –73 (d), 80 (br). IR (KBr): $\nu_{P-F}$ 843, 556 cm$^{-1}$; $\nu_{Nb-F}$ 598, 581 cm$^{-1}$.

If only 1.5 equiv of HPF$_6$ was added to the reduced solution of **1b**, complex **2** was obtained in 50% yield (same workup as described above). This product is contaminated with [Cp$^{\dagger}_2$NbCl$_2$]PF$_6$ (**3**). The ether extract was evaporated and then washed with toluene to remove traces of **1b**. Recrystallization from 1:1 CH$_2$Cl$_2$/toluene gave red crystals of **3** still containing varying amounts of **2**. Examination of a crystal by X-ray diffraction resulted in the adventitious composition [Cp$^{\dagger}_2$NbCl(Cl,F)]PF$_6$ (**4**). C, H analyses gave values between those for **2** and **3**.

**Preparation of [Cp$^{\dagger}_2$NbCl$_2$]PF$_6$ (3). (a) From 2 and Concentrated HCl.** A mixture of 140 mg (0.24 mmol) of **2**, 30 mL of CH$_2$Cl$_2$, and 3 mL of concentrated HCl was stirred for 60 min. After removal of the aqueous phase, the solvent was evaporated to give **3**. Recrystallization from 1:1 CH$_2$Cl$_2$/toluene gave red-violet crystals. Anal. Calcd for C$_{22}$H$_{34}$Cl$_2$F$_6$PNb: C, 43.51; H, 5.64; mol wt, 607.3. Found: C, 43.71; H, 5.35; mol wt, 461.4 (FD-MS from CH$_2$Cl$_2$; calcd 462.34 for C$_{22}$H$_{34}$Cl$_2$Nb). IR (KBr): $\nu_{P-F}$ 840, 565 cm$^{-1}$.

**(b) From Oxidation of 1b by [(C$_5$H$_5$)$_2$Fe]PF$_6$.** A solution of 170 mg (0.37 mmol) of **1b** and 122 mg (0.37 mmol) of [(C$_5$H$_5$)$_2$Fe]PF$_6$ in 30 mL of THF was stirred for 1 h. After evaporation of the solvent (C$_5$H$_5$)$_2$Fe was extracted with 20 mL of toluene. The solid residue was dissolved in 20 mL of CH$_2$Cl$_2$, the solution was filtered, and then the solid recrystallized from 1:1 CH$_2$Cl$_2$/toluene at –25°C to give red-violet **3** in 90% yield.

**Reaction of 2 with Li$_2$S$_2$.** A mixture of 140 mg (0.24 mmol) of **2**, 0.24 mmol of Li$_2$S$_2$, and 40 mL of THF was stirred at room temperature. After 2 h the solvent was removed under vacuum. With chromatography on SiO$_2$ (column 10 × 3 cm), a red-brown band was eluted with ether containing Cp$^{\dagger}_2$NbS$_2$F (**5**) in 40% yield. **5** was recrystallized from 1:1 toluene/ether. Anal. Calcd for C$_{22}$H$_{34}$FNbS$_2$: C, 55.70; H, 7.22; mol wt, 474.6. Found: C, 55.85; H, 7.14; mol wt, 474.4 (FD-MS from toluene). $^1$H-NMR (CDCl$_3$): $\delta$ 0.97 (t, 6), 1.77 (d, $J_{H-F}$ = 0.8 Hz; 6), 1.79 (s, 6), 1.82 (s, 6), 1.83 (d, $J_{H-F}$ = 1.1 Hz, 6), 2.21 (m, 4). IR (KBr): $\nu_{Nb-F}$ 538 cm$^{-1}$, $\nu_{S-S}$ 485 cm$^{-1}$.

**X-ray Crystallography and Structure Solution.** Data were collected on a Syntex R3 (**1b**, **4**) or a Siemens Stoe AEDII diffractometer (**2**) at room temperature. Relevant crystal and data collection parameters are given in Table I. The structures were solved by using standard Patterson methods, least-squares refinement, and Fourier techniques. All calculations were performed with the SHELXTL PLUS program.[10]

**Cp$^{\dagger}_2$NbCl$_2$ (1b).** A green prism of the dimensions 0.1 × 0.1 × 0.4 mm$^3$ was obtained from CH$_2$Cl$_2$. The unit cell was determined and refined from 27 reflections (4.5 < 2$\theta$ < 26°) to be monoclinic. Cell reduction alternatively gave an orthorhombic *C* cell, but from intensity measurements (two pairs of equal intensities instead of four equal intensities for symmetry-related reflections) a monoclinic cell followed unequivocally. The solution of the structure required the assumption of a mirror plane with a statistical distribution of the ring carbons (56:44%). For this reason only Nb and Cl atoms were refined anisotropically; the hydrogen atoms have not been calculated.

**[Cp$^{\dagger}_2$NbF$_2$]PF$_6$ (2).** A yellow needle of the approximate dimensions 0.06 × 0.08 × 0.95 mm$^3$ was obtained from 10:1 CH$_2$Cl$_2$/toluene. The unit cell was determined and refined from 24 reflections (8 < 2$\theta$ < 22°). Because of the limited number of reflections, only the Nb, F, and P atoms were refined anisotropically. The PF$_6$ anion was slightly disordered. The hydrogen atoms were included riding on calculated positions (HFIX option of SHELXTL[10]).

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(10) SHELXTL PLUS (release 3.4), Siemens Analytical X-Ray Instruments, 1989.

**Table 5. Electrochemical[a] and Electron Spin Resonance[b] Data for Niobocene Dihalide Derivates**

| compd | $E_{1/2(\mathrm{Red})}$, V | $E_{1/2(\mathrm{Ox})}$, V | $A_{\mathrm{iso}}$, G | $g_{\mathrm{iso}}$ | ref |
|---|---|---|---|---|---|
| $(C_5Me_5)_2NbCl_2$ (**1a**) | −1.60 | +0.04 | 109.4 | 2.0019 | this work |
| $(C_5Me_4Et)_2NbCl_2$ (**1b**) | −1.61 | +0.07 | 115.4 | 1.999 | this work |
| $(C_5Me_4Et)_2NbF_2$ | −2.38 | −0.38 | 114.2 ($A_{\mathrm{Nb}}$)<br>20 ($A_F$) | 1.956 | this work |
| $(C_5H_4SiMe_3)_2NbCl_2$ | −1.19 | +0.34 | 115.4 | 2.0018 | 4b |
| $[1,3\text{-}C_5H_3(SiMe_3)_2]_2NbCl_2$ | −1.28 | +0.40 | 112.7 | 1.989 | 4c |
| $(C_5H_4CMe_3)_2NbCl_2$ | −1.27 | +0.26 | 109.3 | 1.997 | this work |
| $(C_5H_5)_2NbCl_2$ | −1.29 | +0.36 | 112.4 | 2.0075 | 4a |

[a] THF with 0.2 M $n$-$Bu_4NPF_6$; dropping Hg electrode ($m$ = 3 mg·s$^{-1}$, $\tau$ = 0.5 s); potentials vs SCE. [b] THF, 20 °C.

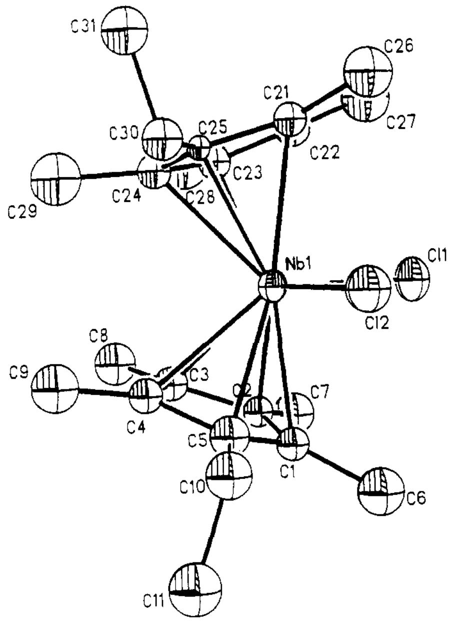

**Figure 1.** Structure of 1 (ORTEP plot). The thermal ellipsoids are drawn at a 50% probability level.

**[$\mathbf{Cp^{\dagger}_2NbCl(Cl,F)]PF_6}$ (4).** A dark red irregular crystal of the dimensions 0.4 × 0.5 × 0.6 mm$^3$ was obtained from 1:1 $CH_2Cl_2$/toluene. The unit cell was determined and refined from 23 reflections (4 < 2$\theta$ < 38.3°). All non-hydrogen atoms were included riding on calculated positions (HFIX option of SHELX-TL[10]). The occupancy factor of Cl2 is 0.85; this means about $^2/_3$ of the site are occupied by Cl and $^1/_3$ by F atoms.

## Results and Discussion

$Cp^{\dagger}_2NbCl_2$ (**1b**) was synthesized from $NbCl_5$ and 2.4 equiv of $Cp^{\dagger}Li$ in boiling dimethoxyethane. As reducing agent 1.5 equiv of $NaBH_4$ was employed, which gave also rise to the formation of a dinuclear complex comprising the $B_2H_6^{2-}$ unit as bridging ligand.[8] $Cp^*_2NbCl_2$ (**1a**) was obtained by the same procedure in about 50% yield.[8] The green complexes **1a,b** exhibit ten-line ($^{93}$Nb, $I = {}^9/_2$) EPR spectra (Table V) with $g$ values and coupling constants typical of $Cp_2NbCl_2$ derivatives.[2] These parameters are not significantly influenced by the nature of the Cp ligand. The same observation is valid for the solid-state structure of **1b** when compared to that of $(C_5H_5)_2NbCl_2$.[11] An X-ray diffraction analysis of **1b** (Figure 1; Tables II and VI) reveals the same pseudotetrahedral geometry and an angle Cl1–Nb–Cl2 (85.2(1)°) very close to that in the unsubstituted complex (85.6°). The Cp rings are disordered in a way that they give rise to a statistic distribution of 56 and 44%, respectively. As a consequence larger standard deviations for the ring carbon parameters are noted.

**Table 6. Selected Distances and Angle for 1b**

| Distances (Å) | | | |
|---|---|---|---|
| Nb–Cl1 | 2.461(2) | Nb–C5 | 2.418(13) |
| Nb–Cl2 | 2.460(3) | Nb–C21 | 2.521(11) |
| Nb–C1 | 2.383(8) | Nb–C22 | 2.536(12) |
| Nb–C2 | 2.413(9) | Nb–C23 | 2.466(15) |
| Nb–C3 | 2.476(11) | Nb–C24 | 2.488(13) |
| Nb–C4 | 2.500(10) | Nb–C25 | 2.485(11) |

| Angle (deg) | |
|---|---|
| Cl1–Nb–Cl2 | 85.2(1) |

Electrochemical studies of **1a,b** showed that an exhaustive electrolysis at the potential of the reduction wave (−1.6 V for both complexes) consumed 2 equiv of electrons. This means a significant difference compared to the other $Cp_2NbCl_2$ derivatives investigated thus far,[4] which generally do not consume more than 1 e$^-$. The influence of the peralkylated Cp ligands is also expressed by a drastic shift to more negative reduction potentials when compared to the lower substituted compounds (Table V). From several experiments solutions were obtained whose EPR spectra exhibit multiline spectra of two new paramagnetic species which are similar to those obtained by 2 e$^-$ chemical reduction of **1a,b**.

The reduction of **1a,b** with 2 equiv of Na/Hg was monitored by EPR spectroscopy. In dimethoxyethane, toluene, and THF a simple ten-line spectrum ($A_{\mathrm{Nb}}$ = 55 G) was obtained for sublimed starting material (Figure 2a). Additional, but not well-resolved, satellites for the inner signals may be interpreted as Nb–H couplings of the order of 11 G. All reduced solutions are very sensitive to air and moisture rendering the investigations very difficult. The EPR spectra of recrystallized samples are more complex, for they contain three paramagnetic Nb species (Figure 2b). Spectrum analysis shows the presence of **1a** (or **1b**), traces of the spectrum type shown in Figure 2a, and a third species of coupling constant $A_{\mathrm{Nb}}$ = 100 G. The value of this coupling is close to that observed for "$(C_5H_5)_2Nb$" so that a bent 15 e$^-$ niobocene structure **1A** may be assumed by analogy. Unsubstituted niobocene has been independently obtained by two different ways,[3a,12] and because of its simple ten-line spectrum ($g$ = 2.001, $A_{\mathrm{Nb}}$ = 103 G) association of two or more molecules or solvent coordination at the niobium center has been excluded.[13]

It is not yet clear how the different EPR signals can be influenced by external factors. Neither influence of different solvents nor of $N_2$ has been observed. An explanation of the spectral type shown in Figure 2a may involve species of the fulvene-like structure **1B**. There may be an equilibrium between **1A** and **1B** by transfer of an

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(11) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr., Sect. B.* **1974**, *30*, 2290.

(12) Elson, I. H.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 1262.

(13) "$Cp_2Ti$" solutions are able to coordinate THF: Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219. Van Tamelen, E. E.; Cretney, W.; Klaentschi, N.; Miller, J. S. *J. Chem. Soc., Chem. Commun.* **1972**, 481.

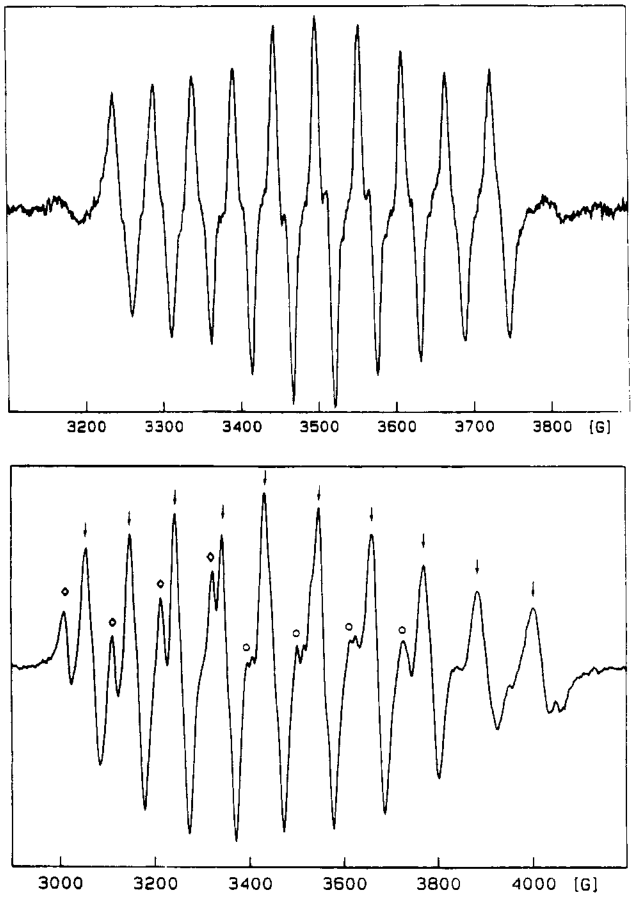
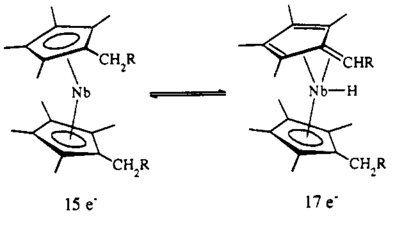


**Figure 2.** EPR spectra for reduced $Cp^{\dagger}_2NbCl_2$ (2 equiv of Na/Hg): (a, top) Spectrum with $A_{Nb}$ = 55 G, solvent dimethoxyethane; (b, bottom) spectrum containing **1b** (◊) and two species with the coupling constants $A_{Nb}$ = 100 G (↓) and $A_{Nb}$ = 55 G (O).



**1A** **1B**

α-alkyl hydride to the metal, which would increase the electron configuration around Nb from 15 to 17, but further studies will be required to confirm this assumption. Nevertheless, the peralkylated niobocenes resemble more $(C_5Me_5)_2Ti$,[14] for which a bent metallocene structure has been established in an equilibrium with a fulvene-like structure, than the classical sandwich type structure reported for $(C_5Me_5)_2V$.[15] This interpretation is supported by the observation that products arising from attack at ring alkyls may be quenched in the reaction of reduced **1a,b** with sulfur.[16] In this regard it will be of interest to investigate how the nature of the reduced solution does affect the chemical results.

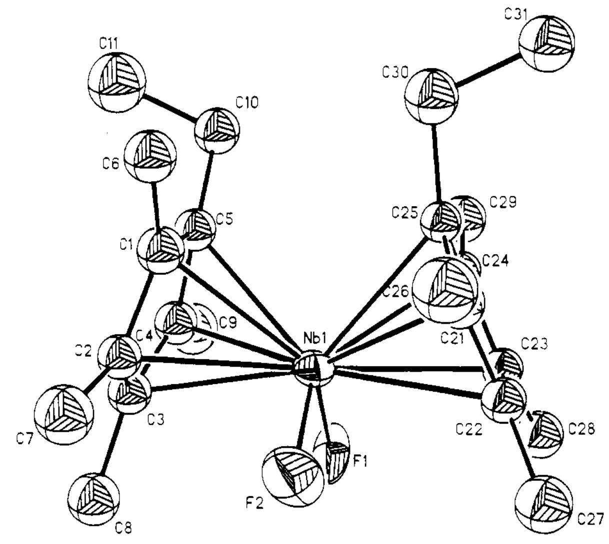


**Figure 3.** Structure of **2** (ORTEP plot), with anion not shown. The thermal ellipsoids are drawn at a 50% probability level.

**Table 7. Selected Distances and Angles for 2**

| | | | |
|---|---|---|---|
| | Distances (Å) | | |
| Nb–F1 | 1.920(8) | Nb–C5 | 2.471(15) |
| Nb–F2 | 1.906(10) | Nb–C21 | 2.432(13) |
| Nb–C1 | 2.451(17) | Nb–C22 | 2.473(15) |
| Nb–C2 | 2.470(16) | Nb–C23 | 2.469(16) |
| Nb–C3 | 2.437(15) | Nb–C24 | 2.420(14) |
| Nb–C4 | 2.434(15) | Nb–C25 | 2.451(14) |
| | Angles (deg) | | |
| F1–Nb–F2 | 102.3(4) | $Cp1_{cent}$–Nb–$Cp2_{cent}$ | 140.7 |

The reduced solution of **1a,b** readily react with $HPF_6$ under spontaneous evolution of $H_2$. The product obtained is dependent on the stoichiometry. When a 15-fold excess of acid is employed, a yellow salt is isolated in good yield which analyses as $[Cp^{\dagger}_2NbF_2]PF_6$ (**2**). In the case of **1a** yellow oils were obtained which did not crystallize. The IR spectrum of **2** consists of each of two strong absorptions for the $PF_6^-$ and the $NbF_2$ moieties. The presence of two chemically very different fluoro ligands is proven by the $^{19}F$ NMR spectrum: A well-resolved doublet ($J_{P-F}$ = 712 Hz) attributed to the hexafluorophosphate anion appears at −73 ppm, whereas a broad resonance at +80 ppm is in agreement with Nb-coordinated fluoro ligands. An X-ray diffraction analysis confirms the pseudotetrahedral environment of the Nb center (Figure 3; Tables III and VII): Two fluoro ligands are attached to the Nb center at an average distance of 1.91(1) Å, while the $PF_6$ unit serves as counterion without closer contacts.[17] Only two $Cp_2Nb$ fluoro derivatives have been structurally described thus far with Nb–F distances of striking difference (Δ = 0.28 Å).[18] The large F–Nb–F angle (102.3(4)°) when compared to Cl–Nb–Cl in **1b** (85.2(1)°) is a consequence of the absence of any unpaired electron at Nb which would exert a repulsive influence on the other ligands lying in the same plane.[2] Cyclovoltammetry of **2** in THF of $CH_2Cl_2$ shows a reversible system $E'/E$ (Figure 4). For sweep rates ($v$) between 0.01 and 0.20 V/s the ratio $i_p/v^{1/2}$ was constant

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[14] Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087.

[15] Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882. Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1984**, *23*, 1739.

[16] Manuscript in preparation.

[17] An example for a coordinating hexafluoroanion in metallocene chemistry is $(C_5H_5)_2VAsF_6$: Gorwik, P.; Klapötke, T. M.; Siems, K.; Thewalt, U. *J. Organomet. Chem.* **1992**, *431*, 47.

[18] $[(MeC_5H_4)_2Nb(CH_2SiMe_3)F]PF_6$ ($d_{Nb-F}$ = 1.910(2) Å): Fu, P.-F.; Khan, M. A.; Nicholas, K. M. *Organometallics* **1992**, *11*, 2607. $[(Me_3SiC_5H_4)_2Nb(\eta^2\text{-}(C,N)\text{-}Ph_2HCCNPh)F]PF_6$ ($d_{Nb-F}$ = 2.199(5) Å): Antiñolo, A.; Fajardo, M.; Gil-Sanz, R.; López-Mardomingo, C.; Martin-Villa, P.; Otero, A.; Kubicki, M. M.; Mugnier, Y.; El Krami, S.; Monrad, Y. *Organometallics* **1993**, *12*, 381.

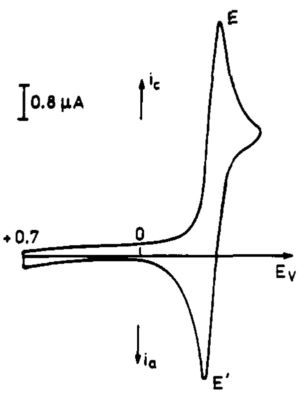

**Figure 4.** Cyclic voltammogram of $[Cp^{\dagger}_2NbF_2]PF_6$ (**2**) in $CH_2Cl_2$: Starting potential 0.7 V; sweep rate 0.020 V $s^{-1}$.

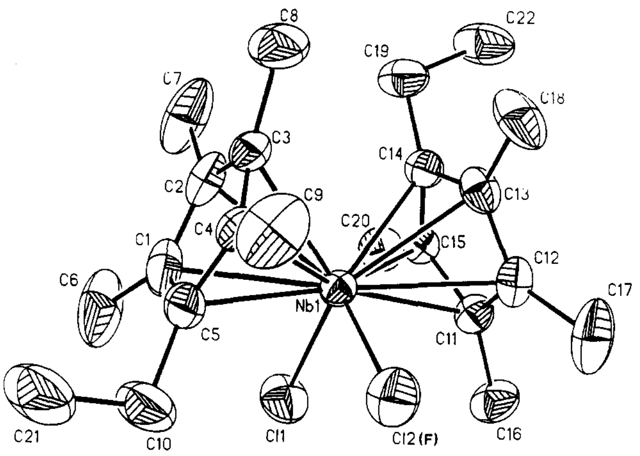

**Figure 5.** Structure of the cation of **4** (ORTEP plot), with Cl2 is replaced by $^1/_3$ F. The thermal ellipsoids are drawn at a 50% probability level.

**Table 8. Selected Distances and Angles for 4**

| | Distances (Å) | | |
|---|---|---|---|
| Nb–Cl1 | 2.352(2) | Nb–C5 | 2.434(5) |
| Nb–Cl2 | 2.269(2) | Nb–C11 | 2.476(5) |
| Nb–C1 | 2.461(5) | Nb–C12 | 2.492(5) |
| Nb–C2 | 2.432(4) | Nb–C13 | 2.431(5) |
| Nb–C3 | 2.454(4) | Nb–C14 | 2.451(5) |
| Nb–C4 | 2.449(5) | Nb–C15 | 2.445(5) |
| | Angles (deg) | | |
| Cl1–Nb–Cl2 | 96.8(1) | $Cp1_{cent}$–Nb–$Cp2_{cent}$ | 137.6 |

and $i_{pa}/i_{pc}$ = 1.0 in accord with diffusion control. A potential separation between cathodic and anodic peaks was about 0.070 V for a sweep rate of 0.30 V/s. After 1 $e^-$ reduction of **2** in $CH_2Cl_2$ at −15°C the paramagnetic complex $Cp^{\dagger}_2NbF_2$ was obtained which exhibits a ten-line EPR spectrum with a triplet hyperfine structure ($g$ = 1.956; $A_{Nb}$ = 114.2 G; $A_F$ = 20 G). Attempts to isolate this compound were unsuccessful because of its instability.[19] The negative oxidation potential ($E_{1/2}$ = −0.38 V) of $Cp^{\dagger}_2NbF_2$ may explain the relatively easy formation of the Nb(V) compound **2** in the presence of $HPF_6$. We have verified that the addition of $HPF_6$ on electrogenerated $Cp^{\dagger}_2NbF_2$ yields complex **2**. The fate of the $PF_6^-$ anion during oxidation of the Nb(II) species has not been followed, but it may be supposed as in previous work[20] that $PF_5$ has been formed after $F^-$ transfer to the complex giving rise to a polymerization of THF. In this regard it is important to note that "$Cp^{\dagger}_2Nb$" containing solutions with HCl form $Cp^{\dagger}_2NbCl_2$ in good yield. No hint for any Nb(V) compound was obtained because of the positive oxidation potential of **1b** (Table V).

The interaction of "$Cp^{\dagger}_2Nb$" with smaller amounts of $HPF_6$ (e.g. 1.5 equiv) gave complex **2** and two byproducts, which were identified as $[Cp^{\dagger}_2NbCl_2]PF_6$ (**3**) and $[Cp^{\dagger}_2NbCl(Cl,F)]PF_6$ (**4**). The latter complex, which apparently is the result of a cocrystallization of **2** and **3**, was only detected by an X-ray diffraction analysis (Figure 5; Tables IV and VIII): The structure solution required the occupation of one chloro site by $^1/_3$ of a fluoride. Another hint for the presence of a fluoro ligand in the crystal is the unusual difference of 0.083 Å between both Nb–Cl distances. The overall geometry of **4** is the same as in **1b** and **2**, but the angle Cl1–Nb–Cl2 (96.8(1)°) is much closer to the value observed in **2** than in **1b** and is thus indicative for a Nb(V) compound.

Complex **3** has been characterized by comparison with independently synthesized samples (see below). The degree of cocrystallization between **2** and **3** obviously depends on crystallization conditions. It is responsible for color variations of the products from yellow to deep red, and it can roughly be examined in the IR spectra by the intensity ratio of the $\nu_{Nb-F}$ and the $\nu_{P-F}$ absorptions. As the slightly positive oxidation potential of **1b** (Table V) does not allow its oxidation by $H^+$, the formation of **3** (and **4**) must be interpreted as a substitution of fluoride in preformed **2** by chloride, which is present from the reduction process. In a control experiment **2** was reacted with an excess of HCl giving pure **3** in good yields. More convenient for the preparation of **3** is the oxidation of $Cp^{\dagger}_2NbCl_2$ by means of $(C_5H_5)_2FePF_6$.[21] Both methods produced compounds slightly contaminated by traces of the starting material, which gave rise to broadened $^1H$ NMR signals.

The difference in the potentials ($\Delta E_{1/2(Ox)}$ = 0.45 V, Table V) of **2** and **3** is also expressed in their reactivity toward $Li_2S_2$: Whereas **3** is reduced to give **1b** in 45% yield, **2** forms the neutral Nb(V) compound **5**, in which one fluoro ligand is replaced by a $\eta^2$-$S_2$ ligand. From spectroscopic data one may deduce a similar structure as in related diamagnetic group V metallocene disulfides.[22] This means that a symmetry plane divides the molecule into two equivalent halves. Therefore, the duplication of two of the ring methyl resonances in the $^1H$ NMR spectrum is attributed to a weak $^{19}F$–$^1H$ coupling in the range between 0.8 and 1.1 Hz. Such a coupling is not present in **2**.

## Conclusions

The electron-donating effect of the ring alkyl groups exerts a considerable influence on the electrochemical and chemical reduction of the peralkylated $Cp_2Nb$ dihalides. The resulting low-valent niobocene species exist in two forms as has been established by EPR studies. Further proofs will be needed however to establish the proposed

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(19) The formation of the "extremely air sensitive" $(C_5H_5)_2NbF_2$ has already been observed in a fluoride transfer from hexafluorobutyne to $(C_5H_5)_2NbH_3$: Sala-Pala, J.; Amaudrut, J.; Guerchais, J. E.; Mercier, R.; Douglade, J.; Theobald, J. G. *J. Organomet. Chem.* **1981**, *204*, 347.

(20) Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718.

(21) This method has already been employed for the synthesis of other niobocene(V) halides: Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1987**, *6*, 473.

(22) Bach, H.-J.; Brunner, H.; Wachter, J.; Kubicki, M. M.; Leblanc, J.-C.; Moise, C.; Volpato, F.; Nuber, B.; Ziegler, M. L. *Organometallics* **1992**, *11*, 1403 and references cited therein.

hydride transfer from a ring alkyl group to the Nb center of the completely reduced niobocenes "Cp*$_2$Nb" and "Cp$^†_2$-Nb". The reduced species exhibit a pronounced reduction potential which permits the synthesis of novel fluoroniobocene derivatives. An extension of this behavior to other inorganic redox systems seems to be promising, and we are going to investigate the nucleophilic fragmentation of sulfur and the activation of $CO_2$ in our laboratories. The carbenoid character of electron-rich niobocenes with respect to unsaturated organic compounds[1,5,23] and a comparison to "reactive" titanocene may also be worthy of further investigations.[24]

**Acknowledgment.** We are grateful to the Deutsche Forschungsgemeinschaft and Electricité de France (Novelect Bourgogne) for financial support. We thank Dr. Y. Mowad for his helpful interest, Mrs. M. T. Compain for her technical assistance, and Dr. J.-C. Leblanc for taking the $^{19}$F NMR spectra. Prof. G. Huttner is acknowledged for financial support of X-ray crystallography.

**Supplementary Material Available:** Tables S1–S3, listing the anisotropic thermal parameters for non-hydrogen atoms (2 pages). Ordering information is given on any current masthead page.

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[23] Fermin, M. C.; Hneihen, A. S.; Maas, J. J.; Bruno, J. W. *Organometallics* **1993**, *12*, 1845.

[24] Shur, V. B.; Berkovich, M. E.; Vol'pin, M. E.; Lorenz, B.; Wahren, M. *J. Organomet. Chem.* **1982**, *228*, C36. Schobert, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 855.