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Quantitative Oxidation of Organovanadium(IV) and -niobium(IV) Complexes: Synthesis of $Cp_2V(SbF_6)_2$, $[Cp_2VCl_2][AsF_6]$, and $[Cp_2V(AsF_6)_2][AsF_6]$. Crystal Structure of $[Cp_2NbCl_2][SbF_6]$

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Niobocene dichloride, Cp_2NbCl_2 (1), reacts with SbF_5 to give $[Cp_2NbCl_2][SbF_6]$ (2). The X-ray structure of 2 has been determined and shows 2 to consist to discrete SbF_6^- anions, which show the usual octahedral geometry but are slightly disordered in the crystal, and $Cp_2NbCl_2^+$ cations with an approximate tetrahedral coordination of the Nb atom. The average Nb–Cl distance is 2.341 Å; the Nb–C distances range from 2.354 to 2.455 Å with an average of 2.404 Å. The mean distance from Nb to the Cp ring centroids is 2.087 Å. The angle Cl–Nb–Cl is 98.10°; the average of the centroid–Nb–Cl angles is 106°, the angle at Nb between the centroids 131°, and the angle between the ring planes 51.4°. 2 crystallizes in the orthorhombic space group $P2_1cn$ with cell constants $a = 8.557$ (3) Å, $b = 12.753$ (4) Å, $c = 13.839$ (6) Å, $V = 1510.2$ Å^3, $Z = 4$, and $R(F) = 3.3\%$. The oxidation of vanadocene dichloride, Cp_2VCl_2 (3), which is not possible by common agents such as Ag^+, with AsF_5 has been estimated to be thermodynamically favored by simple Born–Haber cycles and has been proved to be a convenient and quantitative synthesis of novel organovanadium(V) species. $[Cp_2VCl_2][AsF_6]$ (5) and $[Cp_2V(AsF_6)_2][AsF_6]$ (6) were prepared and characterized by elemental analysis, IR, ^1H NMR, and ^{19}F NMR spectroscopy (5: $\delta = -58.75$ ppm, q; relative to $CFCl_3$; $J = 937 \pm 5$ Hz). The preparation and characterization of the paramagnetic $Cp_2V(SbF_6)_2$ (4) is also reported. The EPR spectrum of 4 shows a nicely resolved eight-line spectrum ($g = 1.9738$), indicating that the unpaired electron is mainly localized at the ^{51}V.

Introduction

Currently we are investigating routes to high oxidation state transition-metal complexes containing highly fluorinated ligand systems.[1,2] Recently we prepared $Cp_2Ti(AsF_6)_2$ (from Cp_2TiCl_2 and $AgAsF_6$ or from Cp_2TiF_2 and AsF_5) which was the first fluorine coordinated hexafluoropnicogenate complex of an electron-deficient metallocene derivative.[1,2] From these results our interest arose to investigate also other transition-metal groups. Especially the chemistry of group 5 seemed to be interesting (cf. ref 3–5), as two further aspects, one thermodynamic/kinetic and one steric, are of importance: (i) Will Cp_2MCl_2 (M = V, 3; M = Nb, 1) react with $AgAsF_6$ in analogy to Cp_2TiCl_2 by substitution of the chloro ligands remaining in oxidation state IV or will the metallocene fragment be oxidized (Ag^+/Ag) yielding a species like $Cp_2MCl_2(AsF_6)$? (ii) Which structure will be realized in derivatives of the type $Cp_2MCl_2(AsF_6)$? Will they contain (for electronic reasons) a direct M···F···As bond with coordination number five in analogy to the structurally characterized $Cp_2Ti(AsF_6)_2$[1] or will an ionic species of the type $[Cp_2MCl_2][AsF_6]$ be obtained due to steric reasons in analogy to $[Cp_2Ti(CH_3CN)_n]^{2+}[AsF_6]_2^-$?[6]

Quite recently the first niobocene(V) hexafluorophosphate was prepared by reaction of $Cp_2NbCl(SiMe_3)$ with ferrocenium hexafluorophosphate.[7] However, oxidation of $Cp_2NbCl(SiMe_3)$ with $[Cp_2Fe][PF_6]$ results in a complex reaction that produces Me_3SiCl, Me_3SiF, $[Cp_2Nb(CH_2SiMe_3)Cl][PF_6]$, and $[Cp_2NbCl_2][PF_6]$.

We were particularly interested to plan our synthesis on the basis of simple thermodynamic estimations. By doing this and simple mechanistical reactions, we try to achieve one of our goals of preparing the compounds in one single step in quantitative or high yields.

Results and Discussion

Preparation and Properties of $[Cp_2NbCl_2][SbF_6]$ (2). We have shown that the direct oxidation of an organometallic compound with agents such as Ag^+, NO^+, I_3^+, AsF_5, SbF_5, and F_2 seems to be not only of potential but also of general interest for the preparation of numerous of high oxidation state organometallic complexes.[8] Although 2 can be prepared by the oxidation of 1 with $AgSbF_6$, $NOSbF_6$, or I_3SbF_6 very conveniently (see also thermodynamic aspects), we got the best orange-red crystals suitable for X-ray diffraction by preparing 2 according to eq 1 and recrystallizing the product twice from SO_2. The characterization of 2 was achieved by microanalysis, ^1H NMR, ^{19}F NMR, IR, and mass spectroscopy (see Experimental Section). The ^1H NMR spectrum of 2 in SO_2 consists of one singlet at $\delta = 6.97$ ppm (relative to TMS in SO_2) due to the 10 equivalent Cp protons. The ^{19}F NMR spectrum shows a complex multiplet at $\delta = -110$ ppm (relative to $CFCl_3$) due to the couplings ^{19}F to ^{121}Sb and ^{123}Sb. In the IR spectrum (CsI) the absorptions of the Cp ring, the octahedral (not coordinated!) SbF_6^- anion, and the Nb–Cl stretching modes were observed. SbF_3 was identified by IR spectroscopy in the reaction residue as it is insoluble in SO_2. Due to the ionic character of 2 in the mass spectrum (EI, 70 eV) only fragments of both the cation and the anion could be observed.

$$\underset{1}{2Cp_2NbCl_2} + 3SbF_5 \xrightarrow{SO_2} \underset{2}{2[Cp_2NbCl_2][SbF_6]} + SbF_3 \qquad (1)$$

Structural Aspects of 2. The X-ray structure analysis shows 2 to consist of discrete SbF_6^- anions, which show the usual octahedral geometry but are slightly disordered in the crystal, and $Cp_2NbCl_2^+$ cations with an approximately

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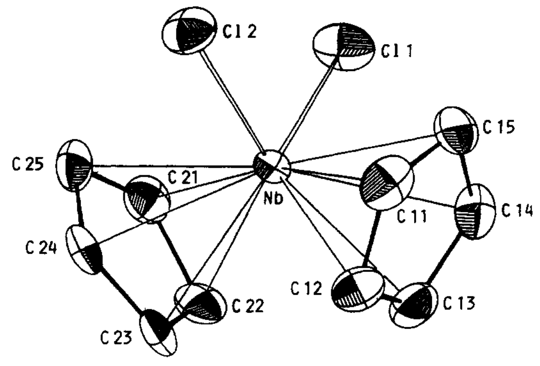
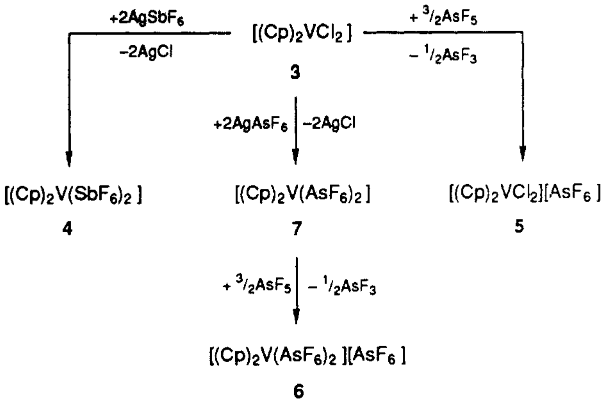


Figure 1. Structure of the $Cp_2NbCl_2^+$ cation in $[Cp_2NbCl_2][SbF_6]$ (2).

Scheme I. Reactions of Cp_2VCl_2 (3)



tetrahedral coordination of the Nb atom (Figure 1). The average Nb–Cl distance is 2.341 Å, which is considerably shorter than the Nb–Cl distance of 2.470 Å in 1,[9] as is to be expected, but comparable with the Nb–Cl distance of 2.370 Å in $[Cp_2NbCl]_2O^{2+}[BF_4]^-{}_2$.[9] Nb–C distances range from 2.354 to 2.455 Å with an average of 2.404 Å. The mean distance from Nb to the Cp ring centroids is 2.087 Å, which agrees well with the values of 2.09 Å in 1 and 2.10 Å in $[Cp_2NbCl]_2O^{2+}[BF_4]^-{}_2$, respectively; the angle Cl1–Nb–Cl2 is 98.10°, compared with 85.6° in 1 and 96.2° in $[Cp_2NbCl]_2O^{2+}[BF_4]^-{}_2$, this is well in agreement with both the positive charge at the metallocene fragment and therefore the shorter Nb–Cl bond compared with those in neutral 1. The average of the centroid–Nb–Cl angles is 106°, the angle at Nb between the centroids 131°, and the angle between the ring planes 51.4°.[10]

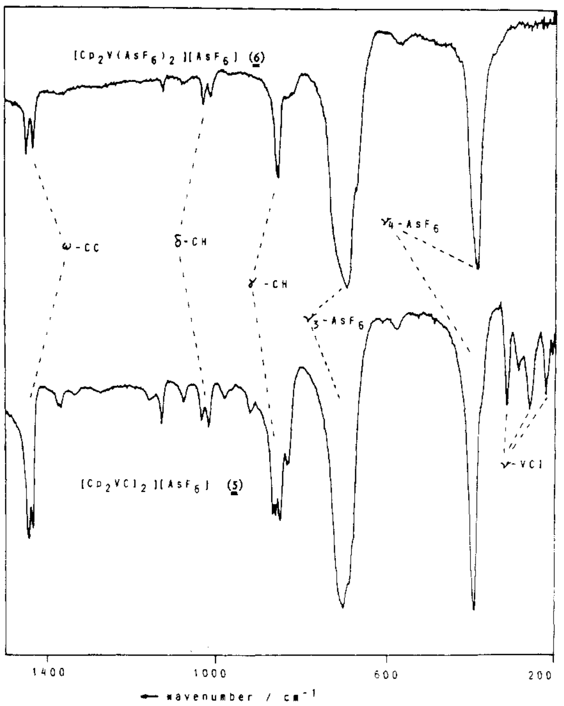


Figure 2. Infrared spectra (CsI) of 5 and 6.

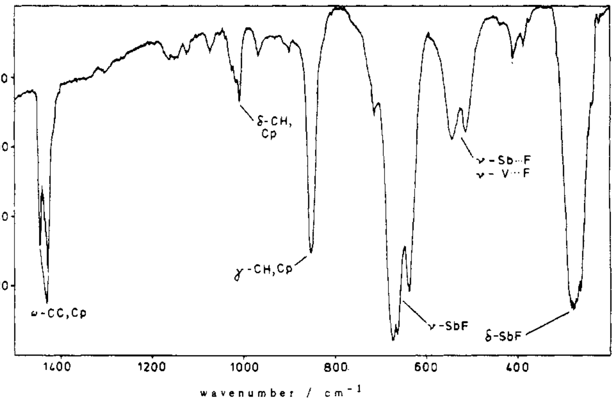


Figure 3. Infrared spectrum (CsI) of 4.

While in $Cp_2Ti(AsF_6)_2$ the AsF_6 unit is directly coordinated to the Ti center (linear Ti···F···As unit)[1] in 2, there is no F coordination to the $Cp_2NbCl_2^+$ cation. So only superficially the high oxidation state niobocene species can be seen in analogy to the titanocene(IV) derivatives (as IV is the highest stable oxidation state for Ti).

Preparation and Properties of $Cp_2V(SbF_6)_2$ (4), $[Cp_2VCl_2][AsF_6]$ (5), and $[Cp_2V(AsF_6)_2][AsF_6]$ (6). Scheme I illustrates all the reactions that have been carried out in vanadium chemistry yielding the products nearly quantitatively. Although Ag^+ thermodynamically should be able to oxidize Cp_2VCl_2 (3), only substitution of the chloro ligands could be observed and the redox reaction is supposed to be kinetically hindered. On the other hand, AsF_5 oxidizes 3 yielding the cationic 5 which is, as far as we are aware, the first example of a stable vanadocene(V) dichloride cation and one of the few organovanadium(V) species. $Cp_2V(AsF_6)_2$ (7) was prepared according to Scheme I, but not isolated, and directly oxidized yielding the quite unstable tris(hexafluoroarsenate) derivative 6.

The IR spectra of 5 and 6 are similar (Figure 2) but clearly show the V–Cl stretching modes in the case of 5. The IR spectrum of 4 (Figure 3) shows all expected absorptions. The splitting of the ν_3 and the ν_4 modes of the SbF_6 unit as well as V···F and Sb···F bands are indicative

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[10] Crystal data: $C_{10}H_{10}Cl_2F_6NbSb$, M = 529.8, orthorhombic, space group $P2_1cn$ (nonstandard setting of $Pna2_1$, No. 33), a = 8.557 (3), b = 12.753 (4), c = 13.839 (6) Å; V = 1510.2 Å^3; Z = 4; D_{calcd} = 2.33 g cm^{-3}; $F(000)$ = 1000; crystal size 0.5 × 0.4 × 0.1 mm; μ(Mo Kα) = 2.93 mm^{-1}. Data were collected by using a four-circle diffractometer Syntex $P2_1$: Mo Kα radiation (graphite monochromator, λ = 0.71069 Å); 1996 unique reflections with $2\theta_{max}$ = 55° measured; 1634 with $I \geq 2\sigma(I)$ used for calculations (program system SHELX-76); numerical absorption correction; transmissions 0.28–0.77; Sb and Nb located by the Patterson method and C and F from difference maps; hydrogen positions calculated and eventually refined with fixed thermal parameters, non-hydrogen atoms refined anisotropically on F to R = 0.033 and R_w = 0.034; weighting scheme $w^{-1} = \sigma^2(F) + 0.00056F^2$; 273 parameters; S = 1.27; maximum shift/esd = 0.2; maximum residual electron density = 0.75 e Å^{-3} near the Sb atom. The $[SbF_6]^-$ anion shows a rotational disorder. One of the Cp rings (ring 2) is also disordered; it exists in two orientations; both were taken into account in the refinement, but only one is shown in the plot. Further details of the structure determination have been deposited with the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany, and may be obtained by quoting a full literature citation and the reference number CSD-53613.

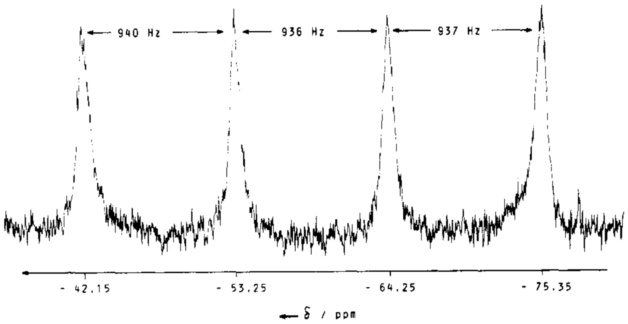


Figure 4. ^{19}F NMR spectrum of **5** (SO_2, 20 °C, relative to $CFCl_3$).

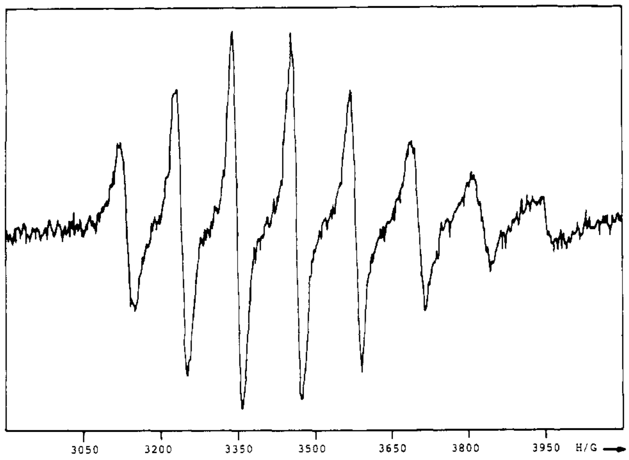


Figure 5. EPR spectrum of **4** (benzene solution, saturated, 25 °C).

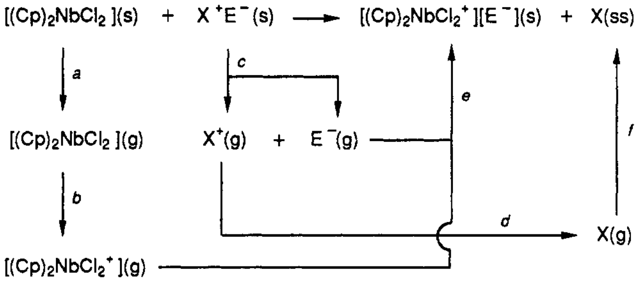
for the covalent structure as observed for $Cp_2Ti(AsF_6)_2$ (X-ray structure analysis).[1]

The ^{19}F NMR spectrum of **5** in SO_2 (Figure 4) shows one nicely resolved quartet at $\delta = -58.75$ ppm (relative to $CFCl_3$) due to the $^{19}F-^{75}As$ couplings (^{75}As, $I = {}^{3}/_{2}$) with a coupling constant of 937 ± 5 Hz. The broad and badly resolved multiplet in the ^{19}F NMR spectrum of **6** is well in agreement with its composition with two coordinated and one ionic AsF_6 units.

Instead of NMR data for the paramagnetic **4**, EPR spectra were recorded. A nicely resolved eight-line spectrum (benzene solution) was observed (Figure 5), indicating that the unpaired electron is mainly localized at the ^{51}V (^{51}V, $I = {}^{7}/_{2}$; $g = 1.9738$). From IR and ^{19}F NMR data it can be concluded that **5** exists isostructural to **2** which was characterized by X-ray diffraction (see above). Due to steric reasons the coordination number four is highly favored for most of the early transition element metallocene complexes and **2** and **5** may very well be regarded as an analogue of $[Cp_2Ti(CH_3CN)_n][AsF_6]_2$, which, however, was prepared on a very different route.[6] While the acetonitrile complex is one derivative of the well-known group of Lewis base coordinated titanocene cations,[11-14] **2** represents as far as we know the first completely characterized example of a cationic niobocene complex of the composition $[Cp_2MCl_2][XF]$ where X is a Lewis acidic perfluoro nonmetal species (e.g. X = BF_3, AsF_5, SbF_5).[4]

Thermodynamic Aspects. We estimated that the oxidation reactions leading to niobocene(V) and vanadocene(V) species were thermodynamically allowed on the basis of simple Born–Haber cycles. A cycle representing the oxidation of **1** with $NOSbF_6$, I_3SbF_6, $AgAsF_6$, and $NOBF_4$ is given in Scheme II. Using a similar approach,

Scheme II. Energy Cycle for the Formation of $[Cp_2NbCl_2]^+[E]^-$



[a] $\Delta H_{subl}(Cp_2NbCl_2)$ was taken to be equal to $\Delta H_{subl}(Cp_2ZrCl_2)$, 23 kcal/mol.[15a] [b] Ionization potential of Cp_2NbCl_2 estimated as $I_p(Cp_2NbCl_2) = 0.5(1.00 + 0.77)I_p(Cp_2VCl_2) = 134$ kcal/mol, calibrated on $I_p(Cp_2VCl_2) = 152$ kcal/mol.[16] The first I_p of Nb relative to V is 1:1, but the fifth I_p of Nb relative to V is 0.77:1.00.[17,18] This calibration is possible as the nonbonding a_1 orbital in Cp_2MX_2 complexes is primarily derived from orbital $1a_1$ (with metal character).[19] [c] Crystal lattice energy (U_L in kcal/mol), calculated from the molecular volume (V_M in Å^3) using the linear relationship: $U_L = 556.3\,(V_M)^{-0.33} + 26.3$.[20,21] $V_M(I_3^+) = 135$ Å^3,[22,23] $V_M(AsF_6^-) = 105$ Å^3,[23] $V_M(Ag^+) = 26$ Å^3 (estimated from $d(AgF) = 5.852$ g/cm^3,[24] $V_M(F^-)$ was taken to be equal to 10 Å^3), $V_M(NO^+) = 16.5$ Å^3,[24-26] $V_M(SbF_6^-) = 123$ Å^3,[27,28] and $V_M(BF_4^-) = 72.6$ Å^3.[24-26] This gives $U_L(I_3AsF_6) = 116$ kcal/mol, $U_L(NOSbF_6) = 134$ kcal/mol, $U_L(AgAsF_6) = 136$ kcal/mol, and $U_L(NOBF_4) = 151$ kcal/mol. [d] Oxidation potential $I(NO(g) \rightarrow NO^+(g)) = 215$ kcal/mol,[18] $I(Ag(g) \rightarrow Ag^+(g)) = 176$ kcal/mol,[18] and $I(3I(g) \rightarrow I_3^+(g)) = 170$ kcal/mol (calculated from $3I(g) \rightarrow I_2(g) + I(g) \rightarrow I_2^+(g) + I(g) \rightarrow I^+(g) + 2I(g) \rightarrow I_3^+(g)$; for details see ref 23). [e] U_L, see c. $V_M(Cp_2NbCl_2^+) = 252$ Å^3.[10] This gives $U_L(Cp_2NbCl_2^+SbF_6^-) = 103$ kcal/mol, $U_L(Cp_2NbCl_2^+AsF_6^-) = 105$ kcal/mol, and $U_L(Cp_2NbCl_2^+BF_4^-) = 107$ kcal/mol. [f] $\Delta H_{subl}(Ag) = 68.1$ kcal/mol;[18] $\Delta H_{atomization}(I_2(s)) = 25.6$ kcal/mol[18] (ss = standard state).

Table I. Estimated Heats of Reactions for the Formation of $[Cp_2MCl_2][X]$ (M = V, Nb; X = SbF_6, AsF_6, BF_4) from Cp_2MCl_2 and the Corresponding Oxidizing Agent According to Scheme II

oxidizing agent	ΔH_r/kcal·mol^{-1} (per mol of $[Cp_2MCl_2][X]$)
$NOSbF_6$	−27
I_3AsF_6	−79
$AgAsF_6$	−56
$NOBF_4$	−14
AsF_5[a]	−71
AsF_5[b]	−63

[a] $Cp_2NbCl_2 + {}^{3}/_{2}AsF_5 \rightarrow [Cp_2NbCl_2][AsF_6] + {}^{1}/_{2}AsF_3$. [b] $Cp_2VCl_2 + {}^{3}/_{2}AsF_5 \rightarrow [Cp_2VCl_2][AsF_6] + {}^{1}/_{2}AsF_3$.

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we showed that the oxidation of **1** with AsF_5 (which is very similar to SbF_5; SbF_5 should even be a better oxidizing agent) and **3** with AsF_5 (yielding **5**) are also thermodynamically favorable. The heats of the reactions are summarized in Table I.

Experimental Section

All techniques have been described previously.[8] The reactions were done in SO_2(l) between −30 °C and room temperature. All byproducts were either volatile (AsF_3) or insoluble in SO_2 (Ag, AgCl, SbF_3) and could be separated by pumping or filtration, respectively. The products were recrystallized from either SO_2 or a mixture of $SO_2/CFCl_3$ or SO_2/SO_2ClF. Elemental analyses were performed by Malissa & Reuter, Analytische Laboratorien, Engelskirchen, or recorded on a Hewlett-Packard 185. ^1H NMR spectra were recorded at 80 MHz with a Bruker WP 80 or at 60 MHz with a Varian EM 360. ^{19}F NMR spectra were recorded with a SXP 90 at 84 MHz. Infrared spectra were recorded on a Perkin-Elmer 580B; EPR spectra were recorded on a Varian E-300 spectrometer.

1 and **3** were used after recrystallization from SO_2 as commercially available (Aldrich). AsF_5 (Union Carbide) was purified by condensation, SbF_5 (Alfa) was purified by destillation. $AgAsF_6$ and $AgSbF_6$ were prepared from AgF and AsF_5 or SbF_5 as described previously.[6]

$[Cp_2NbCl_2][SbF_6]$ (2). A cold solution (−30 °C) of **1** (0.5610 g, 1.908 mmol) in SO_2 (10 mL) was added to a cold solution (−30 °C) of SbF_5 (0.6182 g, 2.852 mmol) in SO_2 (10 mL). After the solution was stirred for 30 min at −30 °C, the color changed from dark brown to orange. The solution was then allowed to warm to room temperature. After filtration (orange solution of **2**, white solid of SbF_3) the solvent was evaporated and the orange-red product was recrystallized twice from SO_2 (10 mL) giving red crystals (mp 164 °C dec) in 98% yield (1.11 g).

Anal. Calcd for $C_{10}H_{10}Cl_2F_6NbSb{\cdot}SO_2$: C, 20.23; H, 1.70. Found: C, 19.96; H, 1.63. IR (CsI, cm^{-1}): 3125 (m, ν(CH)), 1738 (w, br, ν(NbH)), 1438 (m, ω(CC)), 1368 (w, δ(CH)), 1172 (w, δ(CH)), 1126 (w, δ(CH)), 1070 (vw, Δ(CCC)), 1029 (w, Δ(CCC)), 1014 (w, δ(CH)), 965 (vw, δ(CH)), 863 (s, γ(CH)), 743 (m, ν_{as}(NbONb)), 660 (vs, $\nu_3(SbF_6^-)$), 645 (sh, $\nu_3(SbF_6^-)$), 578 (w, Δ(CCC)), 398 (w, ring tilt), 380 (w, ν(NbCp)), 345 (m, ν(NbCl)), 288 (vs, $\nu_4(SbF_6^-)$). ^1H NMR (SO_2, 20 °C, relative to TMS, ppm): 6.97 s. ^{19}F NMR (SO_2, 20 °C, relative to $CFCl_3$, ppm): −110 m. MS (EI, 70 eV, 60 °C, *m/z* (rel intens); *m/z* >64 (rel intens >4%)): 293 (5, $Cp_2NbCl_2^+$), 274 (5, Cp_2NbClO^+), 258 (8, Cp_2NbCl^+), 228 (8, $CpNbCl_2^+$), 197 (8, SbF_4^+), 193 (5, $CpNbCl^+$), 178 (11, SbF_3^+), 163 (11, $NbCl_2^+$), 159 (11, SbF_2^+), 140 (8, SbF^+), 128 (11, $NbCl^+$), 85 (100, $CpFH^+$), 84 (39, CpF^+), 65 (32, Cp^+).

$Cp_2V(SbF_6)_2$ (4). At room temperature a solution of **3** (0.5786 g, 2.296 mmol) in SO_2 (10 mL) was added to a solution of $AgSbF_6$ (1.5790 g, 4.595 mmol) in SO_2 (15 mL). The mixture was stirred for 30 min at room temperature and filtered (dark solution of **4**, residue of AgCl), and the solution was concentrated to dryness. The remaining black solid was recrystallized from $SO_2/CFCl_3$ (15 mL), and black crystals were isolated (1.147 g, 76%).

Anal. Calcd for $C_{10}H_{10}F_{12}Sb_2V$: C, 18.40; H, 1.54. Found: C, 18.17; H, 1.38. IR (CsI, cm^{-1}): 3108 (m, ν(CH)), 1443 (m, ω-CC), 1428 (s, ω(CC)), 1122 (w, δ(CH)), 1025 (sh, δ(CH), 1010 (m, δ(CH)), 900 (w, γ(CH)), 850 (s, γ(CH)), 665 (vs, $\nu_{eq}(SbF_6)$), 660 (sh, ν-(SbF_6)), 640 (sh, $\nu_{ax}(SbF_6)$), 545 (m, ν(Sb···F) and ν_s(V···F)), 515 (m, ν(Sb···F) and ν_{as}(V···F)), 410 (ring tilt), 390 (w, ν(VCp)), 280 (vs, $\delta(SbF_4$, eq) in SbF_6), 275 (sh, $\delta(SbF_4$, eq) in SbF_6). MS (EI, 70 eV, 20 °C, *m/z* (rel intens); *m/z* >64 (rel intens >3%)): 178 (100, SbF_3^+), 159 (78, SbF_2^+), 140 (36, SbF^+), 135 (12, $CpVF^+$), 129 (18, $C_{10}H_9^+$), 121 (28, Sb^+), 70 (14, SbF^{2+}), 65 (39, Cp^+). EPR (benzene, 25 °C, $\nu = 9.73 \times 10^9$ Hz): $H = 3522$ G, $A = 116.3$ G, $g = 1.9738$, eight-line spectrum.

$[Cp_2VCl_2][AsF_6]$ (5). **5** was prepared completely in analogy to the synthesis of **2**. As AsF_3 is volatile, the solvent (SO_2) and the byproduct (AsF_3) were removed by pumping. **3** (0.9150 g, 3.63 mmol) was reacted with AsF_5 (0.9260 g, 5.45 mmol) yielding **5** quantitatively. **5** was recrystallized from SO_2/SO_2ClF giving a black microcrystalline product in 84% yield (1.34 g). The solution of **5** in SO_2 is dark blue-green.

Anal. Calcd for $C_{10}H_{10}AsCl_2F_6V$: C, 27.24; H, 2.28. Found: C, 26.91; H, 2.16. IR (CsI, cm^{-1}): 3135 (m, ν(CH)), 1442 (s, ω(CC)), 1433 (m, ω(CC)), 1129 w (δ(CH)), 1030 (sh, δ(CH)), 1015 (w, δ(CH)), 868 (sh, γ(CH)), 860 (sh, γ(CH)), 850 (s, γ(CH)), 835 (sh, γ(CH)), 700 (vs, br, $\nu_3(AsF_6^-)$), 398 (vs, $\nu_4(AsF_6^-)$), 320 (m, ν(VCl)), 268 (m, ν(VCl)), 225 (m, ν(VCl)). ^{19}F NMR (SO_2, 20 °C, relative to $CFCl_3$, ppm): −42.15, −53.25, −64.25, −75.35; $J = 937 \pm 5$ Hz.

$[Cp_2V(AsF_6)_2][AsF_6]$ (6). A cold solution (−30 °C) of **3** (0.437 g, 1.734 mmol) in SO_2 (10 mL) was added to a cold solution (−30 °C) of $AgAsF_6$ (1.030 g, 3.471 mmol) in SO_2 (10 mL) and allowed to warm to room temperature. After filtration the remaining residue (AgCl) was washed several times with SO_2. The dark brown solution (20 mL) containing **7** was then recooled and frozen at −196 °C. Onto the frozen solution was condensed AsF_5 (0.44 g, 2.60 mmol), and the mixture was allowed to warm to −20 °C (red-brown solution). After the mixture was stirred for 30 min at −20 °C, SO_2 and AsF_3 were removed in a dynamic vacuum at +5 °C. The remaining black product (1.15 g, 89%) was characterized without further purification due to its instability.

Anal. Calcd for $C_{10}H_{10}As_3F_{18}V$: C, 16.06; H, 1.35. Found: C, 15.79; H, 1.20. IR (CsI, cm^{-1}): 3130 (m, ν(CH)), 1450 (m, ω(CC)), 1448 (m, ω(CC)), 1130 (w, δ(CH)), 1035 (w, δ(CH)), 1020 (w, δ(CH)), 860 (s, γ(CH)), 700 (vs, br, $\nu(AsF_6)$), 395 (vs, $\delta(AsF_6)$). ^{19}F NMR (SO_2, 20 °C, relative to $CFCl_3$, ppm): −47.55 (s, br, $\nu/2$ = 1850 Hz).

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Supplementary Material Available: Structure determination summary and tables of final atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom coordinates in German (7 pages); a listing of final observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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