Stable NMR- and EPR-Active 17-Electron Chromium(III) Half-Sandwich Compounds

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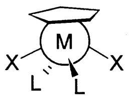
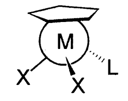
Formerly elusive 17-electron half-sandwiches of chromium(III) were isolated after stabilization with isocyanide ligands by using different approaches. Thus, reaction of Cp_2Cr with CF_3SO_3H and $CNCH_3$ gave $[CpCr(CNCH_3)_4]^{2+}$ ($\mathbf{7}^{2+}$) as a triflate, while $[(R_nCp)CrCl_2]_2$ (R = Me, H (**3** and **5**, respectively), $n = 5$; R = *t*-Bu, $n = 1$ (**8**)) reacted with $Tl(CF_3SO_3)$ to give $\mathbf{7}^{2+}$, $[(C_5Me_5)Cr(CNCH_3)_4]^{2+}$ ($\mathbf{2}^{2+}$), and $[(t\text{-BuCp})Cr(CNCH_3)_4]^{2+}$ ($\mathbf{10}^{2+}$) again as triflates in up to 59% yield. The precursor **8** was synthesized from (*t*-BuCp)Na and $CrCl_3(THF)_3$. The dication $\mathbf{2}^{2+}$ was also obtained electrochemically from $[(C_5Me_5)Cr(CNCH_3)_4]^+[PF_6]^-$ ($\mathbf{2}^+[PF_6]^-$), which was synthesized by reaction of $[(C_5Me_5)Cr(C_6H_3Me_3)]^+[PF_6]^-$ with $CNCH_3$ in 86% yield. Conversely, the dication $\mathbf{7}^{2+}$ could be reduced to $\mathbf{7}^+$ obtained as $[PF_6]^-$ and $[B(C_6H_5)_4]^-$ salts. The crystal structure of $\mathbf{10}^{2+}[CF_3SO_3]^-{}_2$ confirmed the four-legged piano-stool structure of $\mathbf{10}^{2+}$; no interaction of the chromium centers $\mathbf{10}^{2+}$ with the two triflates per formula unit could be detected. Cyclic voltammetry showed a reversible conversion between the cations $\mathbf{2}^{2+/1+}$, $\mathbf{7}^{2+/1+}$, and $\mathbf{10}^{2+/1+}$. By contrast, further oxidation to the trication and reduction to the neutral molecules proved to be irreversible. The dications were shown by NMR and EPR spectroscopies to contain one unpaired electron in the chromium d_{z^2} orbital. With ^1H and ^2H NMR spectroscopy the remote protons of substituted Cps and (after labeling) the deuterons of Cp and methylisocyanide ligands, respectively, were detected. The signs of the NMR signal shifts established negative spin density in the Cp π systems.

Introduction

Half-sandwich compounds of the type $[CpML_n]^{m+/-}$ (where Cp is cyclopentadienyl and L is a variety of ligands) are ubiquitous in organometallic chemistry, and yet they continue to be the focus of much current research. Thus, they are tunable reagents in organic synthesis,[2] they allow the assembly of ligands in such a way that the transition metal becomes chiral,[3] and they are key compounds in the study of electron transfer processes[4] and in olefin polymerization.[5] In addition, half-sandwiches are illuminating examples for demonstrating how the structure and the reactivity of organometallic compounds are related to their spin state.[6] A most remarkable difference emerged for the half-sandwiches of Cr(III), Mo(III), and W(III). They could adopt a piano-stool structure with four legs (**A**) or three legs (**B**), thus arriving at an electron count of 17 (S = 1/2) and 15 (S = 3/2), respectively. It turned out that, whenever the metal is molybdenum and tungsten, the piano-stool has four legs, while for chromium it usually has only three legs. This is also true when **A** and **B** are charged species, i.e., when the number of neutral ligands L and halogens X (and the like) are changed.



A



B

Since a few organometallic 17-electron chromium(III) compounds with structures other than **A** do exist ($CpCr(allyl)_2$,[7a] $[CpCr(2,4\text{-}Me_2Pdl)CO]^+$ (Pdl = pentadienyl),[7b] $(R_nCp)Cr(allyl)_2$[7c]), Poli and co-workers tested the stability limits of 17-electron chromium(III) half-sandwiches.[8] They found that the $CpCrX_2$ fragment does not add chelating phosphine ligands to yield type-**A** compounds, and they ascribed this to the high spin-pairing energy that is necessary for passing from the S = 3/2 to the S

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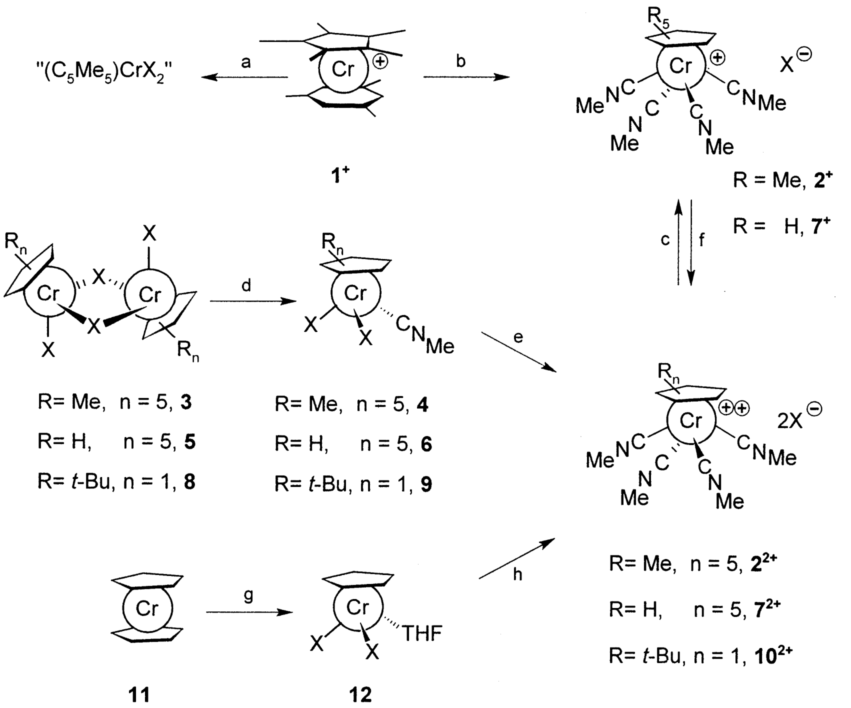
Scheme 1[a]



[a] Key: (a) CH_2Cl_2, 25 °C, $X^- = Cl^-/F^-/PF_6^-$; (b) CH_2Cl_2, CH_3NC, 25 °C, $X^- = PF_6^-$, $R = CH_3$; (c) electrochemical oxidation; (d) $CNCH_3$, $(CH_3)_2CO$, $X = Cl$; (e) $Tl(CF_3SO_3)$, $CNCH_3$, $(CH_3)_2CO$, $X^- = CF_3SO_3^-$; (f) (1) Zn, THF, (2) NH_4PF_6 or $NaB(C_6H_5)_4$, $R = H$; (g) CF_3SO_3H, THF; (h) $CNCH_3$, $X^- = CF_3SO_3^-$.

$= 1/2$ species.[8a,b] However, when the halide X^- was replaced by CN^-, $[(C_5R_5)Cr(CN)_4]^{2-}$ (R = Me, H) and $CpCr(CN)_2L_2$ (L_2 = chelating diphosphine or two PR_3) could be shown in solution to coexist with their precursors $[(C_5R_5)Cr(CN)_3]^-$. The equilibrium did not allow the isolation of a 17-electron chromium(III) half-sandwich, so that it remained an elusive species.

We came across stable $[(C_5R_5)Cr(CNCH_3)_4]^{2+}$ ions while investigating $[(C_5Me_5)Cr(arene)]^+$ derivatives.[9] These ions are simple representatives of the type of compounds in question. In what follows we report on synthetic approaches, spectroscopic and redox properties of the compounds, and their structure.

Results and Discussion

Syntheses. The key for the entry into the chemistry of the title compounds was the observation that $(C_5Me_5)Cr(arene)$ compounds may be easily oxidized to $[(C_5Me_5)Cr(arene)]^+$ isolated as PF_6^- salts and that these cations decompose in the presence of CH_2Cl_2 by splitting off the arene ligand. When the arene was hexamethylbenzene, the decomposition could be stopped at $[(C_5Me_5)Cr(C_6Me_6)]^+[(C_5Me_5)CrCl_3]^-$.[9] The mesitylene derivative $[(C_5Me_5)Cr(C_6H_3Me_3)]^+$ (**1**$^+$) slowly decomposed to a blue solid which contained $(C_5Me_5)Cr(III)$ fragments as shown by ^1H NMR spectroscopy and to a mixture of chloride, fluoride, and hexafluorophosphate (Scheme 1, step a). Since the blue solid could not be further characterized, the reaction of CH_2Cl_2 with **1**$^+[PF_6]^-$ was carried out in the presence of methylisocyanide in order to obtain the known compound $(C_5Me_5)CrCl_2(CNCH_3)$.[10] However, the reaction took a different course, and $[(C_5Me_5)Cr(CNCH_3)_4]^+[PF_6]^-$ (**2**$^+[PF_6]^-$) was isolated instead in more than 80% yield (Scheme 1, step b).

2$^+[PF_6]^-$ is a red crystalline diamagnetic compound which is soluble in polar solvents such as CH_2Cl_2 and CH_3CN. The ^1H and ^{13}C NMR spectra displayed two and three signals, respectively, and were thus consistent with a four-legged piano-stool structure. More specifically, the IR spectrum showed two ν(CN) bands at 2110 cm^{-1} (E) and 2170 cm^{-1} (A_1) as expected for local C_{4v} symmetry. Parallel to this work[1] Ernst's group prepared the ion $[CpCr(CNCMe_3)_4]^+$ from $[CpCr(2,4\text{-}Me_2Pdl)CO]^+[BF_4]^-$ and confirmed the structure of two salts by X-ray crystallography.[7b]

The formation of **2**$^+[PF_6]^-$ suggested that the replacement of the mesitylene ligand of **1**$^+[PF_6]^-$ by four $CNCH_3$ ligands (Scheme 1, step b) is faster than the electron transfer to CH_2Cl_2 (Scheme 1, step a). Also, it should be more difficult to oxidize **2**$^+$ than **1**$^+$. When this was confirmed by cyclic voltammetry (CV; see Electrochemistry below) it turned out that the electron transfer was chemically reversible and that the resulting dication $[(C_5Me_5)Cr(CNMe)_4]^{2+}$ (**2**$^{2+}$; Scheme 1, step c) was a stable species, at least on the CV time scale.

Since the starting cation **1**$^+$ had been prepared from $[(C_5Me_5)CrCl_2]_2$[9] (**3**), it seemed advantageous to synthesize **2**$^{2+}$ directly by starting from **3**. The reaction of **3** with $CNCH_3$ gave a blue solution of $(C_5Me_5)CrCl_2(CNCH_3)$ (**4**; Scheme 1, step d), which could be isolated in good yield.[10] Further reaction with excess $CNCH_3$ was only observed when the chloride ligands were split off with $Tl(CF_3SO_3)$ (Scheme 1, step e). This approach, which was realized in a one-pot reaction, gave pure

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$\mathbf{2}^{2+}[CF_3SO_3]^-{}_2$ in almost 60% yield. Similarly, $[CpCrCl_2]_2$ (**5**) and $[(t\text{-}BuC_5H_4)CrCl_2]_2$ (**8**) gave the intermediates $CpCrCl_2(CNCH_3)$ (**6**) and $(t\text{-}BuC_5H_4)CrCl_2(CNCH_3)$ (**9**), respectively, which may also be isolated,[10] and finally $[CpCr(CNCH_3)_4]^{2+}$ ($\mathbf{7}^{2+}$) and $[(t\text{-}BuC_5H_4)Cr(CNCH_3)_4]^{2+}$ ($\mathbf{10}^{2+}$) as triflate salts. Depending on whether the solvent contained acetone or acetonitrile, the isolated compounds were $\mathbf{7}^{2+}[CF_3SO_3]^-{}_2\cdot(CH_3)_2CO$ and $\mathbf{7}^{2+}[CF_3SO_3]^-{}_2\cdot CH_3CN$, respectively, while $\mathbf{10}^{2+}[CF_3SO_3]^-{}_2$ crystallized free of solvent. All salts were readily soluble in nitriles and acetone to form red solutions. The same color was observed when **5** was dissolved in CH_3CN and treated with $AgBF_4$, but $[CpCr(NCMe)_4]^{2+}$, which would correspond to $\mathbf{7}^{2+}$, could not be isolated as a BF_4^- salt.[11]

Another approach was realized by starting from chromocene (**11**). Reaction of **11** with trifluormethanesulfonic acid in THF gave $CpCr(CF_3SO_3)_2(THF)$[10] (**12**), which gave $\mathbf{7}^{2+}$ upon addition of an excess of $CNCH_3$. The reaction sequence (Scheme 1, steps g and h) can be monitored straightforwardly, because red **11** is converted to deep blue **12** and subsequently to orange-yellow $\mathbf{7}^{2+}$. The advantage of the approach is that triflate is split off from **12** more easily than chloride from **6**. This proved to be particularly useful for the selective deuteriation of $\mathbf{7}^{2+}$, which was necessary for the NMR experiments (see below). Thus, starting from Cp_2Cr and using $CNCD_3$ in step h of Scheme 1 gave $[CpCr(CNCD_3)_4]^{2+}$ ($\mathbf{7}^{2+}\text{-}d_{12}$), while $CpCr\text{-}d_{10}$ and $CNCH_3$ gave $[(C_5D_5)Cr(CNCH_3)_4]^{2+}$ ($\mathbf{7}^{2+}\text{-}d_5$).

The reaction was also carried out in acetonitrile and by starting from $CpCr(CF_3SO_3)_2(NCCH_3)$. This suggests that, generally, triflates of the type $CpCr(CF_3SO_3)_2$ (donor) are useful starting compounds. But there is also a limitation of the approach, because the reaction of $(C_5Me_5)_2Cr$ with CF_3SO_3H stops at $[(C_5Me_5)_2Cr]^+[CF_3SO_3]^-$ even at elevated temperature.

The dication $\mathbf{7}^{2+}$ could be reduced straightforwardly to $[CpCr(CNCH_3)_4]^+$ ($\mathbf{7}^+$) (Scheme 1, step f), which was obtained as $[PF_6]^-$ and $[B(C_6H_5)_4]^-$ salts. Thus, in principle, monocations $[(R_nCp)Cr(CNCH_3)_4]^+$ may be synthesized by starting from $[(R_nCp)CrCl_2]_2$, chromocenes, and $(R_nCp)Cr(arene)$. The first two routes proceed via half-sandwiches $(R_nCp)CrX_2(donor)$ like **4**, **6**, **9**, and **12** and, subsequently, $[(R_nCp)Cr(CNCH_3)_4]^{2+}$ like $\mathbf{2}^{2+}$ and $\mathbf{7}^{2+}$. The last two routes are limited by the fact that for some substituted Cp ligands the synthesis of the sandwich cations corresponding to $\mathbf{1}^+$ is not straightforward[9] and that not all chromocenes may be converted to the half-sandwiches (see above).

The conversion of the half-sandwich monocations to dications may be followed conveniently by using IR spectroscopy: The ν(CN) A_1 and E bands of $[(C_5R_5)Cr(CNCH_3)_4]^{2+}$ appear at roughly 100 cm^{-1} higher frequencies (2250 cm^{-1} $\geq \nu \geq$ 2200 cm^{-1}) than those of $[(C_5R_5)Cr(CNCH_3)_4]^+$ (2170 cm^{-1} $\geq \nu \geq$ 2110 cm^{-1}). This corresponds to the well-known correlation between the electron density at the metal center and ν(CN) of the ligands.[12]

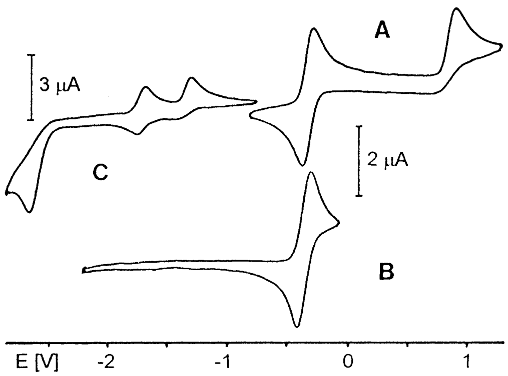

Figure 1. Cyclic voltammograms of $\mathbf{2}^+$, 1.22×10^{-3} mol L^{-1} in propionitrile at 22 °C. Supporting electrolyte 0.1 mol L^{-1} $n\text{-}Bu_4NPF_6$; scan rate 200 mV s^{-1}; scale relative to (internal) Cp_2Fe/Cp_2Fe^+. (A) Oxidations of $\mathbf{2}^+$. (B) Redox stability of $\mathbf{2}^+$ for $-2.2\ V < E < -0.85$ V. (C) CV obtained after cycling four times between −2.85 and −0.85 V (see text).

Electrochemistry. The conversion of the half-sandwich monocations to the dications is also reflected in the cyclic voltammograms. For instance, when the potential applied to a solution of $\mathbf{2}^+[PF_6]^-$ was increased, an oxidative wave developed, which, after cycling the potential, proved to belong to an electron transfer (ET) at −0.38 V relative to the potential of the couple Cp_2Fe/Cp_2Fe^+ (Figure 1). The ET is chemically reversible (ratio of the anodic over cathodic peak current $i_{pa}/i_{pc} = 1.02$) with a quasi-Nernstian wave (difference between anodic and cathodic peak potential $\Delta E_p = 85$ mV). The same ET was recorded when a solution of pure $\mathbf{2}^{2+}[CF_3SO_3]^-{}_2$ was used and when the potential was first decreased, so that it was attributed to the couple $\mathbf{2}^+/\mathbf{2}^{2+}$. When the potential was increased beyond 0 V, a second oxidation showed up at an anodic peak potential of $E_{pa} = 0.78$ V (Figure 1A). We attribute this wave to the formation of the 16-electron trication $[(C_5Me_5)Cr(CNCH_3)_4]^{3+}$, which decomposes before back-reduction can be achieved. As for the reduction, $\mathbf{2}^+$ is stable down to −2.2 V (Figure 1B). At more negative potentials an irreversible reduction is seen at a cathodic peak potential of $E_{pc} = -2.63$ V followed by two new features at −1.78 and −1.40 V on the reverse scan. Reductive waves associated with these features appear when the potential is cycled between −0.85 and −2.85 V, and a new reversible ET develops at −1.78 V with i_{pa} and i_{pc} increasing as cycling continues; Figure 1C selects the fifth cycle of the series. The other new ET is irreversible, and the feature at −1.40 V turns out to be the corresponding anodic peak current. We believe that the origin of the new ETs is the formation of the neutral dimeric species $[(C_5Me_5)Cr(CNCH_3)_3]_2$. This is supported by the recent isolation of $[CpCr(CNCMe_3)_3]_2$ from the reaction of the half-open chromocene CpCr(Pdl) with *tert*-butylisocyanide.[7b] Clearly, dissociation and association of a ligand as well as the dimerization of half-sandwiches is involved. How these chemical steps are coupled with the electrochemical steps will be investigated in a separate study.

CVs were also recorded for $\mathbf{2}^+$ in CH_2Cl_2, for $\mathbf{7}^{2+}$ in EtCN and CH_2Cl_2, and for $\mathbf{10}^{2+}$ in EtCN (Table 1). In CH_2Cl_2 no reliable data could be obtained below −0.5 V, and an electrode stripping peak associated with the

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Table 1. Electrochemical Data[a] Obtained from the Half-Sandwich Cations in Different Solvents

	$[(C_5Me_5)Cr(CNCH_3)_4]^+$		$[CpCr(CNCH_3)_4]^{2+}$		$[(t\text{-BuCp})Cr(CNCH_3)_4]^{2+}$
solvent:	EtCN[b]	CH_2Cl_2[c]	EtCN[d]	CH_2Cl_2[e]	EtCN[f]
$E_{1/2}(1)$	−0.38	−0.36	−0.24	0.23	−0.22
$\Delta E_p(1)$	0.085	0.125	0.100	0.095	0.085
$I_{pa}/i_{pc}(1)$	1.02	0.99	0.97	0.95	0.94
$E_{pa}(2)$	0.79	0.85	1.11	1.04	1.10
$E_{pc}(3)$	−2.63	*h*	−2.50	*h*	−2.56
$E_{1/2}(4)$	−1.78[g]	*h*	−1.67[i]	*h*	−1.67[i]
$\Delta E_p(4)$	0.065[g]	*h*	*i*	*h*	*h*
$I_{pa}/i_{pc}(4)$	1.1[g]	*h*	*i*	*h*	*h*
$E_{pa}(5)$	−1.40[g]	*h*	−1.27	h	−1.27

[a] Potentials in V, ETs relative to the couple Cp_2Fe/Cp_2Fe^+, supporting electrolyte 0.1 M n-Bu_4NPF_6, scan rate 200 mV s^{-1}, temperature 22 °C. The features of the CVs are numbered (1)−(4). [b] 1.22 mmol L^{-1}. [c] 0.78 mmol L^{-1}. [d] 1.24 mmol L^{-1}. [e] 1.75 mmol L^{-1}. [f] 1.92 mmol L^{-1}. [g] Observed after five cycles between −2.85 and −0.85 V (see text). [h] Not observed. [i] Irreversible, E_{pa} rather than $E_{1/2}$ is given.

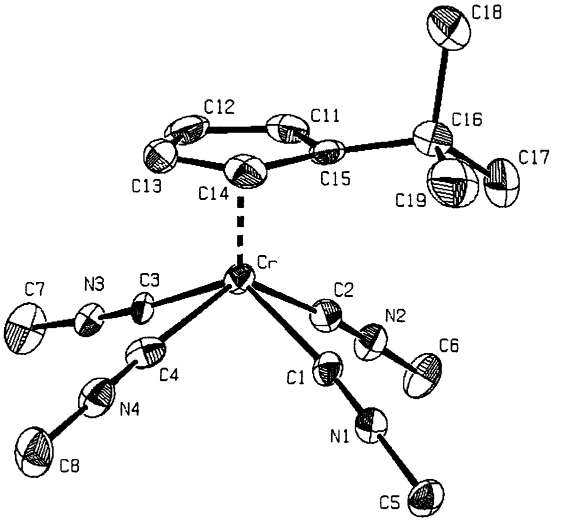

Figure 2. Structure of the half-sandwich cation $[(t\text{-BuCp})Cr(CNCH_3)_4]^{2+}[CF_3SO_3]^-_2$ (ORTEP plot, 50% probability level, H atoms omitted). For unit cell see Supporting Information.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of $\mathbf{10}^{2+}[CF_3SO_3]^-_2$

Cr−C1	2.011(4)	N1−C1	1.138(6)
Cr−C2	1.998(4)	N1−C5	1.444(6)
Cr−C3	2.005(4)	N2−C2	1.147(6)
Cr−C4	1.998(4)	N2−C6	1.440(6)
Cr−C11	2.235(5)	N3−C3	1.140(6)
Cr−C12	2.223(5)	N3−C7	1.435(6)
Cr−C13	2.164(4)	N4−C4	1.139(6)
Cr−C14	2.151(5)	N4−C8	1.452(7)
Cr−C15	2.241(4)		
C1−Cr−C2	84.41(18)	C3−Cr−C4	82.75(18)
C2−Cr−C3	78.36(18)	C1−Cr−C4	78.21(18)
C1−Cr−C3	129.21(19)	C2−Cr−C4	133.16(19)
C1−N1−C5	179.5(4)	Cr−C1−N1	174.5(4)
C2−N2−C6	177.1(4)	Cr−C2−N2	174.9(4)
C3−N3−C7	175.5(5)	Cr−C3−N3	176.0(4)
C4−N4−C8	177.9(5)	Cr−C4−N4	175.5(4)

oxidation above 0.8 V was observed. Aside from this, the data did not change very much with the solvent (Table 1). As expected, the methyl groups of the (C_5Me_5) ligand shift all potentials to more negative values as compared to the Cp and *t*-BuCp ligands. It is worth noting that the oxidation of the half-sandwich $\mathbf{2}^+$ ($E_{1/2}$ = −0.38 V) is considerably more difficult to achieve than that of the sandwich precursor $\mathbf{1}^+$ ($E_{1/2}$ = −1.06 V[9]). This explains why $\mathbf{2}^+$ could be isolated in the presence of CH_2Cl_2, whereas $\mathbf{1}^+$ decomposed (Scheme 1, steps b and a, respectively).

Crystal Structure. An attempt to establish the new 17-electron chromium(III) half-sandwich dications by X-ray crystallography of the well-shaped needles of $\mathbf{7}^{2+}[CF_3SO_3]^-_2\cdot CH_3CN$ failed probably due to disorder of the Cp ligand. In an attempt to lock Cp in the lattice it was substituted by a *tert*-butyl group, and the investigation of $\mathbf{10}^{2+}[CF_3SO_3]^-_2$ was actually successful.

As shown in Figure 2, $\mathbf{10}^{2+}$ has a four-legged piano-stool structure (for selected bond lengths and angles see Table 2). The essentially linear isocyanide ligands (average angle C−N−C 177.5°) have mean angles C−Cr−C of 80.2° and 131.2° when the ligands are *cis* and *trans*, respectively. Furthermore, the isocyanide ligands form a mean angle θ of 114.4° with the vector Cr−D (where D is the midpoint of the Cp plane). All these angles are in the range expected for compounds of the type $CpML_4$,[13a,b] including 17-electron derivatives.[13c] It is worth noting that the angle θ pronouncedly reflects the substitution pattern of the Cp ligand. Thus, the *tert*-butyl group pushes away the adjacent $CNCH_3$ ligand (D−Cr−C1 = 119.0°), while this seems to be compensated by the opposite ligand (D−Cr−C3 = 111.8°). The remaining angles are D−Cr−C2 = 114.1° and D−Cr−C1 = 119.0°. The mean Cr−C distance of the $Cr(CNCH_3)$ fragments (2.003 Å) fits in the known range.[14] For the series $[Cr(CNPh)_6]^{n+}$ it has been shown that the Cr−C distance increases strongly with the charge and that for the dication the mean Cr−C distance is 2.014 Å.[15] This is in agreement with the value found for $\mathbf{10}^{2+}$. There is a structural relationship of $\mathbf{10}^{2+}$ to $[CpCr(CN\textit{t}\text{-Bu})_4]^+$,[7b] to $[CpMoI(CN\textit{t}\text{-Bu})_4]^{2+}$ with an additional iodide ligand,[16a] to $[Cr(CN\textit{t}\text{-Bu})_7]^{2+}$,[16b] and to the carbyne complex $[(C_5Me_5)Cr(CN\textit{t}\text{-Bu})_3(CN(\textit{i}\text{-Pr})_2)]^{2+}$,[16c] which can also be regarded as a four-legged chromium piano-stool derivative.

The distance Cr−D of the chromium atom from the Cp ligand is 1.849 Å. This is much shorter than found for S = 3/2 chromium half-sandwiches, for which Cr−

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Cp is about 1.95 Å.[17] Contractions of this kind are well-known when low-spin configurations are adopted, and in the present case this is in accord with a $S = 1/2$ ground state for the ions $\mathbf{2}^{2+}$, $\mathbf{7}^{2+}$, and $\mathbf{10}^{2+}$. Structurally related $S = 1/2$ CpCr derivatives are CpCr(arene) compounds. Their Cr−Cp distance is 1.80−1.83 Å,[18] which is very close to the value found for $\mathbf{10}^{2+}$.

The two triflates per half-sandwich are well separated from the chromium center, as can be seen from the unit cell (Figure S2, Supporting Information). Likewise, the distance Cr···Cr is large (6.219(1) Å) so that interaction is negligible.

NMR and EPR Spectroscopies. The half-sandwich monocations $\mathbf{2}^{+}$ and $\mathbf{7}^{+}$, being 18-electrons systems, yielded simple ^{1}H and ^{13}C NMR spectra. However, attempts to record a ^{53}Cr NMR signal of a saturated solution of $\mathbf{2}^{+}[PF_6]^{-}$ in acetone were unsuccessful, although the quadrupolar relaxation of compounds with symmetries even lower than O_h and T_d may be slow enough to obtain useful spectra.[19] In the case of $\mathbf{2}^{+}$ broadening of the ^{1}H NMR signals indicated that it is difficult to remove small amounts of the paramagnetic $\mathbf{2}^{2+}$, which would accelerate the ^{53}Cr relaxation excessively.

The half-sandwich dications $\mathbf{2}^{2+}$, $\mathbf{7}^{2+}$, and $\mathbf{10}^{2+}$ are 17-electron species like sandwiches of the type CpCr(arene), for which NMR signals have been obtained.[9] Correspondingly, a 1.06 mol % solution of $\mathbf{2}^{2+}[PF_6]^{-}{}_2$ in CD_3CN gave a ^{1}H NMR signal at −29.3 ppm relative to the solvent signal, which had a half-width of $\Delta\nu_{1/2} = 15$ kHz at 305 K. It was assigned to the (C_5Me_5) protons by analogy with the (C_5Me_5)Cr(arene)derivatives (see below). No signal could be detected for the $CNCH_3$ ligands due to excessive line broadening. Therefore, we resorted to signal narrowing that can be achieved quite generally by using ^{2}H NMR spectroscopy and for which paramagnetic π complexes are illuminating examples.[9,20]

The ^{2}H NMR results of $\mathbf{7}^{2+}$-d_{12} are illustrated in Figure 3. The signal of the isocyanide deuterons appears at 79.3 ppm relative to the solvent signal. When the concentration is increased from 0.39 to 1.06 mol %, $\Delta\nu_{1/2}$ decreases from 8.6 to 2.6 kHz. This demonstrates that the nuclear relaxation is slowed not only by observing ^{2}H instead of ^{1}H but also by intermolecular electron spin interaction. Similarly, $\mathbf{7}^{2+}$-d_5 gave a ^{2}H NMR signal at 135 ppm ($\Delta\nu_{1/2} = 7.4$ kHz) relative to the solvent CD_3CN at 305 K. The isocyanide protons of $\mathbf{7}^{2+}$-d_5 could not be detected by ^{1}H NMR spectroscopy. We conclude that for these dications the isocyanide protons are generally not observable and that this is another reason for assigning the ^{1}H NMR signal of $\mathbf{2}^{2+}$ to the (C_5Me_5) protons. Correspondingly, for $\mathbf{10}^{2+}$ no ^{1}H NMR signals were observed for the protons of $CNCH_3$ and Cp, whereas the protons of the *tert*-butyl group gave a signal that was only little affected by the spin ($\delta = 1.5$, $\Delta\nu_{1/2} = 130$ Hz at 305 K). In solutions of the dications $\mathbf{2}^{2+}$, $\mathbf{7}^{2+}$, and $\mathbf{10}^{2+}$ no proton signal of free methylisocyanide (which should be narrow and clearly visible) could be detected, so that the formation of 15-electron ions of the type $[(R_nCp)Cr(CNCH_3)_3]^{2+}$ is unlikely.

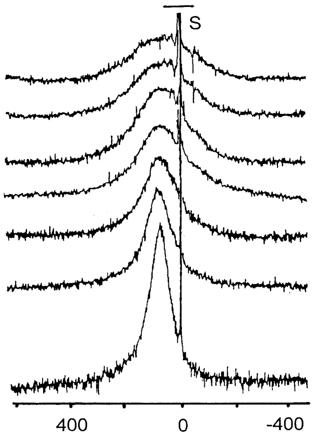

Figure 3. ^{2}H NMR spectra of $\mathbf{7}^{2+}$-$d_{12}[CF_3SO_3]^{-}{}_2$ dissolved in CH_3CN at 305 K, S = solvent, scale in ppm. The concentration increases from top to bottom: 0.39, 0.47, 0.52, 0.63, 0.82, 0.95, 1.06 mol %.

It is instructive to compare the NMR signal shifts of the new dications $[(R_nCp)Cr(CNCH_3)_4]^{2+}$ with those of (C_5R_5)Cr(arene)[9] and (C_5R_5)$CrX_2(CNCH_3)$[10] derivatives (Table 3). While the latter type of compounds are $S = 3/2$ species that have large signal shifts, the other types have small shifts in accord with a $S = 1/2$ ground state.

The sign and the amount of the paramagnetic NMR signal shifts are a measure of the spin-magnetic moment at the nucleus under study.[21a] It is hence possible to map the spin distribution of paramagnetic molecules, and for metallocenes the reliability of the approach has been established.[21b] In the present case the proton signal shifts of (C_5Me_5) and Cp of $\mathbf{2}^{2+}$ and $\mathbf{7}^{2+}$ are negative and positive, respectively. This pattern is the same as that found for (C_5R_5)Cr(arene) compounds;[9] that is, the unpaired electrons in the d_{z^2} orbital of chromium induce negative spin density on the Cp π system. The mechanism of the spin transfer from chromium to the isocyanide ligands is very similar to that between the $CpCrCl_2$ fragment and $CNCH_3$, which has been analyzed previously.[10]

The widths of the NMR signals of $\mathbf{2}^{2+}$ and $\mathbf{7}^{2+}$ and its concentration dependence suggested that EPR spectra should be observable in diluted samples at low temperature. This was verified by investigating a 10^{-3} M liquid solution of $\mathbf{7}^{2+}[CF_3SO_3]^{-}{}_2$ in acetone at 211 K which gave a signal at $g = 1.9832$. It was accompanied by ^{53}Cr satellites with a hyperfine coupling constant of $A(^{53}\mathrm{Cr}) = 1.69$ mT. Both values confirm the data reported by Poli[8c] for nonisolable 17-electron chromium half-sandwiches, e.g., $[(C_5Me_5)Cr(CN)_4]^{2-}$. Additional information was obtained from the EPR spectra of solid samples. Thus, a glassy solution of $\mathbf{10}^{2+}$ in acetone at 138 K gave a pattern characteristic of an axial symmetric species with $g_{\parallel} = 2.0036$ and $g_{\perp} = 1.9901$. Figure 4 shows the EPR spectrum of a diluted powder sample of

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Table 3. $^{1/2}$H NMR Signal Shifts[a] of $S = 1/2$ and $S = 3/2$ Compounds Containing the Fragment (R_nCp)Cr

	(C_5R_5)Cr(arene)[b] $S = 1/2$	$[(R_nCp)Cr(CNCH_3)_4]^{2+}$ $S = 1/2$	(C_5R_5)CrX_2($CNCH_3$)[c] $S = 3/2$
C_5H_5	144	137[d]	248
C_5Me_5	−14	−30	−53
$CNCH_3$		81[d]	166−169

[a] ^{1}H NMR except for *d*. Shifts caused exclusively by the unpaired electrons. [b] Average shifts of several compounds of ref 9. [c] Ref 10. [d] ^{2}H NMR.

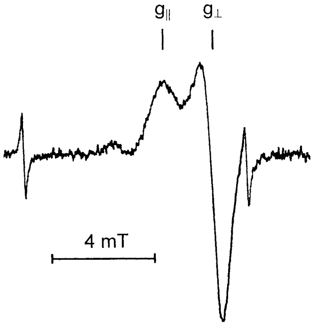

Figure 4. EPR spectrum of $7^{2+}[CF_3SO_3]^-{}_2$ diluted in $7^+[CF_3SO_3]^-$, powder, 133 K. The sharp signals are due to the standard.

$2^{2+}[CF_3SO_3]^-{}_2$ in $2^+[CF_3SO_3]^-$ (ratio 1:19); the *g* factors are $g_{\parallel} = 2.0017$ and $g_{\perp} = 1.9894$. It is gratifying that not only the NMR data described above but also the EPR data of $\mathbf{2}^{2+}$, $\mathbf{7}^{2+}$, and $\mathbf{10}^{2+}$ are very similar to those of CpCr(arene) derivatives.[9] So this is also characteristic for the unpaired electron residing in the d_{z^2} orbital. As the *g*-factor anisotropy is very small, the NMR signal shifts are not affected by dipolar contributions.[22] Therefore, the NMR data in Table 3 can be treated as contact shifts and converted to the hyperfine coupling constants $A(^1H) = 0.19$ mT for Cp and $A(^1H) = 0.10$ mT for $CNCH_3$ of $\mathbf{7}^{2+}$, respectively, by using a known formula.[21] It turns out that these values are too small to be resolved in the EPR spectrum and that NMR and EPR are complementary methods for characterizing the title compounds.

Conclusions

Methylisocyanide is the ligand of choice for stabilizing 17-electron chromium half-sandwiches of the general formula $[CpCrL_4]^{2+}[X]^-{}_2$. These species fill the gap in the series $[CpML_4]^{2+}$ and $CpML_2X_2$ (M = Cr, Mo, W), which is related to the 15-electron half-sandwiches $CpMLX_2$ by loss of one ligand and by a change of the ground state ($S = 1/2$ and $S = 3/2$, respectively). The dications $[CpCrL_4]^{2+}$ are accessible from Cp_2Cr and $[CpCrCl_2]_2$ via compounds of the type $CpCrCl_2$(donor) by removing the halides in the presence of $CNCH_3$; the spin pairing energy is “paid” by the strong bonding of four $CNCH_3$ ligands. When the mesitylene ligand of the mixed-ligand sandwich cation $[(C_5Me_5)Cr(C_6H_3Me_3)]^+$ is replaced by four $CNCH_3$ ligands, this is accompanied by a spin change from $S = 1$ to $S = 0$. Subsequent one-electron oxidation also leads to the desired type of compounds in the form of $[(C_5Me_5)Cr(CNCH_3)_4]^{2+}$ as a triflate salt. The redox chemistry may be followed by cyclic voltammetry, which uncovers oxidation and reduction to unstable Cr(IV) and Cr(0) species, respectively, in addition to the reversible electron transfer between isolable Cr(III) and Cr(II) compounds. From ^{1}H and ^{2}H NMR as well as from EPR spectroscopy it follows that the Cr(III) species $[CpCr(CNCH_3)_4]^{2+}$ is very similar to the Cr(I) species CpCr(arene). Both have one unpaired electron in a chromium d_{z^2} orbital, which induces negative spin density on the Cp ligand. The expected four-legged piano-stool structure is confirmed for $[(t\text{-}BuCp)Cr(CNCH_3)_4]^{2+}[CF_3SO_3]^-{}_2$ by X-ray analysis.

Experimental Section

General Procedures. All synthetic work and physical measurements were performed under purified dinitrogen in Schlenk-type vessels, and cannula were used for transferring liquids. The solvents were dried by standard methods and distilled under dinitrogen before use. $CNCH_3$,[23] $CNCD_3$,[24] *t*-BuCpH,[25] $[(C_5Me_5)Cr(C_6H_3Me_3)]^+[PF_6]^-$,[9] $[(C_5Me_5)CrCl_2]_2$,[17b,26] $[CpCrCl_2]_2$,[10] and $Tl(CF_3SO_3)$[27] were described previously, while $(C_5D_5)Cr(CF_3SO_3)_2$(THF) was prepared from Cp_2Cr-d_{10}[28] as published for the nondeuteriated compound.[10] Cp_2Cr-d_{10} was prepared from C_5D_5Na[29] and $CrCl_2$(THF) by following ref 30. The EPR spectrum was recorded with an X-band spectrometer JEOL JES RE 2X; MnO diluted in MgO was used for calibration. The NMR spectra were run with Bruker CXP 200 and JEOL JNM GX 270 spectrometers. The signal shifts in Table 3 were obtained by measuring relative to the solvent signals, by adding their respective signal shifts, and by subtracting the signal shifts of corresponding nuclei of $\mathbf{2}^+$ and $\delta(^1H) = 4.1$ in the case of the Cp protons of $\mathbf{7}^{2+}$. The IR and mass spectra were recorded by using a Perkin-Elmer 283 B and a Varian MAT 311A (electron impact, 70 eV) apparatus, respectively. The equipment used for the CV measurements has been described previously.[31] The electrolyte was a 0.1 M solution of n-Bu_4NPF_6 in purified propionitrile. The electrolyte was further dried by passing it through activated neutral Al_2O_3 placed in a tube which was integrated in the cell, and, subsequently, the sample was added to give 10^{-3} M solutions. The redox couple Cp_2Fe/Cp_2Fe^+ served as an internal standard. The elemental analyses were carried out by the microanalytical laboratory of the authors' institution.

1. Synthesis of $[(C_5Me_5)Cr(CNCH_3)_4]^+[PF_6]^-$ ($2^+[PF_6]^-$). Immediately after preparing a solution of 170 mg (0.37 mmol)

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of $[(C_5Me_5)Cr(C_6H_3Me_3)]^+[PF_6]^-$ in 10 mL of CH_2Cl_2 an excess of methylisocyanide (150 mg, 3.68 mmol) was added at 25 °C. This was accompanied by an instantaneous color change of the solution from orange-red to red. When the solution was reduced to a volume of 2 mL and 30 mL of diethyl ether was added, a precipitate formed. Recrystallization from CH_2Cl_2/Et_2O gave red crystals of $\mathbf{2}^+[PF_6]^-$ (yield 160 mg, 86%), mp 150 °C (dec). IR (KBr): 2110, 2170 cm^{-1} (νCN). ^1H NMR (acetone-d_6, δ): 1.70 (s, 15H, C_5Me_5), 3.67 (s, 12H, $CNCH_3$). ^{13}C NMR (acetone-d_6, δ): 10.2 ($C_5(CH_3)_5$, 31.4 ($CNCH_3$), 99.2 ($C_5(CH_3)_5$, 190.5 ($CNCH_3$). Anal. Calcd for $C_{13}H_{17}CrF_6N_4P$: C, 36.63; H, 4.02; Cr, 12.12; F, 26.74; N, 13.14. Found: C, 36.61; H, 4.13; Cr, 12.10; F, 26.84; N, 13.45.

2. Synthesis of $[(C_5Me_5)Cr(CNCH_3)_4]^{2+}[CF_3SO_3]^-{}_2$ ($\mathbf{2}^{2+}[CF_3SO_3]^-{}_2$). A 755 mg (18.4 mmol) amount of methylisocyanide was added to a solution of 720 mg (1.4 mmol) of $[(C_5Me_5)CrCl_2]_2$ in 50 mL of acetone. When 1.97 g (5.6 mmol) of $Tl(CF_3SO_3)$ was added and stirred for 1 h, the blue solution turned red, and a white precipitate of TlCl appeared. The mixture was filtered, the solution was reduced until it became saturated, and 10 mL of diethyl ether was added. This gave a precipitate, which was recrystallized from acetone/diethyl ether to yield 1.06 g (59%) of red crystals of $\mathbf{2}^{2+}[CF_3SO_3]^-{}_2$. The crystals decomposed above 120 °C to give a blue solid. IR (KBr): 2200, 2220 cm^{-1} (νCN). Anal. Calcd for $C_{20}H_{27}CrF_6N_4O_6S_2$: C, 36.98; H, 4.19; Cr, 8.01; N, 8.63; S, 9.87. Found: C, 36.87; H, 4.23; Cr, 8.22; N, 8.51; S, 10.19.

3. Synthesis of $[CpCr(CNCH_3)_4]^{2+}[CF_3SO_3]^-{}_2\cdot(CH_3)_2CO$ ($\mathbf{7}^{2+}[CF_3SO_3]^-{}_2\cdot(CH_3)_2CO$) and of $[CpCr(CNCH_3)_4]^{2+}[CF_3SO_3]^-{}_2\cdot CH_3CN$ ($\mathbf{7}^{2+}[CF_3SO_3]^-{}_2\cdot CH_3CN$). The procedure described under 2. was carried out with 755 mg (18.4 mmol) of methylisocyanide, 410 mg (1.1 mmol) of $[CpCrCl_2]_2$, 50 mL of acetone, and 1.55 g (4.4 mmol) of $Tl(CF_3SO_3)$. From the resulting light yellow-brown solution orange crystals (yield 1.68 g, 60%) of $\mathbf{7}^{2+}[CF_3SO_3]^-{}_2\cdot(CH_3)_2CO$ were obtained, which decomposed above 120 °C to give a blue solid. IR (KBr): 2230, 2250 cm^{-1} (νCN). Anal. Calcd for $C_{18}H_{23}CrF_6N_4O_7S$: C, 33.91; H, 3.64; Cr, 8.16; N, 8.79; S, 10.06. Found: C, 33.46; H, 3.53; Cr, 8.31; N, 8.87; S, 10.30.

Recrystallization of $\mathbf{7}^{2+}[CF_3SO_3]^-{}_2\cdot(CH_3)_2CO$, from acetonitrile/diethyl ether gave orange crystals of $\mathbf{7}^{2+}[CF_3SO_3]^-{}_2\cdot CH_3CN$. Anal. Calcd for $C_{17}H_{20}CrF_6N_5O_6S$: C, 32.91; H, 3.25; Cr, 8.38; F, 18.37; N, 11.29; S, 10.33. Found: C, 32.64; H, 3.18; Cr, 8.23; F, 17.47; N, 11.40; S, 10.87.

4. Synthesis of $[(t\text{-BuCp})CrCl_2]_2$ (8). A sample of 4.64 g (38 mmol) of *t*-BuCpH in 50 mL of THF was deprotonated by dropwise addition of 16 mL of a 2.85 M solution of *n*-BuLi in hexane at 25 °C. The resulting solution was slowly added to a stirred suspension of 14.28 g (38 mmol) of $CrCl_3(THF)_3$ in 200 mL of THF, whereupon the color changed from violet to dark blue. The mixture was stirred for 1 h at 25 °C and for 2 h at 65 °C (reflux). Subsequently, the solvents were stripped at 25 °C and 400 mL of toluene was added. From this solution 300 mL was distilled off in order to remove residual THF. The remaining suspension was transferred to a Soxhlet extractor, 250 mL $CHCl_3$ was added, and the blue chromium compound was extracted for 1 day. The volume of the extract was reduced in vacuo, and crystallization of a blue solid was achieved after keeping the remainder at −35 °C. After filtering, the solid was washed with pentane and recrystallized from toluene to yield 5.47 g (59% yield) of dark blue crystals of **8**, mp 234−236 °C. ^1H NMR ($CDCl_3$, 305 K, $\delta/\Delta\nu_{1/2}$ in kHz): 181.7/2.6 (H2/5), 174.6/2.6 (H3/4), 2.9/0.4 (CCH_3). ^{13}C NMR ($CDCl_3$, 305 K, $\delta/\Delta\nu_{1/2}$ in kHz): 186.5/0.25 (C1), 167.1/0.25 (C3/4), 22.7/0.25 (C2/5), 258.5/0.35 (*C*CH3), −0.6/0.08 (C*C*H3); for spectrum and assignment see Supplementary Information. MS (*m*/*z*): 486 (2, M^+), 451 (18, $M^+ - Cl$), 330 (4, $[(t\text{-BuCp})CrCl_3]^+$), 243 (20, M^{2+}), 208 (25, $[(t\text{-BuCp})CrCl]^+$), 192 (35, $[(C_8H_9)CrCl]^+$), 171 (62, $[(C_9H_{11})Cr]^+$), 157 (33, $[(C_8H_9)Cr]^+$), 131 (13, $[(C_6H_7)Cr]^+$), 121 (100, $[t\text{-BuCp}]^+$), 105 (52, $[C_8H_9]^+$), 91 (55, $[C_7H_7]^+$), 77 (32, $[C_6H_5]^+$), 65 (19, $[C_5H_5]^+$), 52 (34, Cr^+). Anal. Calcd for $C_{18}H_{26}Cl_4Cr_2$: C, 44.28; H, 5.37; Cl, 29.05; Cr, 21.30. Found: C, 44.28; H, 5.39; Cl, 28.95; Cr, 21.16.

5. Synthesis of $[(t\text{-BuCp})Cr(CNCH_3)_4]^{2+}[CF_3SO_3]^-{}_2$ ($\mathbf{10}^{2+}[CF_3SO_3]^-{}_2$). The reaction and workup described under 2. were carried out with 0.45 g (0.92 mmol) of $[(t\text{-BuCp})CrCl_2]_2$ dissolved in 50 mL of acetone, with 755 mg (18.4 mmol) of $CNCH_3$, and with 1.30 g (3.7 mmol) of $Tl(CF_3SO_3)$. The yield of orange-red $\mathbf{10}^{2+}[CF_3SO_3]^-{}_2$ after recrystallization at −20 °C was 0.31 g (51%), mp 170−172 °C (slow decomposition above 140 °C was indicated by darkening of the crystals). IR (KBr): 2224, 2250 cm^{-1} (νCN). Anal. Calcd for $C_{19}H_{25}CrF_6N_4O_6S_2$: C, 35.91; H, 3.96; Cr, 8.18; N, 8.82. Found: C, 35.68; H, 3.66; Cr, 8.12; N, 8.78.

6. Reaction of $CpCr(OSO_2CF_3)_2(THF)$ with $CNCD_3$ and of $(C_5D_5)Cr(OSO_2CF_3)_2(THF)$ with $CNCH_3$. A 10 mg (0.02 mmol) sample of $CpCr(OSO_2CF_3)_2(THF)$ was dissolved in 5 mL of diethyl ether. When an excess of 20 mg (0.45 mmol) of methylisocyanide-d_3 was added, an orange-yellow precipitate formed. Filtering and drying in vacuo gave 11.5 mg of a microcrystalline solid, which was identified by IR (νCN: 2230 and 2250 cm^{-1} in KBr) as the deuterio-analogue of $\mathbf{7}^{2+}[CF_3SO_3]^-{}_2$, i.e., $\mathbf{7}^{2+}\text{-}d_{12}[CF_3SO_3]^-{}_2$ (yield 97%).

For the analogous compound that was deuteriated selectively in the Cp ligand (**9**-d_5) the same quantities of starting compounds were employed. Also, the yield of the product $\mathbf{7}^{2+}\text{-}d_5[CF_3SO_3]^-{}_2$ and the νCN frequencies were the same, all within the error limits.

7. Synthesis of $[CpCr(CNCH_3)_4]^+[PF_6]^-$ ($\mathbf{7}^+[PF_6]^-$). A 1.79 g (27.4 mmol) amount of zinc powder was added to a solution of 1.42 g (2.3 mmol) of $\mathbf{7}^{2+}[CF_3SO_3]^-{}_2\cdot CH_3CN$ in 20 mL of THF, and the mixture was stirred for 1 day at 25 °C. The resulting orange solution was filtered, the solvent was stripped, and to the oily remainder was added 100 mL of water. After filtering the solution and adding 550 mg (3.4 mmol) of NH_4PF_6 a precipitate formed. The water was removed by filtration and drying in vacuo, the solid was dissolved in 50 mL of acetone, the solution was filtered, and its volume was reduced until it became saturated at 25 °C. When this solution was covered with a layer of 150 mL of diethyl ether and left alone for 2 days, orange crystals were obtained, which after recrystallizing twice from acetone/diethyl ether gave 470 mg (yield 48%) of $\mathbf{7}^+[PF_6]^-$, mp 140 °C (dec). IR (KBr): 2110, 2180 cm^{-1} (νCN). ^1H NMR (acetone-d_6, δ): 3.60 (s, 12H, $CNCH_3$), 4.65 (s, 5H, Cp). ^{13}C NMR (acetone-d_6, δ): 31.4 ($CNCH_3$), 87.7 (Cp), 185.6 ($CNCH_3$). Anal. Calcd for $C_{13}H_{17}CrF_6N_4P$: C, 36.63; H, 4.02; Cr, 12.12; F, 26.74; N, 13.14. Found: C, 36.61; H, 4.13; Cr, 12.10; F, 26.84; N, 13.45. When $NaB(C_6H_5)_4$ was used instead of NH_4PF_6 to precipitate the product, an orange microcrystalline powder of $[CpCr(CNCH_3)_4]^+[B(C_6H_5)_4]^-$ ($\mathbf{7}^+[B(C_6H_5)_4]^-$) was obtained. ^1H NMR (acetone-d_6, δ): 3.49 (12H, $CNCH_3$), 4.65 (5H, Cp), 7.34 (8H, o-H), 6.93 (8H, m-H), 6.78 (4H, p-H).

Crystal Structure Analysis. Crystals of $\mathbf{10}^{2+}[CF_3SO_3]^-{}_2$ were grown by cooling a concentrated solution in a mixture of CH_2Cl_2 and propionitrile to −20 °C. Preliminary examination and data collection were carried out on a four-cycle diffractometer (NONIUS MACH3) equipped with an area detecting system (NONIUS Kappa-CCD), a rotating anode (NONIUS FR591; 50 kV; 60 mA; 3.0 kW), and graphite-monochromated Mo Kα radiation. Data collection was performed at 143 K within the θ-range of 1.95° < θ < 25.64°. A total number of 13 895 reflections were collected and scaled. Forty systematically absent reflections were rejected from the original data set. After merging a sum of 5081 independent reflections remained and were used for all calculations. The data were corrected for Lorentz and polarization effects.[32a] All nonhydrogen atoms of the asymmetric unit were refined anisotropically. All hydrogen atoms were calculated in ideal positions (riding model; $U_H = 1.2/1.5U_C$). Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with SHELXL-97 weighting scheme and stopped at R1 =

Table 4. Crystallographic Data of the Salt $\mathbf{10}^{2+}[CF_3SO_3]^-_2$

chem formula	$C_{17}H_{25}CrN_4$, 2(CF_3SO_3)
fw	635.57
color/shape	orange-red/fragment
cryst size (mm)	0.23 × 0.18 × 0.05
cryst syst	orthorhombic
space group	$P2_12_12_1$ (No. 19)
a (Å)	10.7930(4)
b (Å)	11.9055(6)
c (Å)	20.9211(10)
V (Å^3)	2688.3(2)
Z	4
T (K)	143
ρ_{calcd} (g cm^{-3})	1.570
μ (mm^{-1})	0.664
F_{000}	1300
θ-range (deg)	1.95−25.64
data collected (h,k,l)	±13, ±14, ±25
no. of reflns collected	13 855
no. of indep reflns/R_{int}	5081 (all)/0.0532
no. of obsd reflns ($I > 2\sigma(I)$)	4371 (obsd)
no. of params refined	344
R1 (obsd/all)	0.0561/0.0705
wR2 (obsd/all)	0.1009/0.1048
GOF(obsd/all)	1.100/1.100
max/min $\Delta\rho$ (e Å^{-3})	+0.67/−0.40

0.0705, wR2 = 0.1048, and shift/err < 0.001. A value of 0.47(3) was obtained for Flack's parameter, which is not meaningful. This indicates that either the data are not of sufficient quality to correctly determine the enantiomorph or the crystal is twinned by a center of inversion. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the calculations were taken from *International Tables for Crystallography*.[32b] All calculations were performed on a DEC 3000 AXP workstation and an Intel Pentium II PC by using the STRUX-V system[32c] including the programs PLATON,[32d] SIR92,[32e] and SHELXL-97.[32f] A summary of the crystal and experimental data is reported in Table 4.

Crystallographic data (excluding structure factors) for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-188843. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: NMR results of [(t-BuCp)$CrCl_2$]$_2$, stereoview of the unit cell of $\mathbf{10}^{2+}[CF_3SO_3]^-_2$, additional crystal data and details of the structure determination, final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms, hydrogen atom positions and isotropic thermal parameters, (an)isotropic thermal parameters, bond distances, bond angles, and a unit cell diagram. This material is available free of charge via the Internet at http://pubs.acs.org.

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