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(Arene)cyclopentadienylchromium Chemistry. Synthesis, EPR, NMR, and Cyclic Voltammetry of Neutral Compounds and Their Monocations

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The unsymmetric sandwich compounds Cp*Cr(arene) (arene = benzene (**3**), benzene-d_6, (**3**$\boldsymbol{d_6}$), toluene (**4**), toluene-d_8, (**4**$\boldsymbol{d_8}$), ethylbenzene (**5**), mesitylene (**6**), ethylmesitylene (**7**), hexamethylbenzene (**8**)) were synthesized from $[\mathrm{Cp^*CrCl_2}]_2$ in yields up to 75% by applying three procedures. Two reaction pathways could be substantiated by NMR measurements and cyclic voltammetry. For comparison $\mathrm{CpCr(C_6H_6)}$ (**1**) and $\mathrm{Cp'Cr(C_6H_6)}$ (**2**) (Cp' = $\mathrm{CH_3C_5H_4}$) were also made in low yield. Well-resolved EPR spectra in liquid and solid solutions were obtained below −120 °C, while ^{1}H and ^{13}C NMR spectra could be recorded at 25 °C and above. From the spectroscopic results a $^2A_1$ (e_2^4, a_1^1) ground state was deduced; its bearing on the electron and nuclear relaxation was analyzed. Appreciable spin density was found on the ligands; in the ligand π orbitals the spin is negative, more spin sits on the arene than on $\mathrm{Cp^{(*)}}$, and the π orbitals dominating the delocalization are antisymmetric. Cyclic voltammetry showed **3**, **6**, and **8** to undergo quasi-reversible electron transfers to $[\mathrm{Cp^*Cr(arene)}]^-$ and $[\mathrm{Cp^*Cr(arene)}]^+$, while the oxidation to the dication was followed by chemical reaction. The hitherto unknown sandwich type $[\mathrm{Cp^{(*)}Cr(arene)}]^+$ could be synthesized in the case of **3**$^+$, **6**$^+$, and **8**$^+$ as $[\mathrm{PF_6}]^-$ and partly as $[\mathrm{B(C_6H_5)_4}]^-$, $\mathrm{I^-}$, $[\mathrm{Cp^*CrCl_3}]^-$, and $[\mathrm{Cp^*CrI_3}]^-$ salts. The ^{1}H and ^{13}C NMR spectra proved that the monocations are paramagnetic having most probably a $^3E_2$ (e_2^3, a_1^1) ground state. Negative spin density was found in the ligand π system so that these cations are potential building blocks in ferromagnetic donor−acceptor stacks.

Introduction

One of the successful concepts on the way to molecule-based magnetic materials[2] is linear stacking of decamethylmetallocenium ions and planar cyano-substituted π anions with $[\mathrm{Cp^*_2Fe}]^+[\mathrm{TCNE}]^-$ being the prototype of the TCNE series.[3] Variation of the organometallic component in this organic/organometallic approach revealed that not any sandwich may be converted to ferromagnetic stacks. Examples are $\mathrm{Cp^*_2Co}$, which gives a diamagnetic cation,[4] $\mathrm{Cp_2Fe}$, whose redox potential is too high,[5] $\mathrm{(C_6H_6)_2V}$, which loses its ligands but yields a spectacular room-temperature ferromagnet,[6] and $\mathrm{Cp^*_2Ni}$. The nickelocene yields antiferromagnetic $[\mathrm{Cp^*_2Ni}]^+[\mathrm{TCNE}]^-$ [5] owing to positive spin density in the ligand π orbital whereas negative spin has been postulated to be necessary[7] and to be actually present[8] when ferromagnetic interaction within the stacks is to be realized.

In this context we have investigated the paramagnetic ($S = {}^1/_2$) mixed-ring sandwich type CpCr(arene). When we started our work the parent compounds $\mathrm{CpCr(C_6H_6)}$,[9] $\mathrm{CpCr(\eta^6\text{-}C_7H_8)}$,[10] $\mathrm{CpCr(\eta^6\text{-}C_8H_8)}$,[10] $\mathrm{CpCr(\eta^6\text{-}C_7H_7C_6H_5)}$,[11] and $\mathrm{Cp^*Cr(C_6Me_6)}$[12] were known while $\mathrm{Cp^*Cr(\eta^6\text{-}C_8H_8)}$,[13] $\mathrm{CpCr(\eta^6\text{-}C_{10}H_8)}$,[14] and $\mathrm{(CpCr)_2(\eta^6,\eta^6\text{-}C_{10}H_8)}$[14] were published recently. The syntheses of these derivatives are rather special, and in some cases the yield is not attractive. Therefore we have undertaken a systematic synthetic study. Parallel to this study Jolly and coworkers developed a procedure that leads to derivatives having hexasubstituted arene ligands.[15] Since sandwich cations are present in the afore-mentioned ferromagnetic stacks and since ions of the type $[\mathrm{CpCr(arene)}]^+$ were unknown, a further goal was to investigate the redox properties of the neutral sandwiches. Among the techniques of characterization emphasis was laid on EPR and NMR spectroscopy in order to elucidate the magnetic orbitals and the distribution of the unpaired electron spin density within the molecules.

Results

Syntheses. The readily available dinuclear half-sandwich $[\mathrm{Cp^*CrCl_2}]_2$[16] was selected as a promising starting compound

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Table 1. Methods Applied for the Synthesis of Cp*Cr(arene) Derivatives

compd	% yield by method AlX_3/Al	 $AlEt_3/\Delta T$	 $AlEt_3/LiAlH_4$
3	39	35	59
3*d*$_6$	51		
4		50	
4*d*$_8$		47	
5			73
6	40	47	
7			17
8	75		

because various Cp*Cr(arene) derivatives should be obtained selectively after only two reaction steps, i.e., reduction and replacement of the chloro ligands by arenes. However, all attempts to reduce $[Cp^*CrCl_2]_2$ in the presence of hexamethylbenzene by sodium amalgam in diethyl ether or THF, by magnesium with ultrasound in THF, by $LiAlH_4$ in diethyl ether or THF, and by isopropylmagnesium bromide in diethyl ether under irradiation[10,17] were unsuccessful.

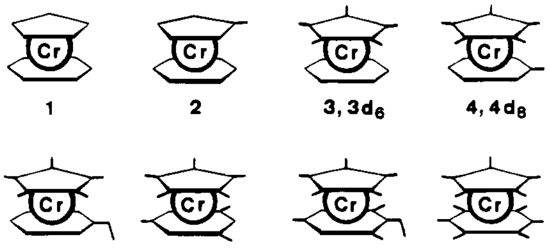
When a mixture of $[Cp^*CrCl_2]_2$ and hexamethylbenzene was heated with the Lewis-acidic reducing reagent $AlCl_3/Al$,[18] a brown mixture was obtained. Further treatment with aqueous dithionate solution, extractive workup, and purification with silica gel gave analytically pure $Cp^*Cr(C_6Me_6)$ (**8**) in 75% yield. For other arenes we found it more convenient to use a mixture of AlX_3, Al, and $LiAlH_4$ which was heated with the arene. After simple extraction with ether and purification $Cp^*Cr(C_6H_6)$ (**3**), $Cp^*Cr(C_6D_6)$ (**3*d*$_6$**), and Cp*Cr(mesitylene) (**6**) were isolated in yields up to 51%. A shortcoming of the $AlCl_3/Al$ method was the redistribution of the arene substituents under Friedel–Crafts conditions. Thus, in the mass spectrum of **6** the molecular ions of $Cp^*Cr(Me_4C_6H_2)$ and $Cp^*Cr(Me_5C_6H)$ were also present.

This problem could be circumvented by allowing a mixture of $[Cp^*CrCl_2]_2$ and the arene to react with $AlEt_3$ above 60 °C. After destruction of unreacted $AlEt_3$ with methanol, Cp*Cr(toluene) (**4**) and Cp*Cr(toluene-d_8) (**4*d*$_8$**) were isolated. For comparison compounds **3** and **6** were also made by the $AlEt_3/\Delta T$ method. The results are collected in Table 1, which shows that the yields of both methods are similar.

Far milder reaction conditions could be realized in a third synthetic variant. Thus, $LiAlH_4$ was added at room temperature rather than heating the mixture of $[Cp^*CrCl_2]_2$, the arene, and $AlEt_3$. As can be seen in Table 1, this increased the yield of **3**. Other compounds made by the $AlEt_3/LiAlH_4$ method were Cp*Cr(ethylbenzene) (**5**) and Cp*Cr(ethylmesitylene) (**7**). It should be noted that decamethylchromocene, Cp^*_2Cr (identified by its ^1H NMR signal at −6.2 ppm and its ^{13}C NMR signals at -418.2 ppm (C1−5) and 807 ppm (CH_3), all at 305 K[19]), was formed as a byproduct. For unknown reasons this was most serious in the case of **7**, which, in addition, was difficult to separate from Cp^*_2Cr.

The compounds synthesized by these methods are represented in Chart 1. They are air-sensitive orange-red crystalline materials except for **5** which is a liquid at room temperature and which gives a glass at −20 °C. They may be sublimed, they are easily soluble in hexane, toluene and ethers, and they are thermally stable at least up to 100 °C; **8** did not decompose below its melting point of 354 °C.

Chart 1



The methods mentioned so far (mostly) failed when applied to the synthesis of $CpCr(C_6H_6)$ (**1**) and $Cp'Cr(C_6H_6)$ (**2**) (Cp′ = $CH_3C_5H_4$). Thus, the reaction of $[CpCrCl_2]_2$ with $AlEt_3$ in boiling benzene or with $AlEt_3/LiAlH_4$ gave a little chromocene as the only product that could be extracted with hexane from the reation mixture. Therefore **1** was prepared in low yield by Fischer's route.[9] **2** could be obtained from $[Cp'CrCl_2]_2$ by using the $AlEt_3/\Delta T$ method albeit only in trace amounts together with Cp'_2Cr (identified by its ^1H NMR signals at 328, 280, and 32 ppm[20]); it was isolated after destroying Cp'_2Cr with silica gel. The AlX_3/Al method gave **2** in low yield only when ether was added to the reaction mixture at ambient temperature rather than heating it to 80 °C.

All compounds were characterized by their mass spectra which in the case of **3*d*$_6$** and **4*d*$_8$** reflected the deuteriation. The relative intensity of the molecular ions increased with the number of methyl groups per sandwich while the fragmentation pattern was similar for all derivatives. In particular, M^+ split off an arene more easily than a Cp or Cp*.

NMR Spectra. The NMR spectra were strongly dependent on the signal half-widths which increased strongly with decreasing temperature and concentration. Therefore some signals could be detected only in a melt containing a few drops of a solvent which was used as an internal standard. A striking example was $CpCr(C_6H_6)$ (**1**): A 20 mol % solution at 392 K yielded ^1H NMR signal half-widths of 20 and 30 kHz, which are about three times larger than found for a polycrystalline sample near room temperature.[21] Under these conditions base line distortions may render the signal integration and thus the distinction between the Cp and the benzene ligand unreliable. This problem was solved by comparing **1** with the Cp* derivatives **3**−**5** having only arene α protons.[22] The corresponding ^1H NMR signal shifts appear all above 240 ppm (Table 2) and leave no doubt that the nuclei of the five-membered ring have smaller signal shifts than those of the six-membered ring.

The ^1H NMR signals of the methyl groups (β protons) are much narrower than those of the α protons. Yet they may be also difficult to integrate because the relaxation rates are rather different (Figure 1). However, when the number of methyl groups per ligand is sufficiently different, as in the case of **4** and **6**, it is clear that the β proton signal of the arene is more shifted than that of Cp*. It follows that, whenever the half-widths of the β proton signals are different, the broader one belongs to the arene.

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Table 2. Paramagnetic ^1H, ^2H, and ^{13}C NMR Results of the CpCr(arene) Derivatives **1**–**8**[a]

nucleus and posn[b,22]	**1**	**2**	**3**, **3**d_6[c]	**4**, **4**d_8[c]	**5**[j]	**6**	**7**[i]	**8**
				Cp				
Hα	143[d] (20[d]) [A, 20]	145[d,e] (12[d,e]) [A, 99]						
Hβ		−10.2[d] (1.0[d]) [A, 99]	−14.7 (0.4) [B,15]	−13.8 (0.5) [A,[f]]	−14.0 (0.3) [A, 61]	−14.4 (0.4) [B, 23]	−13.9 (0.5) [A, 11]	−14.1 (0.7) [B, 0.7]
C1–5	−79.6 (1.0) [A, 20]	−72.7, C1; 70.0, C3/4; −86.9, C2/5	−79.6 (1.0) [A, 99]	−74.5 (0.9[h]) [A,[f]]	−74.5 (0.7[i]) [A, 99]	−79.9 (0.7) [A, 48]	−86.4 (2.5) [A, 11]	*g*
Cα		217 (3.0) [A, 99]	290 (2.2) [A, 99]	299 (4.3[h]) [A[f]]	303 (3.0[i]) [A, 99]	335 (5.0) [A, 48]	*g*	*g*
				Arene				
Hα	252[d] (30[d]) [A, 20]	256[d] (20[d]) [A, 99]	260[d] (20[d]) [A, 99]; *330 (2.6)* [D, 12]	253[d,e] (20[d]) [A[f]]; *259*[h] *(0.7*[h]*)* H2,3,5,6; *242*[h], *(0.7*[h]*)* H4 [C, 99]	329[k,e] (30[k]) [100]	*g*	*g*	
Hβ				−64 (4.0) [A[f]]; *−48.4*[h] *(0.04*[h]*)* [C, 99]	−41.9 (0.8) [A, 61]	−67 (3.8) [B, 23]	−66[e] (4.0) CH$_3$; −29.4, (1.0) CH$_2$ [A, 11]	−72 (13) [B, 0.7]
Hγ					−0.3 (0.2) [A, 61]		−2.5 (0.06) [A, 11]	
C1′–6′	−264 (5.0) [A, 20]	−259 (3.0) [A, 99]	−259 (2.3) [A, 99]	−258[e] (5.3[h]) [A[f]]	−257[e] (4.0[i]) [A, 99]	−255[e] (6.5) [A, 48]	*g*	*g*
Cα				398 (15[h]) [A[f]]	435 (3.5[i]) [A, 99]	474 (8.0[i]) [A, 34]	*g*	*g*

[a] Signal shifts are in ppm; negative sign means to low frequency. ^1H and ^2H NMR at 305 K, ^{13}C NMR at 392 K unless stated otherwise; signal half-width in kHz in parentheses. Solvent and concentration in mol % in brackets; A = toluene-d_8, B = benzene-d_6, C = toluene, D = benzene. [b] See Figures 1 and 3. [c] Data of the ^2H NMR measurements are given in italics. [d] At 392 K. [e] Signals of the nonequivalent nuclei not resolved. [f] Saturated solution. [g] Signal-to-noise ratio not sufficient. [h] At 385 K. [i] At 395 K. [j] The signal of Cβ could not be detected. [k] At 306 K.

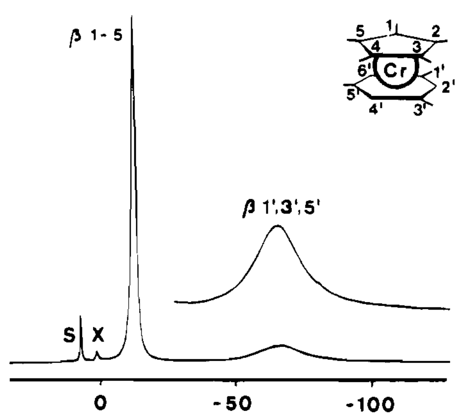

Figure 1. ^1H NMR spectrum of a 23 mol % solution of **6** in C_6D_6 at 305 K, β proton range. S = solvent, and X = impurity. The scale is in ppm.

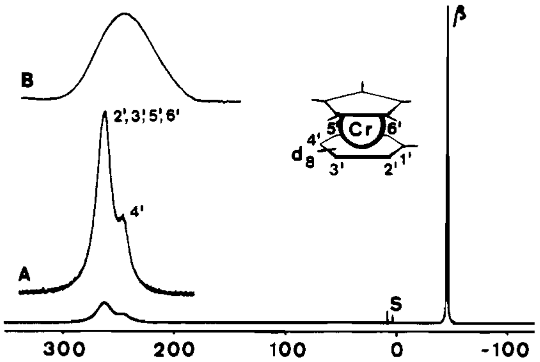

Figure 2. ^2H NMR spectrum of a melt of **4**d_8 containing a drop of toluene-d_8 (S) at 385 K. Inset A: D2–6 amplified. Inset B: H2–6 of **4** at 384 K. The scale is in ppm.

The data collection in Table 2 shows that the α proton signals of **6** and **7** were broadened beyond the detection level and that for **4** and **5** the expected splitting of these signals could not be resolved. Therefore we have made use of the signal-narrowing effect of ^2H NMR spectroscopy which has been previously[19,23] exploited for other sandwiches. A test with Cp*Cr(C_6D_6) (**3**d_6) revealed a remarkable improvement. Thus a 12.2 mol % solution of **3**d_6 at 305 K had a ^2H NMR signal which was almost eight times narrower than the ^1H NMR signal of a melt of **3** (containing a drop of internal standard) at 392 K (Table 2). Dilution to 5.1 and 2.5 mol % broadened the ^2H NMR signal to 5.9 and 8.0 kHz, respectively. The selectively deuteriated toluene derivative **4**d_8 gave the ^2H NMR spectrum represented in Figure 2. Although the α deuteron signals of the arene are resolved only partly, this is useful for the MO considerations described below. Note also that the ^2H NMR spectra independently establish the assignment given above for the α proton signals of the Cp and arene ligands.

The ^{13}C NMR spectra which were desirable as a probe for the spin delocalization could be obtained for most CpCr(arene) derivatives (Table 2). Even for the most simple compound **1** the assignment of the two signals was unclear because the integration was again hampered by rather different relaxation rates (Figure 3A). The signal assignment was established by recording the ^{13}C NMR spectrum of **2** (Figure 3B). On the change from **1** to **2** the less shifted signal splits into a 1/2/2 pattern so that it must originate from the five-membered ring. The α carbon signal of **2** was somewhat noisy; it could be confirmed indirectly by the ^{13}C NMR spectrum of **3** in Figure

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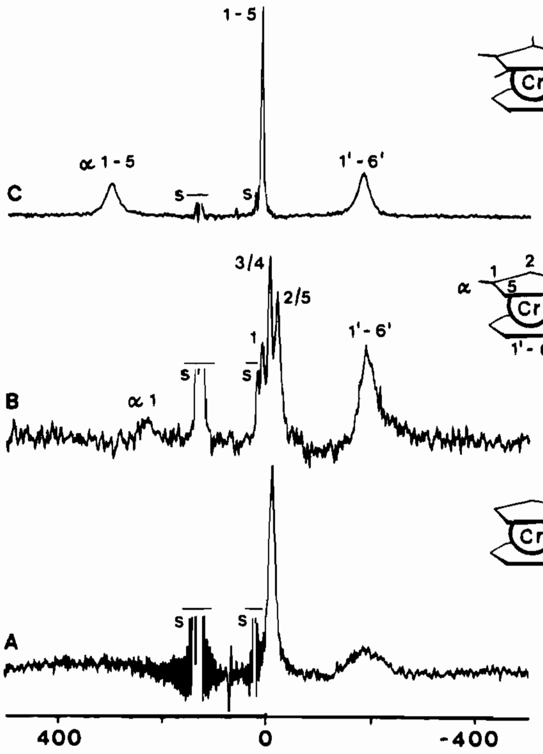


Figure 3. ^{13}C NMR spectra of **1** (A, 20 mol % solution in toluene-d_8), **2**, and **3** (B and C, respectively, both as a melt containing a few drops of toluene-d_8 (S)).

Table 3. EPR Data[a] of the $Cp^{(*)}Cr$(arene) Derivatives **1**, **3**, and **6**

	1[b]	**3**	**6**
g_{iso}		1.9900	1.9923
$g_{\parallel}$	2.0030	2.0019	2.0035
$g_{\perp}$	1.9787	1.9851	1.9846
$\langle g \rangle$	1.9885	1.9907	1.9909
$A(^1H)_{iso}$[c]	0.465	0.490	0.510
$A(^1H)_{\parallel}$[c]		0.450	0.500
$A(^1H)_{\perp}$[c]		0.525	0.525
$\langle A(^1H) \rangle$		0.500	0.515
$A(^{53}Cr)_{iso}$	1.468	1.375	1.365

[a] *A* in mT. [b] From ref 21. [c] Coupling constant of the arene.

3C where the corresponding signal also appears at high frequency. The α carbon signal widths of the arene ligands were particularly broad. Therefore the corresponding signal of **6** could be detected only from a mixture of **6** (34 mol %), **3** (18 mol % as a relaxation aid), and toluene-d_8. We were unable to locate the β carbon resonances of **5** and **7** even after changing the temperature and the solvent.

EPR Spectra. Compounds **3** and **6** were investigated as representative examples (Figure 4). At low temperature the liquid solution spectra display the hyperfine splitting due to the α protons of the arene ligands, while the interaction with the methyl protons is not resolved. For **3** the outer components of the heptet interfere with the satellites of the $I = {}^3/_2$ nucleus ^{53}Cr. This is obvious after comparison with the spectrum of **6**. As expected for molecules with axial symmetry, the frozen solution spectra show a *g* factor anisotropy which is small in this particular case. These results are similar to those of three other derivatives[13,21] of which **1**[21] was included in Table 3 for comparison.

Cp*Cr(arene) Cations. The Cp*Cr(arene) derivatives **3**, **6**, and **8** were investigated as representative examples by cyclic voltammetry (CV). As can be seen in Table 4 and Figure 5, three electron transfer (ET) reactions were observed for a 0.1 M solution of nBu_4NPF_6 in THF at 25 °C. Near −2.9 V (relative to internal Cp_2Fe/Cp_2Fe^+) the neutral compounds were reduced while oxidations were observed around −1 and 0 V. As for **8** this confirms earlier results.[16d] The reversability of the ETs was dependent of the final oxidation state, the arene, and the temperature.

In all cases the oxidation to $[Cp^*Cr(arene)]^{2+}$ was completely irreversible. When the solvent was 1,2-difluorobenzene rather than THF and when the temperature was lowered to −20 °C, a small reverse peak corresponding to $\mathbf{8}^{2+} \rightarrow \mathbf{8}^{+}$ appeared. For **3** and **8** the reduction to $[Cp^*Cr(arene)]^-$ and the oxidation to $[Cp^*Cr(arene)]^+$ were quasi-reversible. This was evident from

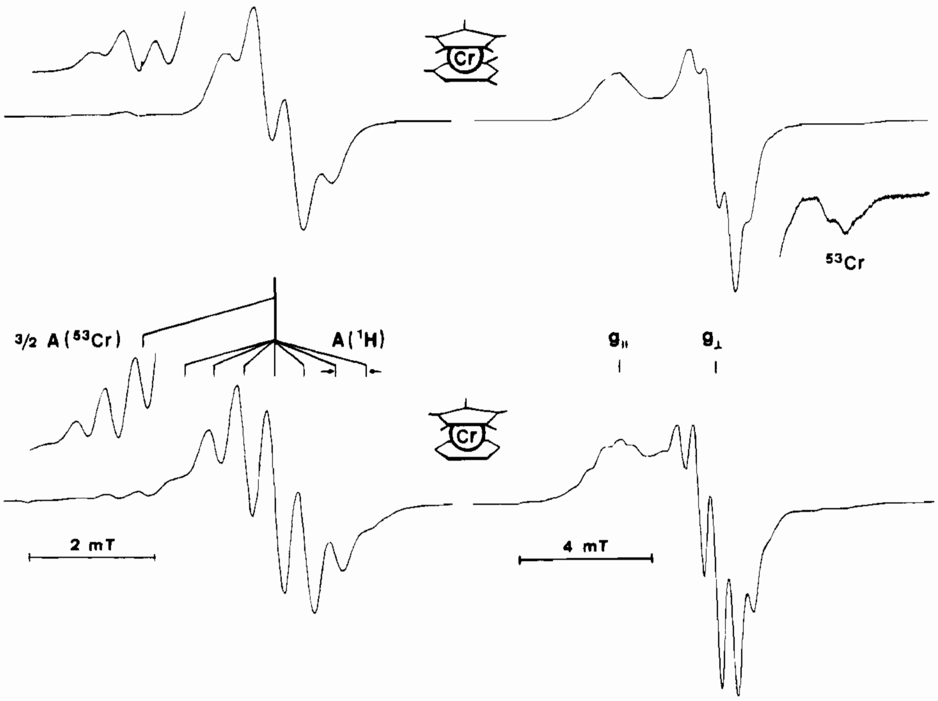


Figure 4. EPR spectra of **3** (bottom) and **6** (top) dissolved in petroleum ether. The liquid solution (left) is at 146 and 153 K, respectively. The glassy solution (right) is at 110 and 108 K, respectively.

Table 4. Electrochemical Results[a] of Cp*Cr(arene) Derivatives **3**, **6**, and **8** in THF

	3	**6**	**8**
$E_{1/2}(-1)^b$	−2815	2940	−2955
$\Delta E_p(-1)$	150	185	125
$i_{pc}/i_{pa}(-1)$	0.99	1.56	1.04
$E_{1/2}(1)$	−855	−1055	−1235
$\Delta E_p(1)$	85	165	120
$i_{pc}/i_{pa}(1)$	1.04	0.67	0.97
$E_{pa}(2)^c$	−60	−80	−25

[a] Potentials given in mV. $E_{1/2}$ values at 25 °C relative to Cp_2Fe/Cp_2Fe^+. [b] Successive cathodic and anodic ETs are numbered in parentheses. [c] Irreversible oxidation.

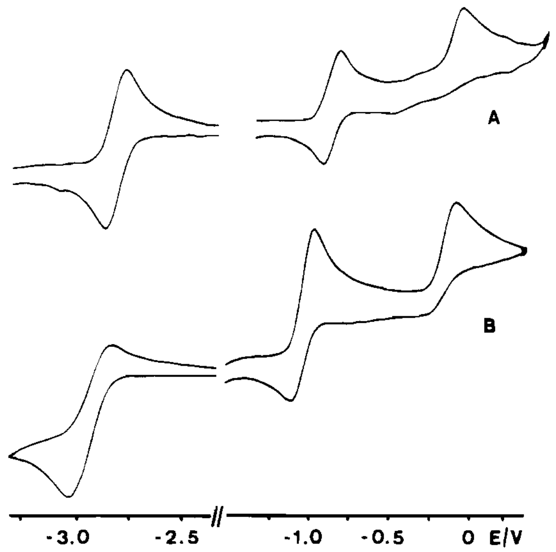


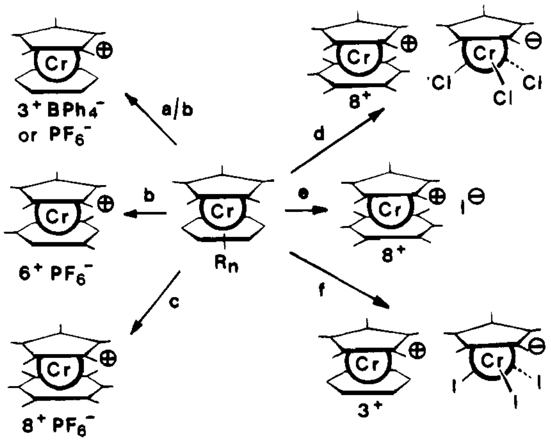
Figure 5. Cyclic voltammograms of $Cp^*Cr(C_6H_6)$ (**3**) (A) and $Cp^*Cr(Me_3C_6H_3)$ (**6**) (B) in THF at 25 °C. The scan rate is 200 mV s^{-1}, and the potential scale is relative to Cp_2Fe/Cp_2Fe^+.

the separation ΔE_p (Table 4) of the anodic and cathodic current peak (E_{pa} and E_{pc}) and from the fact that on stepwise increasing the scan rate v from 50 to 800 mV s^{-1} $i_p/\sqrt{v}$ (where i_p is the peak current) was not constant. The ratio i_{pc}/i_{pa} was close to unity which means that, under CV conditions, the monoanions and -cations are stable. By contrast, the corresponding ETs of **6** were only partly reversible. This is illustrated by comparing the CVs of **3** and **6** (Figure 5), and it is reflected in i_{pc}/i_{pa} which deviates strongly from unity (Table 4).

The oxidation to the monocation was investigated chemically as summarized in Scheme 1. The result depended strongly on the reagent and the counterion. Thus, a simple electron transfer reaction occurred between Cp*Cr(arene) compounds and ferrocenium ions. In this way $\mathbf{6}^+$ was isolated as orange-red $[PF_6]^-$ salt. In solution at room temperature it decomposed to give dark blue products which were chromium(III) half-sandwich derivatives according to their ^1H NMR signals (see below). Solvolysis occurred in 1,2-difluorobenzene within 2 days, in CH_2Cl_2 within hours, and in acetone within minutes. In an analogous reaction $\mathbf{3}^+[PF_6]^-$ could not be obtained free from dark decomposition products. However, rapid investigation by ^1H NMR spectroscopy in CD_2Cl_2 proved the formation of $\mathbf{3}^+$. By contrast, $\mathbf{3}^+$ could be isolated as tetraphenylborate salt.

The Cp*Cr(arene) derivatives were also oxidized by halogenated hydrocarbons. When treated with CH_2Cl_2 or $CHCl_3$, they gave dark blue $[Cp^*CrCl_2]_2$ as the final product. Depending on the arene ligand, a dark green intermediate was observed. For **8** the reaction was sufficiently slow to isolate the intermediate which was $\mathbf{8}^+[Cp^*CrCl_3]^-$ as shown by elemental analysis and NMR spectroscopy (see below). Obviously, under the reaction conditions, the arene of $\mathbf{8}^+$ was partly replaced by three chloro ligands in a further oxidation step. The color of $\mathbf{8}^+[Cp^*CrCl_3]^-$ corresponds to a mixture of orange-red $\mathbf{8}^+$ and the dark blue anion. We have observed a similar reaction for chromocene which was transformed to $[Cp_2Cr]^+[CpCrCl_3]^-$ by $CHCl_3$ or CH_2Cl_2.[24] **8** could also be oxidized by using allyl iodide or iodine. According to elemental analysis the resulting $\mathbf{8}^+I^-$ contained about 18% of $\mathbf{8}^+I_3^-$. Salt metathesis of the iodide and NH_4PF_6 gave pure $\mathbf{8}^+[PF_6]^-$. In a similar reaction **3** and allyl iodide failed to yield $\mathbf{3}^+I^-$. Rather a solid was obtained which analyzed for $\mathbf{3}^+[Cp^*CrI_3]^-$. This means that $\mathbf{3}^+$ splits off the arene more easily than $\mathbf{8}^+$ and that it follows a reaction path analogous to that of $\mathbf{8}^+$ in the presence of CH_2Cl_2. No Cp*Cr(arene) cation could be obtained by oxidation with air. Instead **3** gave red diamagnetic $[Cp^*CrO_2]_2$[12,25] in 50% yield.

Scheme 1[a]



[a] Key: (a) $[Cp^*_2Fe]^+[B(C_6H_5)_4]^-$; (b) $[Cp_2Fe]^+[PF_6]^-$; (c) I_2/NH_4PF_6; (d) CH_2Cl_2; (e) allyl iodide, 1:1; (f) allyl iodide, excess.

NMR spectra have been recorded for all cations. Owing to the limited stability in solution ^{13}C NMR results were obtained only for $\mathbf{8}^+$. Representative examples are selected in Figures 6 and 7, which show that the cations are paramagnetic. The signal assignment is based on the signal areas and the changes of the spectra with the number of methyl substituents. For instance, in the order from $\mathbf{6}^+[PF_6]^-$ and $\mathbf{8}^+[PF_6]^-$ to $\mathbf{8}^+[Cp^*CrCl_3]^-$ (Figure 6) the arene signal disappears, the signals in the methyl range adopt the ratio 5:6, and a new signal appears at −70 ppm which must belong to the $[Cp^*CrCl_3]^-$ ion. This is reminiscent of the signal position of $[Cp^*CrI_3]^-$ (-89.2 ppm).[19] Further details are discussed below, and the results are collected in Table 5.

Discussion

Formation of Cp*Cr(arene). The fact that Cp*Cr(arene) derivatives could be obtained from $[Cp^*CrCl_2]_2$ only in the presence of a strong Lewis acid suggests that the first step of the reaction sequence is the labilization of the Cr−Cl bonds by the attack of the Lewis acid (Scheme 2). In order to substantiate this view a solution of $[Cp^*CrCl_2]_2$ in C_6D_6 was treated with $AlCl_3$ and investigated by ^1H NMR spectroscopy (Figure 8). After addition of excess $AlCl_3$ the color changed from dark blue to blue-green and the spectrum B in Figure 8 was obtained.

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Table 5. Paramagnetic ^1H and ^{13}C NMR Results[a] of Cp*Cr(arene) Salts Compared to Those of Chromocenes at 305 K

nucleus and posn[c]		$3^+[PF_6]^-$	$6^+[PF_6]^-$	$8^+[PF_6]^-$	8^+I^- [d]	$8^+[Cp^*CrCl_3]^-$	Cp_2Cr	Cp^*_2Cr[e]
				Cp				
1−5	^{13}C			−227.9 (0.75)			−311.3 (0.23)	−418.2 (0.26)
α	^1H						308.9 (1.23)	
α	^{13}C			529 (0.60)				807 (0.47)
β	^1H	−18.7 (0.60)	−18.3 (0.25)	−18.8 (0.24)	−18.2 (0.36)	−18.5 (0.17)		−7.9 (0.17)
				Arene				
1′−6′	^{13}C			−250 (0.60)				
α	^1H	290 (2.80)	309 (2.30)					
α	^{13}C			609 (0.96)				
β	^1H		−11.6 (0.25)	−27.1 (0.23)	−27.4 (0.30)	−26.7 (0.20)		
$[Cp^*CrCl_3]^-$						−70.0 (0.70)		

[a] Signal shifts in ppm, negative signs means to low frequency. Signal half-width in kHz in parentheses. Solvent CD_2Cl_2 unless stated otherwise. [b] Taken from refs. 19, 23 and 26 and calculated to 305 K. [c] See Figures 1 and 3. [d] In D_2O. [e] In C_6D_6 or toluene-d_8.

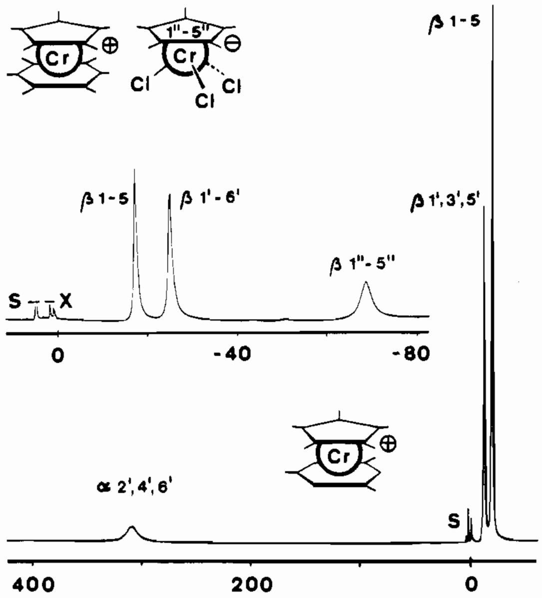


Figure 6. ^1H NMR spectra of $6^+PF_6^-$ (bottom) and $8^+[Cp^*CrCl_3]^-$ (top) dissolved in CD_2Cl_2 at 305 K and 306 K, respectively. S = solvent, and X = impurity. The scales are in ppm. For numbering see also Figures 1−3.

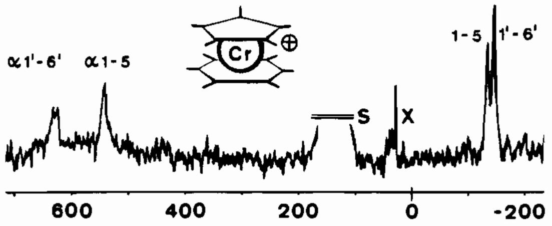
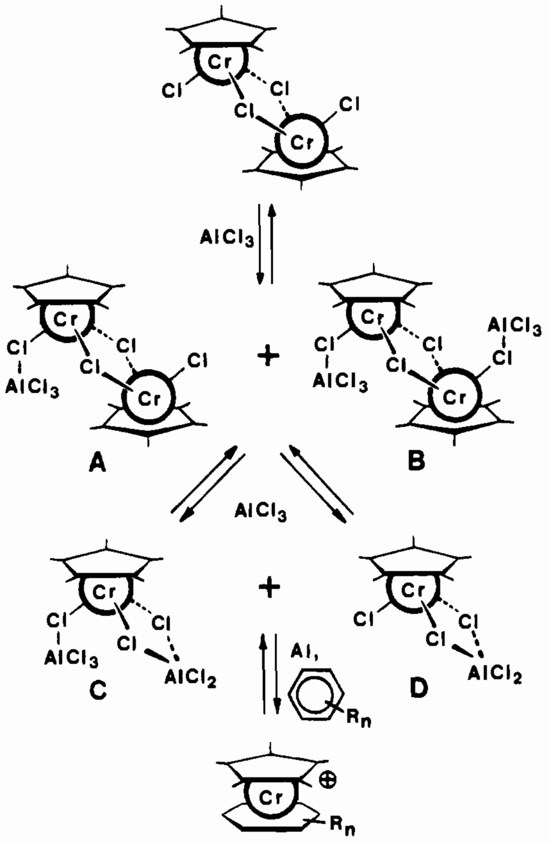


Figure 7. ^{13}C NMR spectrum of $8^+PF_6^-$ dissolved in 1,2-difluorbenzene at 305 K. S = solvent, and X = impurity. The scale is in ppm. For numbering see Figures 1−3.

The signal near −60 ppm is typical of a halogen-bridged dinuclear Cp^*Cr^{III} species.[16c,19] On cleavage of the halogen bridges, the signal is expected to move to low frequency, and therefore, we attribute the signal near −140 ppm to a mononuclear Cp^*Cr^{III} species.

We have verified this by temperature-dependent measurements. They prove that the signal at −140 ppm approximately follows the Curie law whereas that at −60 ppm strongly deviates as expected for a dinuclear species which experiences antiferromagnetic exchange.[16c] A hint to the different magnetic properties comes from the comparison of spectra B and C of Figure 8. Thus, on heating, the signal near −60 ppm hardly moves while that at −140 ppm shifts to high frequency.

Scheme 2



Comparison of spectra A and B of Figure 8 shows that after addition of $AlCl_3$ a dinuclear species is still present but that it is different from $[Cp^*CrCl_2]_2$. We conclude that species like **A** and **B** of Scheme 2 were formed and that the influence of $AlCl_3$ shifts the proton signal of Cp* to low frequency. We cannot rule out species that experience an interaction of $AlCl_3$ with a bridging chloride. However, if ever these species are present, their concentration should be much lower than that of **A** and **B** because *μ*-Cl is already engaged in a donor−acceptor interaction, i.e., the mutual stabilization of two Lewis-acidic fragments Cp^*CrCl_2. Finally, the signal at −140 ppm would belong to species like **C** and **D** of Scheme 2. Its shift would result from moving the signal of, for instance, $[Cp^*CrCl_3]^-$ at −70 ppm (Table 5) to low frequency by action of $AlCl_3$ similar to what was found for the dinuclear species. The spectra B−D of Figure 8 also establish a temperature-dependent equilibrium between mono- and dinuclear species. For unknown reasons the original ratio of the compounds is not fully re-established after heating, cooling back, and standing for 7 days. The labilizing effect of AlX_3 on M−X bonds in organometallic

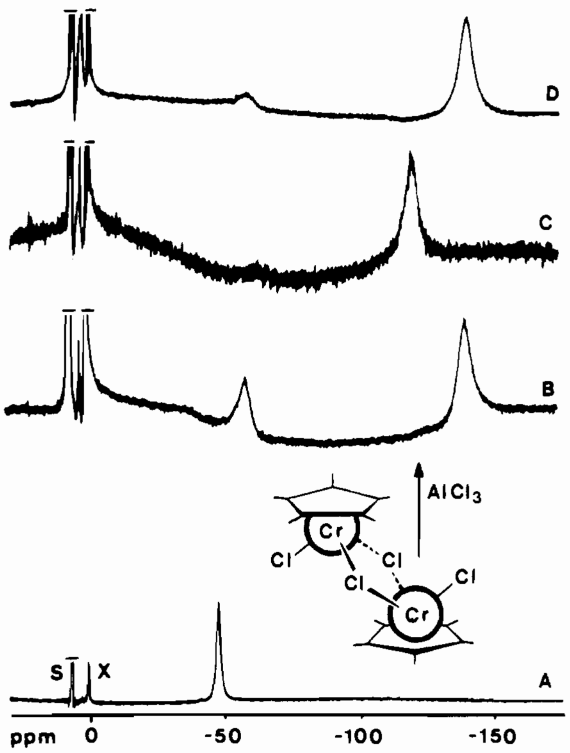


Figure 8. ^{1}H NMR spectra of the reaction of $[Cp^*CrCl_2]_2$ with $AlCl_3$ in C_6D_6: A, unreacted $[Cp^*CrCl_2]_2$ at 305 K; B, after addition of $AlCl_3$ at 305 K; C, as in (B) but at 357 K; D, As in (B) but after heating to 357 K and cooling back. S = solvent, and X = impurity.

chemistry has been discussed previously, e.g., for the formation of $[(C_6H_6)_2Cr]^+$[27] and the activation of Cp_2TiCl_2 and $Cp_2Ti(Cl)R$.[28] It is also interesting that half-sandwiches of the type $(arene)M(\mu_2\text{-}Cl_2AlCl_2)_2$ could be isolated.[29] We can exclude a similar compound $Cp^*Cr(\mu_2\text{-}Cl_2AlCl_2)_2$ having a four-legged piano stool structure because the proton signal of the corresponding 17-electron species $[Cp^*CrL_4]^{2+}$ appears near -28 ppm,[30] a range where no signals were found in the present study.

Most probably the formation of the sandwich (last step in Scheme 2) proceeds only in the presence of a reducing agent because, according to cyclic voltammetry, the dication $[Cp^*Cr(arene)]^{2+}$ is not stable (cf. Figure 5). With aluminum the reduction stops at Cr(II) as demonstrated by the ^{1}H NMR spectrum in Figure 9. It was obtained from the crude product which formed after heating $[Cp^*CrCl_2]_2$, Al, $AlCl_3$, $AlBr_3$, and mesitylene (see Experimental Section) and shows the presence of $[Cp^*Cr(mesitylene)]^+$ (signals near 250, -8, and -13 ppm) and of species of the type **C** and **D** of Scheme 2 (signal near -119 ppm). When these signal shifts are converted to paramagnetic shifts and calculated for 305 K following the Curie law, they are in good agreement with those of $\mathbf{6}^+$ given in Table 5 and the results illustrated in Figure 8. The last step of Scheme 2 is reversible. Thus, when orange-red $\mathbf{8}^+[PF_6]^-$ was dissolved in a melt of $AlCl_3/AlBr_3$ at 390 K, the mixture became dark green and the ^{1}H NMR spectrum showed a signal for free hexamethylbenzene and a second one near -120 ppm. This points to the oxidative cleavage of the arene and to the formation of Cp^*Cr^{III} species like **C** and **D** already seen above. Nothing is known about the redox partner at present.

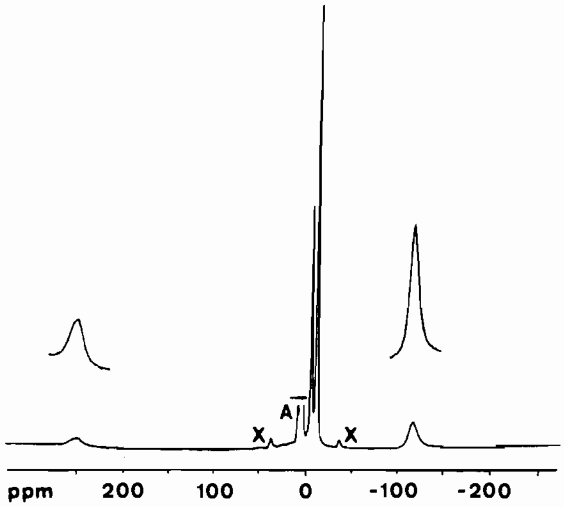
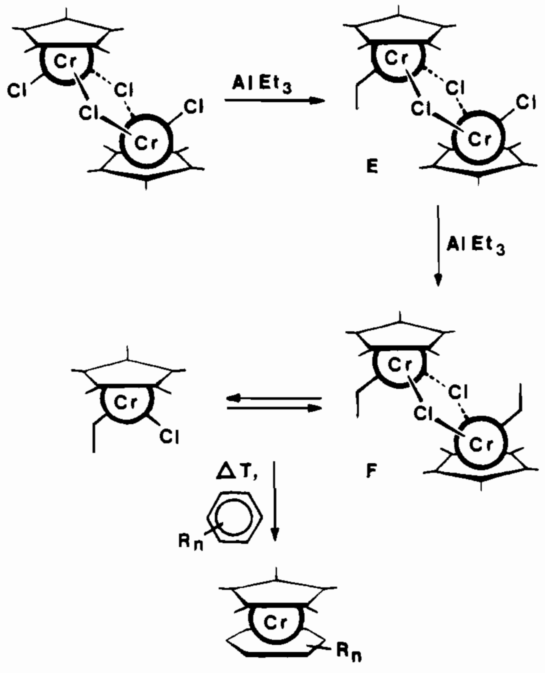


Figure 9. ^{1}H NMR spectrum of the product obtained from the reaction of $[Cp^*CrCl_2]_2$ with AlX_3, Al, and mesitylene dissolved in an eutectic mixture of $AlCl_3/AlBr_3$ at 374 K. See text for details. A = free arene, and X = unidentified paramagnetic species.

Scheme 3



When $AlEt_3$ was used rather than AlX_3, the reaction took a different course (Scheme 3).Thus the reaction of $[Cp^*CrCl_2]_2$ with $AlEt_3$ gave a hexane-soluble dark oil from which a red-violet powder was obtained after addition of ether. Since alkylated derivatives of the type $[Cp^{(*)}Cr(R)\mu\text{-}X]_2$ are known,[16b,d,19,31] it is reasonable to consider the formation of compound **F** in Scheme 3. Indeed the ^{1}H NMR spectrum of the powder dissolved in toluene-d_8 shows a big signal near -9 ppm, exactly where we have found the Cp* signals of *cis*- and *trans*-$[Cp^*Cr(CH_3)\mu\text{-}Cl]_2$ (-9.5 and -10.9 ppm[19]). In addition small signals were found whose shifts were compatible with the Cp* signals of residual starting compound (near -50 ppm[16b]) and a small amount of the partly alkylated compound **E** (near -11 and -43 ppm). A further broad signal near -80 ppm was tentatively assigned to the CH_3 groups of the $CrCH_2CH_3$

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fragments, while the corresponding CH_2 groups could not be observed in accord with earlier findings.[16b] Temperature-dependent spectra showed that all signal shifts deviated from the Curie law as expected for antiferromagnetic dinuclear compounds and as found for $[Cp^*CrCl_2]_2$.[16c,d] In the last step of Scheme 3, which has not been studied in detail, the replacement of the ethyl group and chloride in **F** or possibly its monomer[32] by the arene would finally yield the sandwich. One may also think of intermediates in which $AlEt_3$ interacts with chromium fragments similarly as does $AlCl_3$ (see discussion accompanying Scheme 2). In the case of $AlEt_3$ we have no experimental evidence for these intermediates.

Electronic Ground State and Spectrum Optimization of the Neutral Sandwiches. The electronic ground state of $CpCr(C_6H_6)$ is $^2A_1$ (e_2^4, a_1).[33] This was derived from the similarity of its EPR spectrum with those of bis(arene)chromium cations.[21] For the latter $g = 2$, a small g factor anisotropy, and the uniform $A(^1H)$ values of bis(toluene)chromium cation were taken as evidence that the unpaired electron sits in an orbital which has essentially chromium $3d_{z^2}$ character.[34] Later this was confirmed by MO calculations.[35]

The ground state is of paramount importance for the observation of EPR or NMR signals. In the case of d^5 sandwiches both $^2E_2$ (a_1^2, e_2^3) and $^2A_1$ are known. It turns out that the NMR signals of $^2E_2$ compounds like ferrocenium ions[8] and low-spin manganocenes[36] are rather narrow, while they are very broad for the $^2A_1$ chromium compounds of this work. Other sandwiches which are known or supposed to have a $^2A_1$ ground state and which yield only very broad or no solution NMR signals are $(C_6H_6)_2V$,[37] $[(C_6H_6)_2Cr]^+$,[37] $CpV(C_7H_7)$,[38] $[CpCr(C_7H_7)]^+$,[8] and $CpTi(C_8H_8)$.[39] By contrast, well-resolved EPR spectra were obtained for these compounds at or not far below room temperature.[8,38–40] We conclude that, generally, the nuclear relaxation of low-spin d^5 sandwiches should allow us to determine their electronic ground state.

A striking relaxation feature is the decrease of the signal half-width W with increasing sample concentration. This can be understood when we recall that, for small paramagentic molecules, W may be approximated by $\pi W = 1/T_{2n}^{dip} + 1/T_{2n}^{con}$, where T_{2n}^{dip} and T_{2n}^{con} are the transverse nuclear relaxation times due to dipolar and contact interaction, respectively, between the nucleus and the paramagnetic metal center. On the basis of earlier treatments[41] and with assumption that the fast motion limit applies, we can write

$$1/T_{2n}^{\mathrm{dip}} = C^{\mathrm{dip}}\gamma_n^{\,2} r^{-6}\tau_c \qquad (1)$$

$$1/T_{2n}^{\mathrm{con}} = C^{\mathrm{con}}\gamma_n^{\,2}(\delta^{\mathrm{con}})^2\tau_2 \qquad (2)$$

Here γ_n is the nuclear gyromagnetic ratio, r is the distance between the nucleus under study and the metal, δ^{con} is the contact shift of the signal, τ_c and τ_e are correlation times, and C^{dip} and C^{con} are constants for a given molecule at a given temperature.

Equations 1 and 2 are a useful experimental guide. First they show that, independent of the relaxation mechanisms, W decreases with γ_n^2. This is why the ^{13}C NMR signals are narrower than similar ^1H NMR signals (Table 2) and why ^2H NMR spectroscopy is advantageous. In addition the ratio

$$T_{2n}^{\mathrm{dip}}/T_{2n}^{\mathrm{con}} = 4.8 \times 10^5 r^6(\delta^{\mathrm{con}})^2 \qquad (3)$$

allows us to determine the dominating relaxation mechanism. Equation 3 applies for 305 K, $g = 2$, $S = {}^1/_2$, and $\tau_c \approx \tau_e$. δ^{con} can be safely approximated by the shifts given in Table 2 as will be shown below. r values may be obtained from Cp*−Cr and arene−Cr distances of 1.80−1.83 Å and 1.35−1.57 Å,[15] respectively, and from standard C−C and C−H distances. When corresponding δ^{con} and r values are inserted into eq 3, it turns out that T_{2n}^{dip} and T_{2n}^{con} are comparable for all ring-C and Hβ nuclei while the contact relaxation dominates for all other nuclei. A dominating contact relaxation means that W is determined by the electron spin relaxation time (via τ_e in eq 2) unless some exchange is taking place.[41]

This has practical consequences when rather slow electron spin relaxation leads to broad signals as for **1−8**. Apart from changing γ_n, signal narrowing can be achieved by intermolecular electron exchange interaction which, of course, increases with the concentration of the sample. In our case this mechanism seems to be particularly efficient because the spin-carrying d_{z^2} orbital partly penetrates the arene ligand.[42]

Distribution of the Electron Spin in Cp^(*)Cr(arene) Compounds. The paramagentic NMR signal shift is proportional to the hyperfine coupling constants A(X), and thus it is a measure of the electron spin density at the nucleus X, provided contact shifts δ^{con} are available. For **1−8** δ^{con} is obtained by calculating the dipolar shifts δ^{dip} [43] and subtracting them from the data given in Table 2. Here we confine ourselves to the metal-centered dipolar shifts which depend on the g factor anisotropy and the position of nucleus X relative to the metal. Taking the geometric data of ref 15 and the data of Table 3, δ^{dip} at 305 K varies ±0.3 ppm for the protons of **1−8** and between −0.2 and 1.6 ppm for ^{13}C. Hence we can neglect δ^{dip} and consider the signal shifts given in Table 2 as δ^{con}. This is confirmed by the $A(^1H)$ values which can be calculated[43] from δ^{con}. For the arene protons of **1** and **3** we obtain 0.45 and 0.47 mT (0.44 mT from ^2H NMR), respectively, which agrees with the EPR data of Table 3 within the error limits and with the previous findings.[21]

It is clear from the EPR and the NMR data that appreciable spin density must be present on the ligands. With regard to any stacking of sandwiches mentioned in the introduction it is important to know in which ligand orbitals the spin resides and what sign it has. From $\delta^{con} \sim \varrho$ (with ϱ being the spin density) it follows that the spin at all ring-C atoms is negative. In order to see whether the spin sits in the ligand π system we have developed a selective NMR method which is based on the signal shifts of Hβ or, preferably, Cβ.[8] Suitable molecules are Cp*Cr(ethylbenzene) (**5**) and Cp*Cr(ethylmesitylene) (**7**), which were

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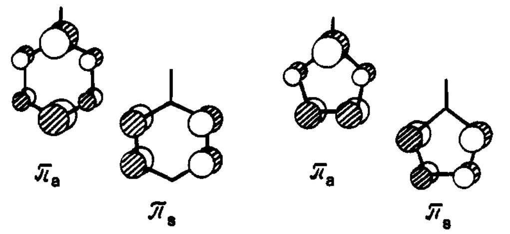

Figure 10. e_1-type ligand π orbitals involved in spin delocalization. Radii approximate the coefficients of the carbon $2p_z$ orbitals.

synthesized for this purpose. While the Cβ signals could not be found the Hβ signals worked well. In the order from **5** to **7** the signal moved from -41.9 to -29.4 ppm, i.e., to high frequency. This is indicative of negative spin in the ligand π system[8,44] and sheds new light on the delocalization:[21] The electrons in the e_2 and e_1 orbitals must be engaged in spin polarization.

Predominating π delocalization also follows from the fact that the sign of δ^{con} changes on going from the ring-C atoms to Cα (or Hα) and further to Hβ (Table 2). However, in contrast with typical π-delocalized spin in sandwiches like nickelocenes[45] the magnitude of the shift $|\delta(\text{ring-C})|$ is smaller than $|\delta(\text{C}\alpha)|$ and the ratio $|\delta(\text{H}\alpha)|/|\delta(\text{H}\beta)|$ is much bigger. This is expected when the spin is partly delocalized into the ligand σ system. Then additional positive spin appears at all nuclei thus decreasing the magnitude of the spin at the ring-C atoms and Hβ while increasing it at Cα and Hα. Since the singly occupied MO of Cp*Cr(arene) has mainly d_{z^2} character, the ligand σ orbitals appropriate for mixing are the σ-a_1'(CH) orbitals.[46] Their energy is rather different from that of the d-block, but the overlap should be good.

When any cyclic ligand of a sandwich is substituted with, for instance, one methyl group, the signal of the ring-C atoms and that of Hα splits. The nature of this splitting has been described in some detail previously[8,20,47] so that we just summarize the consequences for the present $S = 1/2$ case. When π polarization predominates, i.e., when the ligand content of the (bonding) e_1-type orbitals (Figure 10) reflects the spin distribution, the signal sequence of the ring-C atoms and Hα should follow the relative (squared) orbital coefficients of π_s or π_a shown in Figure 10. Two independent experiments establish that the π_a orbital is more engaged in the spin delocalization than π_s. Thus, the Cp signal sequence of Cp′Cr(C$_6$H$_6$) is $|\delta(\text{C1})| < |\delta(\text{C3/4})| < |\delta(\text{C2/5})|$ (Figure 3B) and the arene signal sequence of Cp*Cr(toluene-d_8) is $\delta(\text{D4}) < \delta(\text{D3/5}) \approx \delta(\text{D2/6})$ (Figure 2). The splitting of these signals is remarkably small and seems to be a typical feature of the $^2A_1$ ground state. We speculate that the signal splitting expected from the π_a orbitals in Figure 10 is partly compensated by the σ delocalization. A hint comes from the squared carbon 2s coefficients of the σ-a_1'orbital of Cp′$^-$ which increases on passing from C3/4 to C2/5 and C1.[46c]

The $\delta(^{13}\text{C})$, $\delta(^1\text{H})$, and $A(^1\text{H})$ values of Tables 2 and 3 clearly indicate that more spin is induced on the arene than on the Cp ligand. This originates mainly from the fact that the arene π orbitals are lower in energy than those of Cp$^-$ so that the ligand content of the e_2 and e_1 orbitals engaged in spin polarization is bigger for the arene.[35] It is tempting to quantify the ratio of the spin densities by comparing the NMR or EPR results of corresponding nuclei of both ligands. However, this ratio changes when passing from the ring-C atoms to Hα (or Cα) and Hβ because two delocalization mechanisms are operating and the relative π and σ contributions change from one nucleus to the next.

Cp*Cr(arene) Cations. The monocations form at potentials that depend on the number of CH$_3$ substituents; a preliminary estimate from Table 4 is -60 mV per additional CH$_3$ group. This trend corresponds to what is known for other sandwich compounds[48] although the potential difference per CH$_3$ group may change considerably. Extrapolation leads to $E_{1/2} = -0.55$ V for CpCr(C$_6$H$_6$) (**1**), which is somewhat more anodic than found previously (irreversible ET at -0.65 V[49]). The oxidation of **1** occurs about 0.6 V more anodic than that of the (closed-shell) sandwiches (C$_6$H$_6$)$_2$Cr (-1.29 V) and CpCr(C$_7$H$_7$) (-1.18 V).[50] This may explain why (C$_6$H$_6$)$_2$Cr$^+$ and CpCr(C$_7$H$_7$)$^+$ are stable while **1**$^+$ decomposes rapidly in solution. Note that the CH$_3$ groups of Cp*Cr(C$_6$Me$_6$) (**8**) lower $E_{1/2}$ to -1.24 V and that therefore **8**$^+$ is considerably more stable than **1**$^+$.

From the CV experiments and the preparative results it follows that the decomposition of Cp$^{(*)}$Cr(arene) cations can be slowed down by optimizing the following points. (i) The counterion should be noncoordinating; PF$_6^-$ is satisfactory in many cases. (ii) The solvent should be polar and a bad donor; 1,2-difluorobenzene proved more suitable than CH$_2$Cl$_2$ probably because the C$-$Cl bond is more labile. (iii) When experiments are performed in solution, the temperature should be low. (iv) The oxidation potential should be kept low by introducing donor substituents.

As for the ground state, the d^4 complex [Cp*Cr(arene)]$^+$ could be diamagnetic ($^1A_1$ (e_2^4, a_1^0)) or paramagnetic. According to the NMR results there is no doubt that the cations are paramagnetic. This confirms the suspicion that a $^1A_1$ ground state found by INDO calculations is not very likely.[35] In the further discussion we relate the cations to the d^4 sandwich chromocene for which a $^3E_2$ ground state rather than other triplet states or quintet states fits the experimental results.[51] Actually, the NMR data of both sandwich types are very similar. In the order from Cp*Cr(arene) (Table 2) to [Cp*Cr(arene)]$^+$ (Table 5) the signal half-widths W decrease up to a factor of more than 10, and if any concentration dependence of W is left it is much less pronounced. This corresponds to what is known for chromocenes (Table 5) although the various W values of [Cp*Cr(arene)]$^+$ remain roughly twice as big. The NMR signal shifts of analogous protons of both d^4 sandwich types are also very similar while those of ^{13}C are larger for chromocenes than

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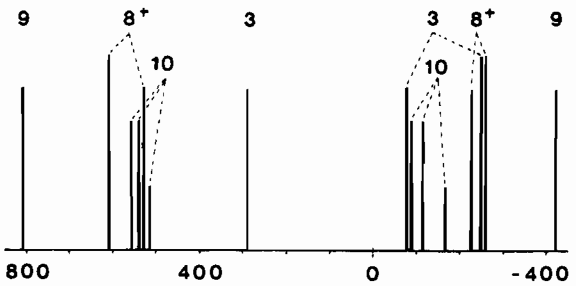

Figure 11. Comparison of the signals of the ring-C atoms (negative shifts) and of Cα (positive shifts) for $[Cp^*Cr(C_6Me_6)]^+$ (**8**$^+$), $Cp^*Cr(C_6H_6)$ (**3**), Cp^*_2Cr (**9**), and $[(EtMe_4C_5)_2Mn]^+$(**10**) at 305 K. The scale is in ppm. The relative intensities refer to six- and five-membered rings or to the symmetry-related signal splitting of **10**.

for $[Cr^*Cr(arene)]^+$. In summary it is reasonable to assume a $^3E_2$ ground state for $[Cp^*Cr(arene)]^+$.

The electron delocalization follows from the NMR signal pattern of e.g. **6**$^+$ and **8**$^+$ (Table 5). Like for the neutral precursors the signal shift of the ring-C atoms is negative and the sign changes on going to α and β nuclei. This is characteristic of a predominating π polarization and of negative spin in the ligand π orbitals. Hence $[Cp^*Cr(arene)]^+$ cations should be suitable building blocks for ferromagnetic donor–acceptor chains. The fact that $\delta(C\alpha)$ is bigger than $|\delta(\text{ring-C})|$ indicates that σ delocalization is also present (again similar to the neutral precursors). Finally, dipolar shifts must be considered as well. For a rough estimate of the metal-centered dipolar shifts[43] we assume the metal–ligand distances to be 10 pm longer than in the neutral precursors and take the remaining parameters from chromocenes.[51] This yields values which are 20–30 times larger than the dipolar shifts calculated for Cp*Cr(arene) (vide supra) but which are still too small as to change the general trends.

These trends are illustrated in Figure 11 where we compare the ^{13}C NMR signal shifts of the cation **8**$^+$ with those of **3**, Cp^*_2Cr, and the manganocenium ion $[(EtMe_4C_5)_2Mn]^+$:[8] (i) The unpaired spin on the ligands increases in the order **3** < **8**$^+$ < Cp^*_2Cr. (ii) The imbalance of spin in the five- and six-membered ring decreases considerably on going from **3** to **8**$^+$. (iii) The spin distribution within $[(EtMe_4C_5)_2Mn]^+$, the only other well-studied d^4 sandwich cation known so far, is very similar to that within **8**$^+$. Comparison of $|\delta(C\alpha)|$ and $|\delta(\text{ring-C})|$ suggests that in **8**$^+$ the π polarization is more efficient. It follows that, when the chemical stability is sufficient, $[Cp^*Cr(arene)]^+$ cations should behave like $[Cp^*_2Mn]^+$ which gives the highest Curie temperatures of ferromagnetic donor–acceptor stacks.[52] Corresponding experiments are in progress and will be reported in due course.

Conclusion

For the synthesis of Cp*Cr(arene) derivatives three methods have been developed that are generally applicable. The reactions proceed only after activation of the starting $[Cp^*CrCl_2]_2$ either by cleaving it with $AlCl_3$ or by partial exchange of Cl for alkyl. Subsequent reduction from Cr(III) to Cr(I) proceeds step by step or, when Cp*Cr(Cl)R species are engaged, by reductive elimination.

The oxidation of Cp*Cr(arene) compounds yields a new family of paramagnetic sandwich cations that meet the electronic requirements of building blocks in ferromagnetic stacks: delocalization of spin onto the ligands in such a way that negative spin appears in the ligand π orbitals. These properties are due to the fact that the two unpaired electrons sit in e_2-type ($d_{xy}/d_{x^2-y^2}$ character) and a_1-type (d_{z^2} character) MOs. In the neutral precursor just one unpaired electron in an a_1-type MO leads to a similar, albeit less pronounced, induction of spin on the ligands.

NMR and EPR prove to be efficient methods for obtaining this information. In the case of CpCr(arene) compounds a delicate balance of sample concentration and temperature allows one to shift the relaxation either into the EPR or the NMR regime.

Experimental Section

A combined Schlenk tube/Teflon cannula technique was used for the synthesis and the characterization of all compounds under purified nitrogen. The solvents were dried by standard methods and freed from oxygen. Analytically pure $CpCr(C_6H_6)$ was prepared according to the literature.[9] The melting points were determined in sealed capillaries, and the elemental analyses were carried out by the Inorganic Microanalytical Laboratory at Garching, Germany.

Cp*Cr (arene) from $[Cp^*CrCl_2]_2$ and AlX_3/Al. (1) (η-Pentamethylcyclopentadienyl)(η-benzene)chromium (3). A stirred dark blue mixture of 1.49 g (2.88 mmol) of $[Cp^*CrCl_2]_2$,[16] 2.10 g (15.8 mmol) of $AlCl_3$, 0.80 g (21.1 mmol) of $LiAlH_4$, 0.50 g (18.5 mmol) of aluminum, and 20 mL of benzene was heated to reflux. After 1 h the liquid phase was colorless and a red brown solid had formed. The mixture was cooled to 25 °C and 10 mL of Et_2O was added whereupon the solid partly dissolved and hydrogen was evolved. After the solution was stirred for 2 h, the solvents were removed under reduced pressure, the residue was extracted with 100 mL of pentane, and the yellow solution was passed over silica gel (Merck 60, 63–200 μm, column height/diameter 30/20 mm). The silica gel was washed with 100 mL of pentane, and from the combined solutions the solvent was evaporated. Sublimation (0.13 Pa, 75 °C bath temperature) of the residue gave orange crystals of **3** (yield 0.60 g, 39%), mp 98 °C. MS (*m/z* (%)): 265 (77), M^+; 187 (96), Cp^*Cr^+; 133 (26) $Cp^{*+} - 2H$; 130 (2), $(C_6H_6)Cr^+$; 78 (26), $C_6H_6^+$; 52 (100), Cr^+. Anal. Calcd for $C_{16}H_{21}Cr$: C, 72.43; H, 7.97; Cr, 19.59. Found: C, 72.78; H, 8.20; Cr, 18.89.

(2) (η-Pentamethylcyclopentadienyl)(η-hexadeuteriobenzene)chromium (3*d*$_6$). The synthesis was analogous to that of **3**, wherein 2.21 g (4.3 mmol) of $[Cp^*CrCl_2]_2$, 3.60 g (27.0 mmol) of $AlCl_3$, 1.04 g (38.5 mmol) of aluminum, 1.04 g (27.4 mmol) of $LiAlH_4$, and 10 mL of C_6D_6 yielded 1.19 g (51%) of **3*d*$_6$**, mp 98 °C. MS (*m/z* (%)): 271 (58), M^+; 187 (77), Cp^*Cr^+; 136 (5), $(C_6D_6)Cr^+$; 133 (17), $Cp^{*+} - 2H$; 84 (47), C_6D_6; 52 (100), Cr^+.

(3) (η-Pentamethylcyclopentadienyl)(η-mesitylene)chromium (6). A mixture of 5.96 g (22.3 mmol) of $AlBr_3$ and 2.15 g (26.5 mmol) of $AlCl_3$ was dried by heating it with 5 mL of cyclohexane and 2 mL of a 1.7 M solution of nBuLi in hexane to reflux for 30 min. Then 2 mL (14.4 mmol) of mesitylene, 1.00 g (37.1 mmol) of aluminum, and 1.33 g (2.6 mmol) of $[Cp^*CrCl_2]_2$ were added at room temperature. Heating under reflux for 1 h gave a brown product a small quantity of which was investigated directly by ^1H NMR spectroscopy. It showed the signals of the cation $[Cp^*Cr(mesitylene)]^+$. After addition of 0.90 g (23.7 mmol) of $LiAlH_4$ at room temperature 50 mL of Et_2O and 50 mL of THF were dropped into the mixture whereupon hydrogen was evolved. When the reaction was finished, most of the solvents were stripped and the remainder was extracted with two 100 mL portions of boiling hexane. The extract was reduced to 100 mL and worked up as described under part 1. Sublimation at 1.3 Pa and 100 °C bath temperature gave little oily product which was rejected. Raising the temperature to 120 °C gave red-brown crystalline **6** (yield 0.64 g, 40%), mp 170 °C. MS (*m/z* (%)): 307 (100), M^+; 187 (71), Cp^*Cr^+; 172 (10), $(Me_3C_6H_3)Cr^+$; 133 (25), $Cp^{*+} - 2H$; 120 (25), $Me_3C_6H_3^+$; 52 (63), Cr^+. Anal. Calcd for $C_{19}H_{27}Cr$: C, 74.23; H, 8.85; Cr, 16.91. Found: C, 74.39; H, 9.00; Cr, 16.56.

(4) (η-Pentamethylcyclopentadienyl)(η-hexamethylbenzene)chromium (8). A mixture of 3.07 g (5.94 mmol) of $[Cp^*CrCl_2]_2$, 4.00 g

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(24.6 mmol) of hexamethylbenzene, 7.40 g (55.5 mmol) of $AlCl_3$, and 2.00 g (74.1 mmol) of aluminum was heated to 160 °C for 5 min, and the resulting brown melt was stirred for 6 h at 100 °C. On being cooled to ambient temperature, the product solidified. After addition of 300 mL of ether the product was grinded, a solution of 10.00 g (57.4 mmol) of $Na_2S_2O_4$ and 25.0 g (445 mmol) of KOH in 200 mL of water was poured into the flask, and the mixture was stirred for 18 h. The yellow-brown ether phase was separated, the aqueous phase was extracted with 400 mL of hexane, and the solvents were stripped from the combined organic solutions. The remaining solid was dissolved in 500 mL of hexane and passed over silica gel as described under part 1. After stripping of the solvent, excess hexamethylbenzene was sublimed off for 3 h at 1.3 Pa and a bath temperature of 70 °C. Recrystallization from hot hexane gave red-brown crystals of **8** (yield 3.14 g, 75%), mp 354 °C (dec). MS (*m/z* (%)): 349 (100), M^+; 214 (6), $(Me_6C_6)Cr^+$; 187 (20), Cp^*Cr^+; 162 (21), $Me_6C_6^+$; 133 (18), $Cp^{*+} - 2H$; 52 (78), Cr^+. Anal. Calcd for $C_{22}H_{33}Cr$: C, 75.61; H, 9.51; Cr, 14.88. Found: C, 75.58; H, 9.54; Cr, 14.96.

(5) (*η*-Methylcyclopentadienyl)(*η*-benzene)chromium (2). The synthesis was carried out with 10.3 g (37.6 mmol) of $AlBr_3$, 3.30 g (122 mmol) of aluminum, 10.00 g (263 mmol) of $LiAlH_4$, 30 mL of benzene, and 5.37 g (13.3 g) $[Cp'CrCl_2]_2$[19] as described under part 1 except that the temperature was kept below 25 °C. Final sublimation and recrystallization (pentane, −40 °C) of the oily product gave orange platelets of **2** (yield 30 mg, 0.5%), mp 116 °C. MS (*m/z* (%)): 209 (37), M^+; 131 (85), $(MeCp)Cr^+$; 79 (2), $MeCp^+$; 78 (7), $C_6H_6^+$; 52 (100), Cr^+. Anal. Calcd for $C_{12}H_{13}Cr$: C, 68.88; H, 6.26; Cr, 24.85. Found: C, 68.77; H, 6.00; Cr, 24.13.

Cp*Cr(arene) from $[Cp^*CrCl_2]_2$ and $AlEt_3/\Delta T$. (6) (*η*-Pentamethylcyclopentadienyl)(*η*-toluene)chromium (4). A 30 mL volume of a 0.48 M commercial solution of Al_2Et_6 (28.8 mmol $AlEt_3$) in toluene was diluted with 30 mL of toluene. When 5.40 g (10.5 mmol) of $[Cp^*CrCl_2]_2$ was added under stirring at 25 °C, the mixture became dark wine-red. After the mixture was heated to reflux for 1 h and cooled to 25 °C, excess $AlEt_3$ was destroyed by dropwise addition of 15 mL of methanol, the reaction mixture was filtered over silica gel, and the solvents were removed under reduced pressure. Sublimation (1.3 Pa, 80 °C bath temperature) gave orange crystals of **4** (yield 2.93 g, 50%), mp 98 °C. MS (*m/z* (%)): 279 (100), M^+; 187 (99), Cp^*Cr^+; 92 (67), $MeC_6H_5^+$; 91 (90), $C_7H_7^+$; 52 (80), Cr^+. Anal. Calcd for $C_{17}H_{23}Cr$: C, 73.09; H, 8.30. Found: C, 71.99; H, 8.23.

(7) (*η*-Pentamethylcyclopentadienyl)(*η*-octadeuteriotoluene)chromium (4*d*$_8$). The synthesis was similar to that of **4**. A 30 mL volume of a 0.5 M solution of Al_2Et_6 in hexane (30.0 mmol $AlEt_3$), 7.5 mL (70.4 mmol) of toluene-d_8, and 1.83 g (3.5 mmol) of $[Cp^*CrCl_2]_2$ yielded 0.95 g (47%) of **4*d*$_8$**, mp 98 °C. MS (*m/z* (%)): 287 (52), M^+; 187 (100), Cp^*Cr^+; 100 (43), $CD_3C_6D_5^-$; 98 (50), $C_7D_7^+$; 52 (86), Cr^-.

By the same method 1.80 g (35%) of **3** was obtained from 5.00 g (9.7 mmol) of $[Cp^*CrCl_2]_2$, 50 mL of a 0.5 M solution of Al_2Et_6 (50 mmol $AlEt_3$), and 20 mL of benzene and 3.83 g (57%) of **6** from 5.61 g (10.9 mmol) of $[Cp^*CrCl_2]_2$, 62.2 mL of a 0.5 M solution of Al_2Et_6 in hexane (62.2 mmol $AlEt_3$), and 15 mL of mesitylene.

Cp*Cr(arene) from $[Cp^*CrCl_2]_2$ and $AlEt_3/LiAlH_4$. (8) (*η*-Pentamethylcyclopentadienyl)(*η*-ethylbenzene)chromium (5). To a wine-red solution of 20 mL of ethylbenzene, 15.5 mL of a 0.5 M solution of Al_2Et_6 in hexane (15.5 mmol $AlEt_3$), and 3.10 g (6.0 mmol) of $[Cp^*CrCl_2]_2$ was added 1.55 g (40.8 mmol) of $LiAlH_4$. After being stirred for 24 h at 25 °C the mixture was diluted with 100 mL of hexane and 20 mL of ether, and the new mixture was stirred for 1 h and filtered. Excess reagents were destroyed with 3.0 mL (75 mmol) of methanol. When the evolution of gas was terminated, the solution was filtered over silica gel, the solvents were removed in vacuo, and the remaining oil was distilled (1.3 Pa, 130 °C bath temperature) in an apparatus described earlier.[53] This yielded 2.58 g (73%) of **5** as a yellow-brown oily liquid. MS (*m/z* (%)): 293 (100), M^+; 187 (89), Cp^*Cr^+; 158 (1) $(C_2H_5C_6H_5)Cr^+$; 133 (18), $Cp^{*+} - 2H$; 106 (7), $C_2H_5C_6H_5^+$; 52 (58), Cr^-. Anal. Calcd for $C_{18}H_{25}Cr$: C, 73.68; H, 8.58; Cr, 17.72. Found: C, 73.40; H, 8.53; Cr, 17.71.

(9) (*η*-Pentamethylcyclopentadienyl)(*η*-1-ethyl-2,4,6-trimethylbenzene)chromium (7). The synthesis was carried out as described under part 8 with 2.12 g (14.3 mmol) of ethylmesitylene,[54] 5.53 g (10.7 mmol) of $[Cp^*CrCl_2]_2$, 25.0 mL of a 0.5 M solution of Al_2Et_6 in hexane (25.0 mmol $AlEt_3$), and 1.14 g (30.0 mmol) of $LiAlH_4$. Prior to sublimation an oily impurity was distilled off at 1.3 Pa up to 100 °C bath temperature. After the temperature was increased to 130−140 °C, 1.58 g of an orange-red crystalline product was obtained which contained about 50% of Cp^*_2Cr (identified by ^1H and ^{13}C NMR). This corresponds to a 17% conversion of ethylmesitylene to **7**. Further purification steps included sublimation at 1.3 Pa/130 °C yielding 1.24 g of solid, a second sublimation at 1.3 Pa/110 °C yielding 0.90 g of solid, chromatography (silica gel Merck 60, 63−200 *μ*m, column height/diameter 20/5 mm, hexane) yielding 0.66 g of solid, and sublimation at 1.3 Pa/110 °C yielding 0.58 g of solid. Final crystallization from hexane gave orange-red crystals of **7** (yield 0.22 g, 5% relative to ethylmesitylene), mp 130 °C. According to ^1H NMR spectroscopy this product contained ca. 1% of Cp^*_2Cr. MS (*m/z* (%)): 335 (32), M^+; 322 (2), $Cp^*_2Cr^+$; 187 (12), Cp^*Cr^+; 148 (28), $C_2H_5(CH_3)_3C_6H_2^+$; 133 (100) $Cp^{*+} - 2H$; 52 (13), Cr^+. Anal. Calcd for $C_{21}H_{31}Cr$: C, 75.18; H, 9.31; Cr, 15.49. Found: C, 74.09; H, 9.29; Cr, 15.31.

By the same method 1.22 g (59%) of **3** was obtained from 25 mL of benzene, 10 mL of a 0.5 M solution of Al_2Et_6 in hexane (10 mmol $AlEt_3$), 2.00 g (3.9 mmol) of $[Cp^*CrCl_2]_2$, and 1.15 g (30.3 mmol) of $LiAlH_4$.

$[Cp^*Cr(arene)]^+$ Cations. (10) (*η*-Pentamethylcyclopentadienyl)(*η*-benzene)chromium(II) Tetraphenylborate ($3^+[B(Ph)_4]^-$). A 0.49 g (1.8 mmol) amount of **3** was added to a green solution of 1.04 g (1.6 mmol) of $[Cp^*_2Fe]^+[B(Ph)_4]^-$ in 15 mL of 1,2-difluorobenzene at −30 °C, and the mixture was stirred until a clear red solution was obtained. Upon addition of 50 mL of hexane a red precipitate formed which was washed with three 50 mL portions of hexane and dried in vacuo. $\mathbf{3}^+[B(Ph)_4]^-$ was obtained as a red powder (yield 0.91 g, 96% relative to $[Cp^*_2Fe]^+[B(Ph)_4]^-$) which decomposed above 140 °C without melting. Anal. Calcd for $C_{40}H_{41}BCr$: C, 82.18; H, 7.06; Cr, 8.89. Found: C, 80.29; H, 6.97; Cr, 8.78.

(11) Reaction of 3 with $[Cp_2Fe]^+[PF_6]^-$. A 0.92 g (3.5 mmol) amount of **3** and 1.01 g (3.1 mmol) of $[Cp_2Fe]^+[PF_6]^-$ were grinded, and 10 mL of CH_2Cl_2 was added at -78 °C. The mixture was stirred at this temperature until the violet solid had disappeared and a red solution had formed. When 100 mL of ether was added at −78 °C, a solid precipitated which after filtration and dying in vacuo yielded 0.28 g of an orange-red powder. The powder contained dark decomposition products and decomposed above 150 °C. A solution in CD_2Cl_2 showed the ^1H NMR signals expected for the cation $\mathbf{3}^+$.

(12) (*η*-Pentamethylcyclopentadienyl)(*η*-mesitylene)chromium(II) Hexafluorophosphate ($6^+[PF_6]^-$). The synthesis was carried out as described under part 11 with 0.85 g (2.8 mmol) of **6** and 0.82 g (2.5 mmol) of $[Cp_2Fe]^+[PF_6]^-$ and 20 mL of CH_2Cl_2. Rapid recrystallization of the resulting precipitate from CH_2Cl_2/Et_2O at 25 °C gave orange-red microcrystals of $\mathbf{6}^+[PF_6]^-$, which were washed with ether and dried in vacuo (yield 0.93 g; 83% relative to $[Cp_2Fe]^+[PF_6]^-$). The compound decomposed above 180 °C without melting accompanied by a color change to blue. Anal. Calcd for $C_{19}H_{27}CrF_6P$: C, 50.44; H, 6.01; Cr, 11.49; F, 25.20. Found: C, 50.39; H, 6.05; Cr, 11.40; F, 26.10.

(13) (*η*-Pentamethylcyclopentadienyl)(*η*-hexamethylbenzene)chromium(II) Hexafluorophosphate ($8^+[PF_6]^-$). A 0.204 g (0.8 mmol) amount of I_2 dissolved in 45 mL of THF was added dropwise at −20 °C to a stirred solution of 0.62 g (1.8 mmol) of **8** in 100 mL of THF. The orange precipitate which formed was washed with a little THF and ether, dried in vacuo, and disssolved in 100 mL of H_2O. After filtering of the mixture, the product was precipitated with 0.63 g (3.9 mmol) of NH_4PF_6, washed with H_2O, and dried in vacuo. Recrystallizing twice from acetone/H_2O gave orange-red microcrystals of $\mathbf{8}^+[PF_6]^-$ (yield 0.40 g, 52% relative to I_2), which decomposed above 180 °C. Anal. Calcd for $C_{22}H_{33}CrF_6P$: C, 53.44; H, 6.73; Cr, 10.51; F, 23.05. Found: C, 53.46; H, 6.63; Cr, 10.25; F, 24.48.

(14) (*η*-Pentamethylcyclopentadienyl)(*η*-hexamethylbenzene)chromium(II) (*η*-pentamethylcyclopentadienyl)trichlorochromate(III) ($8^+[Cp^*CrCl_3]^-$). A 0.46 g (1.3 mmol) amount of **8** was dissolved in 50 mL of CH_2Cl_2. When the solution was kept at 25 °C for 2 weeks,

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the color changed slowly from yellow to dark green. The volume was reduced to 20 mL by evaporation, and 100 mL of hexane was added whereupon green glittering crystals formed. Recrystallization from CH_2Cl_2/hexane gave 0.11 g of $\mathbf{8}^+[Cp^*CrCl_3]^-$ (yield 26%), which decomposed above 200 °C. Anal. Calcd for $C_{32}H_{48}Cr_2Cl_3$: C, 59.76; H, 7.52; Cr, 16.17; Cl, 16.54. Found: C, 59.58, H, 7.70; Cr, 16.21; Cl, 16.54.

(15) (η-Pentamethylcyclopentadienyl)(η-benzene)chromium(II) (η-pentamethyl)cyclopentadienyltriiodochromate(III) ($\mathbf{3}^+[Cp^*CrI_3]^-$). A 1 mL (10.9 mmol) volume of allyl iodide was added dropwise at 25 °C to a solution of 0.16 g (0.6 mmol) of **3** in 5 mL of ether. After the solution stood for for 12 h, dark green fibrous microcrystals had formed. Filtering, washing with ether, and drying in vacuo gave 0.21 g of $\mathbf{3}^+[Cp^*CrI_3]^-$ (yield 84%) which decomposed above 150 °C. Anal. Calcd for $C_{26}H_{36}Cr_2I_3$: C, 37.48; H, 4.35; Cr, 12.48; I, 45.69. Found: C, 36.79; H, 4.15; Cr, 12.60; I, 45.46.

(16) Reaction of 8 with Allyl Iodide. When the reaction described under part 15 was carried out with 70 mg (0.2 mmol) of **8** and 37 mg (0.2 mmol) of allyl iodide, a yellow solid was obtained which analyzed as follows: C, 52.14; H, 6.53. The ^1H NMR spectrum of the sample taken in D_2O at 305 K showed the signals expected for $\mathbf{8}^+$ ($\delta^{para} = -18.2$ and -27.4 at 305 K for Cp* and C_6Me_6, respectively) and no signal of $[Cp^*CrI_3]^-$ near -89 ppm.[19] These results are compatible with the formation of $\mathbf{8}^+I^-$ which contains 18 % $\mathbf{8}^+I_3^-$.

Physical Measurements. The mass spectra were recorded in the electron impact mode (70 eV) at source temperatures varying between 25 and 150 °C with a Varian MAT 311A instrument. The EPR spectra were run with the X-band spectrometer Varian EE 12. The equipment used for the CV measurements has been described previously.[55] The electrolyte was a 0.1 M solution of nBu_4NPF_6 in purified THF. Before addition of an amount of the sample which gave a 10^{-3} M solution, the electrolyte was further dried by passing it through activated neutral Al_2O_3 placed in an tube which was integrated in the cell. The redox couple Cp_2Fe/Cp_2Fe^+ was used as an internal reference. The NMR spectra were recorded with the following spectrometers: Bruker CXP 200, Bruker MSL 300, and Jeol JNM GX 270. The most efficient configuration was a high-power solenoidal probehead and the air-tight rechargeable sample tube shown in Figure 12. The signals were measured relative to solvent peaks and calculated relative to the signal shift of corresponding nuclei of similar diamagnetic compounds: Cp_2Fe,[56ab] $(C_6H_6)_2Cr$,[56c,d] Cp^*_2Fe,[48d] $(Me_3C_6H_3)_2Cr$,[56d,e] $(EtC_6H_5)_2Cr$,[56c,d] $(MeCp)_2Fe$,[56b] $[Cp^*Fe(C_6H_6)]^+[PF_6]$,[56f] and $[Cp^*Fe(C_6Me_6)]^+[PF_6]$.[56f] When the signal assignment was not clear for the reference compounds, a mean value of the corresponding signal shifts was used. As far as the spectra had to be recorded at high temperature, 392 K was chosen as the standard temperature. A few spectra were obtained at slightly different temperatures. Then the signal shifts were calculated to 392 K by assuming that the Curie law holds in the narrow temperature range. The error limits depending on the signal width were estimated as ±0.2, ±2, ±5, and ±10 ppm for W up to 0.25, 1, 5, and 15 kHz, respectively, for ^1H NMR signals and ±0.5, ±5, and ±10 pm for W up to 0.4, 1, 5, and 10 kHz, respectively, for ^{13}C NMR signals.

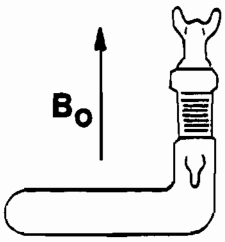

Figure 12. NMR tube used with solenoid probe heads. B_0 = direction of the magnetic induction.

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