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Syntheses, Structures, and NMR Spectroscopy of Paramagnetic Open Vanadocenes and Open Chromocenes

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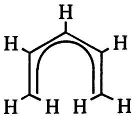
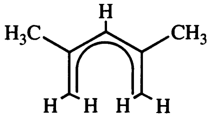
The syntheses and characterizations of the M[1,5-$(Me_3Si)_2C_5H_5$]$_2$ complexes for M = V and Cr have been achieved, as well as that for the unsymmetric Cr[1-Me_3Si-3-MeC_5H_5]$_2$. Structural data for the vanadium complex reveal substantial steric crowding, in accord with the observation that this complex is only weakly coordinated by CO. Structural data have also been determined for $Cr(C_5H_5)(2,4\text{-}C_7H_{11})$ (C_7H_{11} = dimethylpentadienyl), revealing the presence of both eclipsed and staggered conformations in the solid state and much shorter Cr−C bonds for the open dienyl ligand. Proton NMR spectra have been recorded for these and related paramagnetic complexes. While one observes relatively narrow signals and small upfield shifts for methyl and silyl substituents in the chromium complexes, much broader signals and greater shifts, downfield, are observed for hydrogen substituents; furthermore, these resonances are substantially broadened relative to those in chromocene. For $V(2,4\text{-}C_7H_{11})_2$, the broadening is so great that only the methyl signals can be assigned with certainty.

Introduction

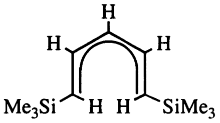
Metallocenes and other complexes with cyclopentadienyl ligands have been intensively studied for over 50 years, leading to many applications as well as a detailed understanding of their structures and bonding.[1] In contrast, relatively little attention has been given to related complexes with pentadienyl ligands, although applications in naked metal reactions,[2] metal film depositions,[3] materials syntheses,[4] doping of semiconductors,[5] and polymerizations[6] have been developed. One of the most interesting aspects of pentadienyl ligands that has emerged from a number of spectroscopic, structural, and theoretical studies is their substantially different electronic behavior relative to C_5H_5.[7] Pentadienyl ligands such as C_5H_7, 2,4-C_7H_{11}, and 1,5-$(Me_3Si)_2C_5H_5$ are sterically much more demanding and generally serve as strong δ acids, so much so that they exhibit a pronounced tendency to bond to metals in low



C_5H_7



2,4-C_7H_{11}



1,5-$(Me_3Si)_2C_5H_5$

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10.1021/om020720+ CCC: $25.00

oxidation states.[7] It has also become clear that pentadienyl ligands may be not only more strongly bound than C_5H_5 but also more reactive. Given these interesting aspects of pentadienyl ligands, it is important to gain some understanding of the electronic structures of their metal complexes. Unfortunately, this can be quite complicated due to substantial metal−pentadienyl orbital mixing,[8] and as a result, a clear MO picture has not been developed, especially for the earlier metals. As NMR spectroscopy of paramagnetic complexes can provide information regarding the constitution of any SOMOs (S = singly),[9] we have carried out such studies on representative open and half-open vanadocenes and chromocenes. Not only do these studies provide important insight into the orbitals in question, they also demonstrate that paramagnetic NMR methods should prove valuable for a much wider variety of organometallic compounds than just the metallocenes, which have attracted most interest in the past.

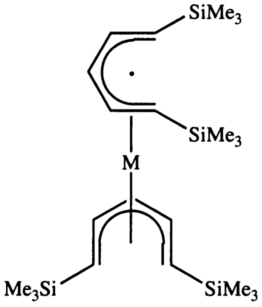
Synthetic and Structural Results

The reactions of appropriate titanium and zirconium chlorides with the 1,5-$(Me_3Si)_2C_5H_5$ anion have already been reported to lead to the diamagnetic, 14-electron M[1,5-$(Me_3Si)_2C_5H_5]_2$ complexes,[10] which are notable for their high thermal stabilities, even allowing for their isolation by sublimation at 120 °C. We now report that the related complexes of vanadium and chromium could readily be prepared from analogous reactions (eq 1).

$$\text{“MCl}_2\text{”} + 2\text{K}[1,5\text{-}(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_5] \rightarrow \text{M}[1,5\text{-}(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_5]_2 \quad (1)$$

$$\text{M} = \text{V, Cr}$$

These species, with respective 15- and 16-electron configurations, are paramagnetic, with one and two unpaired electrons, respectively. In addition to analytical, magnetic susceptibility, and mass spectral characterization (see Experimental Section), the vanadium complex displayed an eight-line spectrum characteristic of an open vanadocene,[11] with a vanadium hyperfine splitting of 81.5 G. This complex can then be formulated straightforwardly as an analogue to the titanium and zirconium complexes (below).



M = Ti, Zr, V, Cr

Although exposure to CO did not lead to a noticeable change in color, there was a decrease in the vanadium hyperfine splitting to 69.0 G; however, attempts to isolate a product led only to recovery of the starting complex. These results indicate that the coordination of CO is reversible (eq 2), which is quite reasonable, given the steric demands of the trimethylsilyl substituents. In contrast to the vanadium complex, Cr[1,5-$(Me_3Si)_2C_5H_5]_2$ was not found to interact with CO, which is consistent with the behavior of other, even less crowded open chromocenes,[12] although chromocenes do form weakly bound carbonyl adducts.[13] From a similar approach utilizing the 1-trimethylsilyl-3-methylpentadienyl anion, the complex Cr(1-Me_3Si-3-$MeC_5H_5)_2$ could be obtained (eq 3), analogous to the diamagnetic iron analogue which had already been reported.[14]

$$\text{V}[1,5\text{-}(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_5]_2 + \text{CO} \rightleftharpoons \text{V}[1,5\text{-}(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_5]_2\text{CO} \quad (2)$$

$$\text{“CrCl}_2\text{”} + 2\text{K}(1\text{-Me}_3\text{Si-3-MeC}_5\text{H}_5) \rightarrow \text{Cr}(1\text{-Me}_3\text{Si-3-MeC}_5\text{H}_5)_2 \quad (3)$$

The structure of Cr[1,5-$(Me_3Si)_2C_5H_5]_2$ has been determined (Figure 1, Table 1). While the related titanium and zirconium complexes exhibited crystallographically imposed C_2 symmetry, that is not the case here, and there exists a slight difference between the ligands, which may be traced to the smaller size of chromium, and the resulting increase in steric crowding for the complex. In particular, the Cr−C(1−5) bond distances are longer than those for C1′−C5′, especially C1 (2.320(3) Å) vs C1′ (2.252(3) Å). Although open metallocenes are well known to experience substantial steric crowding due to the short separations required between the metal centers and their ligand planes, in this complex the crowding appears to have become severe enough that one ligand backs off slightly to help optimize the bonding for the other. This may readily be seen from the metal−ligand plane separations, which are 1.567 and 1.539 Å, respectively. Further evidence of this crowding may be obtained from a comparison with the less crowded Cr(2,4-$C_7H_{11})_2$.[12] On going from 2,4-C_7H_{11} to the silylated dienyl ligands, the average Cr−C

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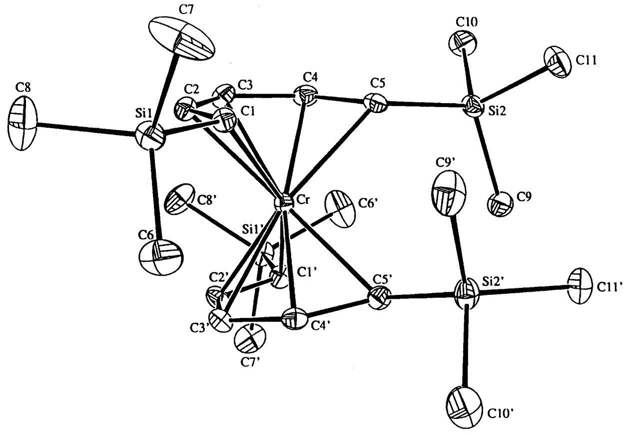
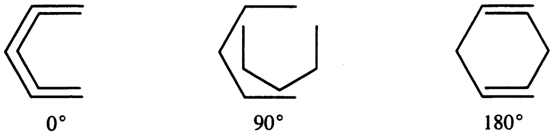
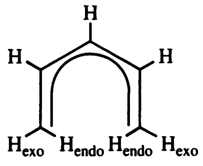


Figure 1. Perspective view of the solid-state structure of Cr[1,5-(Me$_3$Si)$_2$C$_5$H$_5$]$_2$. 30% probability ellipsoids are shown.

distance increases from 2.163 to 2.211 Å, and this increase results almost entirely from the silyl-substituted carbon atoms. However, it appears that these steric effects lead only to a slight change in molecular conformation. Relative to the idealized syn-eclipsed and anti-eclipsed structures, with respective conformation angles of 0° and 180°, Cr(2,4-C$_7$H$_{11}$)$_2$ exhibits a conformation angle of 82.2°, fairly close to the idealized value of 90°, corresponding to a staggered conformation. For Cr[1,5-(Me$_3$Si)$_2$C$_5$H$_5$]$_2$, the conformation angle is 78.7°.



Some additional comparisons may be made regarding the ligand planes. There is first of all a relatively small interligand tilt of 10.6° More notable are the deviations of the substituents from these planes. One typically observes all but the endo-oriented substituents on the terminal carbon atoms tilting significantly toward the metal center. This tilting also occurs for C$_5$H$_5$ ligands,[15] although generally to a much smaller extent. In both cases, the tilting has been attributed to an attempt by the ligand to optimize overlap by pointing its p orbitals more toward the metal center (below). Much greater tilts are therefore typical for the open dienyl ligands,[16] in accord with their greater girths and closer approaches to the metal center. In the present case, the tilts average 12° for the 2,4 positions and 9° for the 3 position. For the Me$_3$Si substituents, the tilts are −0.5°, 1.7°, 4.3°, and 5.5°, respectively, for Si(1,1′,5,5′). These tilts are much smaller than expected for terminal substituents, in accord with the steric crowding. Much larger tilts of 35° are observed for the hydrogen substituents on the 1,5 positions, *away from* the metal center, as expected.[7,17,18]



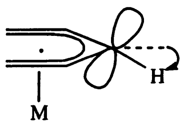
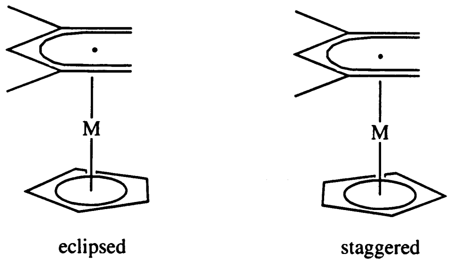


Table 1. Pertinent Bonding Parameters for Cr[1,5-(Me$_3$Si)$_2$C$_5$H$_5$]$_2$

Bond Distances (Å)			
Cr−C1	2.320(3)	Cr−C1′	2.252(3)
Cr−C2	2.217(3)	Cr−C2′	2.185(3)
Cr−C3	2.173(3)	Cr−C3′	2.171(3)
Cr−C4	2.161(3)	Cr−C4′	2.149(3)
Cr−C5	2.247(3)	Cr−C5′	2.239(3)
C1−C2	1.392(4)	C1′−C2′	1.411(4)
C2−C3	1.425(4)	C2′−C3′	1.410(4)
C3−C4	1.415(4)	C3′−C4′	1.423(4)
C4−C5	1.412(4)	C4′−C5′	1.410(4)
Bond Angles (deg)			
Si1−C1−C2	120.2(2)	Si1′−C1′−C2′	120.5(2)
C1−C2−C3	128.7(3)	C1′−C2′−C3′	126.6(3)
C2−C3−C4	127.8(3)	C2′−C3′−C4′	126.7(3)
C3−C4−C5	128.3(3)	C3′−C4′−C5′	129.8(3)
C4−C5−Si2	118.6(2)	C4′−C5′−Si2′	115.3(2)

The structure of Cr(C$_5$H$_5$)(2,4-C$_7$H$_{11}$) has also been determined, revealing a disorder in which the C$_5$H$_5$ ligand adopts both an eclipsed and a staggered orientation relative to the 2,4-C$_7$H$_{11}$ ligand (Figure 2, Table 2). In contrast, the isomorphous iron compound,[19] also positioned on a mirror plane, adopts an apparently eclipsed conformation, although the large anisotropy of the Cp atoms' thermal parameters suggests that the actual conformation is rotated slightly from being perfectly eclipsed. For the chromium complex, the eclipsed orientation also dominates, with a relative occupation of 63%. The differences in conformational preference between the chromium and iron complexes may readily be traced to the larger size of chromium. It has been observed for other ligands that eclipsed and staggered conformations are commonly of similar energies.[20]



The shorter average Cr−C distance for the 2,4-C$_7$H$_{11}$ ligand, 2.129 vs 2.201(4) and 2.194(7) Å for the two Cp images, reflects the stronger bonding that would be expected on the basis of its lesser π-delocalization energy relative to C$_5$H$_5$. A similar trend was evident from structural data for Cr(C$_5$Me$_5$)(C$_5$H$_7$),[12d] for which the average Cr−C distances were 2.117 and 2.194 Å for the

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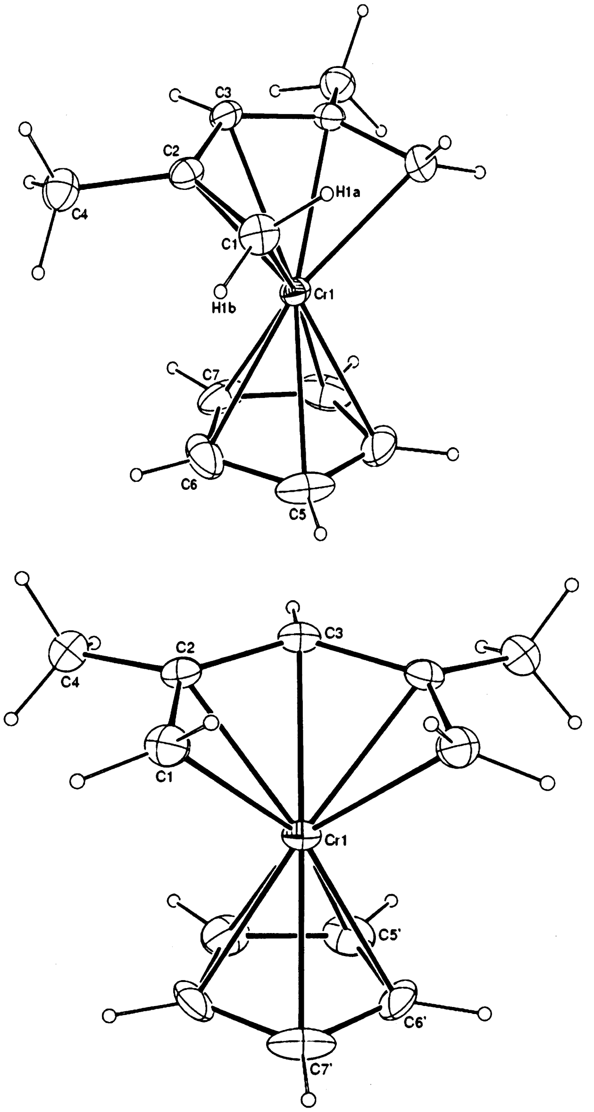


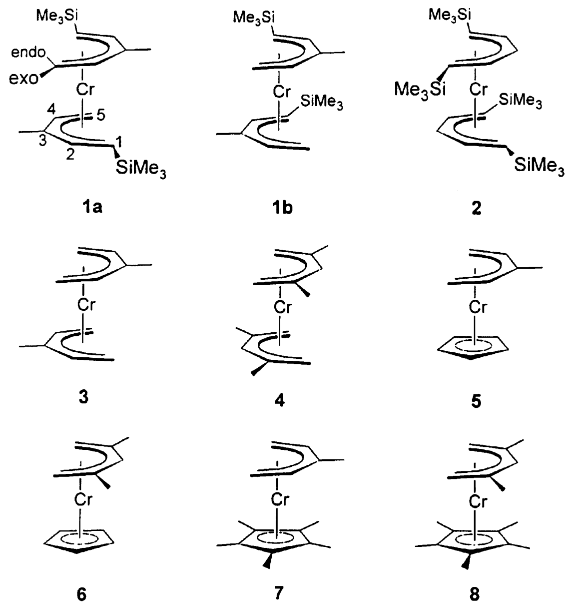
Figure 2. Perspective views of the major (eclipsed, top) and minor (staggered, bottom) isomers of $Cr(C_5H_5)(2,4\text{-}C_7H_{11})$. 30% probability ellipsoids are shown for the non-hydrogen atoms.

Table 2. Pertinent Bonding Parameters for $Cr(C_5H_5)(2,4\text{-}C_7H_{11})$

Bond Distances (Å)			
Cr−C1	2.113(2)	C1−C2	1.427(2)
Cr−C2	2.132(2)	C2−C3	1.425(2)
Cr−C3	2.157(2)	C2−C4	1.507(3)
Cr−C5	2.191(7)	C5−C5	1.385(12)
Cr−C6	2.208(7)	C5−C6	1.401(7)
Cr−C7	2.208(9)	C6−C7	1.397(7)
Cr−C5′	2.216(11)	C5′−C5′	1.389(20)
Cr−C6′	2.177(11)	C5′−C6′	1.385(13)
Cr−C7′	2.183(18)	C6′−C7′	1.353(13)
Bond Angles (deg)			
C1−C2−C3	122.8(2)	C2−C3−C2	127.7(2)
C1−C2−C4	119.2(2)	C3−C2−C4	117.5(2)

open and closed dienyl ligands. The shortening for the M−pentadienyl bonds is not typically observed for the smaller, later metals such as iron, for which both steric (i.e., ligand−ligand repulsions) and overlap problems occur. Both problems arise from the shorter M−ligand plane separations, and in the latter case also from the greater girth of the open ligands.[7] An appreciation for the overlap problems for the open dienyl ligands may be gained by examining the tilts of its various substituents from the ligand planes, each defined by the five metal-bound carbon atoms (cf., discussion for the $Cr[1,5\text{-}(Me_3Si)_2C_5H_5]_2$ structure, vide supra). While in this case negligible tilts are observed for the Cp ligand, the tilts by the open dienyl substituents are substantial, being 13.0°, 12.3°, and 8.4° toward the Cr center, respectively, for H1(exo), C4, and H3. In contrast, the H1(endo) substituents tilt away from the Cr center by 44.0°.

Chart 1



NMR Studies. Previous studies have provided conclusive evidence that open and half-open chromocenes resemble chromocenes,[12] particularly in that they have two unpaired electron spins (although some higher-spin chromocenes are known[21]). The spins of chromocenes relax sufficiently fast so that NMR spectra may be recorded, which yield information on the geometric and electronic structures.[9c,22] The similarity also holds for the ^1H NMR spectra of the open and half-open chromocenes listed in Chart 1. For instance, in the lower part of Figure 3 the spectrum of the methyl-/silyl-substituted derivative **1** is reproduced. When compared to the proton spectra of chromocenes, it shows similarities and differences. As for the similarities, there are strongly shifted signals at high frequency (ca. 250−500 ppm), which correspond to the ring proton signal of the parent chromocene at 316.2 ppm.[23a] The signal of the methyl group at C3 appears at low frequency (−50 to −80 ppm), as in the case of decamethylchromocene (−8.1 ppm[23b]). Finally, the signal shift of the silyl protons is small (−1.0 ppm), which corresponds to what has been found for 1,1′-disilylated chromocene (−2.6 ppm[23c]). An unexpected difference as compared to

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Table 3. Proton NMR Data[a] of Open and Half-Open Chromocenes in Comparison with Those of Chromocenes

signal assignment		compound							
		1	2	3[b]	4	5	6	7[c]	8
exo-H1/5	δ^{exp}	470		470	560	*d*	*d*	*d*	*d*
	$\Delta\nu_{1/2}$	36.5		30.0	35.0				
	δ^{con}	478		585	570				
endo-H1/5	δ^{exp}	260	275	280	300	*d*	*d*	*d*	*d*
	$\Delta\nu_{1/2}$	15.7	23.5	8.0	30.0				
	δ^{con}	266	281	350	307				
H2/4	δ^{exp}	360	435	330		*d*		*d*	
	$\Delta\nu_{1/2}$	22.0	36.5	11.2					
	δ^{con}	365	445	408					
H3	δ^{exp}		435		410		*d*		*d*
	$\Delta\nu_{1/2}$		36.5		15.0				
	δ^{con}		445		415				
Me2/4	δ^{exp}				−61.0		−113		−118
	$\Delta\nu_{1/2}$				1.0		3.7		6.0
	δ^{con}				−64.2		−117		−124
Me3	δ^{exp}	−78.3/−53.9		−43.0		−49.7		−44	
	$\Delta\nu_{1/2}$	2.1/1.4		0.7		2.0		3.5	
	δ^{con}	−81.9/−56.9		−56.0		−52.6		−51	
$SiMe_3$	δ^{exp}	−1.0/−2.3	−0.6						
	$\Delta\nu_{1/2}$	0.15/0.22	0.22						
	δ^{con}	−1.4/−2.4	−1.0						
C_5H_5	δ^{exp}					222	214		
	$\Delta\nu_{1/2}$					6.0	9.0		
	δ^{con}					223	215		
C_5Me_5	δ^{exp}							9.6	9.9
	$\Delta\nu_{1/2}$							0.4	0.4
	δ^{con}							8.0	8.3

[a] Signal shifts in ppm, experimental shifts, δ^{exp}, at 305 K except for **3** and **7**, signal half widths, $\Delta\nu_{1/2}$, in kHz, contact shifts, δ^{con}, at 298 K. [b] Measured at 373 K. [c] Measured at 330 K. [d] Signal not observed.

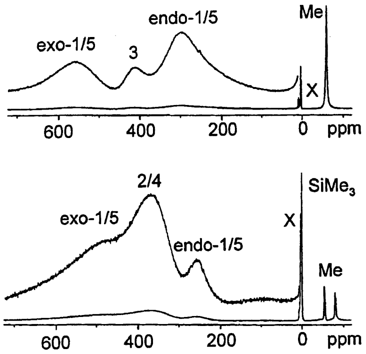

Figure 3. ^{1}H NMR spectra of the open chromocenes **1** (bottom) and **4** (top) dissolved in toluene-d_8 at 305 K. The insets show the amplified ranges of the broad signals. For numbering see Chart 1; X are signals of the solvent and diamagnetic impurities.

chromocenes are the widths of the pentadienyl proton signals, which are up to almost 40 times larger.

Nevertheless, characteristic signal patterns could be resolved in cases for which the shift differences were substantial. For instance, the pentadienyl protons of the tetramethyl derivative **4** gave a 2/1/2 pattern (upper two traces of Figure 3) besides the methyl signal at −61 ppm. From the relative intensities it follows that the signal at 410 ppm belongs to H3, while those at 300 and 560 ppm belong to the *endo*- and *exo*-H1/5, respectively. It will be shown below that the more shifted signals must be assigned to the *exo* protons. The ^{1}H NMR spectrum of compound **1** (lower two traces of Figure 3) is very similar, as it also shows three broad and strongly shifted signals. Two of them appear in ranges that are expected for *endo*-H1/5 (260 ppm) and *exo*-H1/5 (470 ppm), respectively. It follows that the remaining signal at 360 ppm belongs to H2/4. For compound **1** there are two signals rather than one in the shift range of the methyl protons (−53.9 and −78.3 ppm). These signals establish the formation of two diastereoisomers, **1a** and **1b**, following from the planar chirality, which is generated by the unsymmetrically substituted pentadienyl ligand. Correspondingly, there are also two signals for the silyl groups (2.3 and −1.0 ppm, not distinguishable in the overview spectrum given in Figure 3), while the large widths of the pentadienyl protons prevent the resolution of separate signals for the diastereoisomers. Signal intregration shows that within the error limits the diastereoisomers were formed in a 1:1 ratio.

The ^{1}H NMR spectra of the tetrasilyl and the dimethyl derivatives **2** and **3**, respectively, confirm these results. As can be seen in Table 3, the data of compound **3** are similar to those of **4**. The intensity ratio of the signals of **3** in the pentadienyl shift range is 1:1:1, as expected. Compound **2** shows a weakly shifted signal for the silyl groups and very broad signals centered at 435 and 275 ppm for the pentadienyl protons. The signal assignment of all open chromocenes is facilitated by the fact that compound **2**, unlike compounds **1**, **3**, and **4**, lacks a signal in the range of about 450−600 ppm. The reason is that **2** lacks *exo* protons, whereas **1**, **3**, and **4** do not. From the comparison with, for example, the ^{1}H NMR spectrum of **4** discussed above (Figure 3) it follows that *endo* proton signals are less shifted than *exo* proton signals.

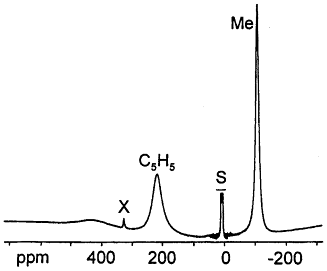

Figure 4. ^{1}H NMR spectrum of the half-open chromocene **6** dissolved in toluene-d_8 at 305 K. S = solvent, X = Cp_2Cr.

The proton spectra of the half-open chromocenes **5**−**8** have also been studied for comparison with compounds **1**−**4**. A representative example is that of compound **6** in Figure 4, which shows signals for the methyl and the Cp protons. The latter signal is nearly 8 times broader than the signal of the parent chromocene Cp_2Cr present as an impurity. The increased broadening appears to result from both geometric and relaxation time differences.[24−26] The latter can be recognized to be more signficant here and points to an increase of the electron relaxation time in the order chromocenes < open chromocenes < half-open chromocenes, paralleling the increase in NMR spectral line widths. Concerning the pentadienyl protons, the very broad and unstructured feature near 430 ppm is the only one we could detect for compounds **5**−**8**. Therefore, its assignment is too speculative, and it must be concluded that NMR spectroscopy of half-open chromocenes is the most problematic.

In addition to the chromium derivatives the tetramethylated open vanadocene, **9**,[12a,b] was investigated (Supporting Information). The ^{1}H NMR spectrum showed two paramagnetically shifted signals. The one at lower frequency ($\delta = -21$ ppm, $\Delta\nu_{1/2} = 3.5$ kHz) was assigned to the methyl protons, the other one ($\delta = 57$ ppm, $\Delta\nu_{1/2} = 25.0$ kHz) to the pentadienyl protons. Additional spectra at 305 and 375 K revealed that the shift decreased upon increasing the temperature as expected. The assignment was based on the signal widths, which, by analogy with the corresponding chromium derivatives, were expected to be larger for protons closer to the vanadium spin center. The pentadienyl protons of the open vanadocene should show a 2:1:2 signal pattern similar to that of the open chromocene **4** in Figure 3. However, only one signal (intensity: two protons, *exo*- or *endo*-H1/5) could be observed (57 ppm) in the range of ±2500 ppm. It must be concluded that the missing signals were too broad to be detected, because the electron relaxation time of the open vanadocene is much longer than for normal vanadocenes, owing to a different ground state. Thus, Cp_2V is a $S = 3/2$ compound with $\delta = 314.2$ ppm and $\Delta\nu_{1/2} = 2.3$ kHz at 298 K,[23a] while compound **9** has a $S = 1/2$ ground state,[12c] leading to smaller signal shifts (as far as detectable) and to different relaxation times. It has been shown that the unpaired electron of the parent open vanadocene occupies a d_{z^2}-type orbital.[27] This situation seems to entail rather long electron relaxation times quite generally.[8,28]

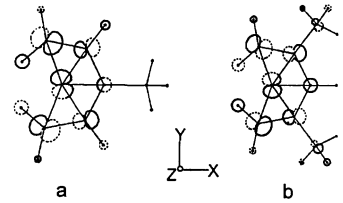

Figure 5. Molecular orbitals reflecting the spin distribution on the pentadienyl ligands of compounds **3** (a) and **4** (b). A view down the ligand−metal−ligand axis is given, and the lower ligand has been omitted for clarity.

From the NMR data useful information can be obtained because the contact shifts, $\delta^{con}{}_T$, at the measuring temperature, T, are proportional to the hyperfine coupling constants, A, which in turn are proportional to the probability of finding the unpaired electrons (or the spin density) at the nucleus under study (eq 4).[9c]

$$\delta^{con}{}_T \propto A \propto |\Psi(0)|^2 \qquad (4)$$

To exploit the proportionality, the experimental NMR signal shifts, $\delta^{exp}{}_T$, must be transformed to the paramagnetic signal shifts, $\delta^{para}{}_T$ (see Experimental Section). The latter shifts are composed of dipolar and contact shifts. It turns out that the dipolar shifts are very small, so that the $\delta^{para}{}_T$ values can be regarded as $\delta^{con}{}_T$ values, and these are also listed in Table 3. Note that all data have been transformed to values at the standard temperature of 298 K and that, therefore, the temperature has been omitted in what follows. The spin density at the observed nucleus and hence the δ^{con} values can be reproduced by MO calculations. The simplest case would be spin density in a MO whose ligand content is a pure π orbital. Then the contact shifts are proportional to the squared coefficients of the respective carbon $2p_z$ orbitals. Because of the low symmetries of pentadienylmetal derivatives, their relevant MOs contain more σ orbital contributions than in the case of chromocenes.[8,9c,22,29] Nevertheless, for a qualitative understanding of the contact shifts of this work extended Hückel calculations are a reasonable approximation.

It has been shown previously[9c,22] that spin-polarized metal−ligand bonding electrons occupy MOs that are derived from metal d_{xz} and d_{yz} orbitals and that the substitution pattern of a given ligand determines which one dominates. In the case of the most simple open chromocenes **3** and **4** the relevant MOs have d_{yz} character. Figure 5 presents a view down the z axis perpendicular to one pentadienyl ligand with the chromium atom below in the middle; the second ligand is not shown for clarity. It can be seen that the (hyperconjugative) spin transfer from the respective pentadienyl carbon atoms to the methyl protons is less efficient for compound **3** than for **4**. If we consider the spin delocalization mechanism at work in chromocenes,[9c] this

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is in line with the fact that the negative signal shift of Me3 is smaller than that of Me2/4 (Table 3). The same applies for the pairs of compounds **5**/**6** and **7**/**8**. It is also obvious from Figure 5 that some negative spin density is delocalized from C1/5 to the adjacent protons. This partly compensates positive spin density, which is induced by polarization of the C−H bonding electrons. Figure 5 shows that the decrease of positive spin is more efficient for the *endo* protons than for the *exo* protons. This is in accord with smaller positive signal shifts of the *endo* protons found throughout the series of open chromocenes.

Conclusions

Several new open and half-open chromocenes and vanadocenes have been synthesized, and structural data for $Cr(C_5H_5)(2,4\text{-}C_7H_{11})$ reveal that the Cr−C bonds for the open dienyl ligand are shorter than those for C_5H_5. ^1H NMR spectra have been recorded for open and half-open chromocenes as well as for an open vanadocene. The signals for the open chromocenes were found in ranges of up to 680 ppm. The informational content of these spectra was found to depend on the electron relaxation time of the $S = 1$ and $S = 1/2$ compounds and on the proton−metal distance. While all expected signals were present in the spectra of open chromocenes, the half-open chromocenes showed only signals for the cyclopentadienyl ligands, while two signals were missing for bis(2,4-dimethylpentadienyl)vanadium. It is possible that future studies with deuterated pentadienyl ligands would reduce the spectral line widths sufficiently to allow for the observation and assignments of these missing signals. In addition to confirming the structure of open chromocenes, the proton spectra shed light on the electron spin delocalization: spin polarization transfers from the metal to the pentadienyl π system and from there to the adjacent protons place positive spin density on these atoms. Correspondingly, negative spin density predominates in the ligand π orbitals. Extended Hückel calculations reproduce the finding that from the pentadienyl core more spin density is transmitted to a methyl group in positions 2/4 than in position 3. The large differences in the spin density on the *exo* and *endo* protons of the ligands result from changes in the interplay of two delocalization mechanisms.

Experimental Section

All synthetic procedures and manipulations of compounds were carried out under an atmosphere of nitrogen gas in Schlenk apparatus or in a glovebox. Hydrocarbon and ethereal solvents were dried by distillation from benzophenone ketyl. ESR spectra were obtained as previously described,[11] while magnetic susceptibilities were determined by the Evans method.

Bis[η^5-1,5-bis(trimethylsilyl)pentadienyl]vanadium, V[η^5-1,5-$(Me_3Si)_2C_5H_5]_2$. A red solution of 0.50 g (1.3 mmol) of $VCl_3(THF)_3$[11,30] in 25 mL of THF was reduced with 0.105 g (1.61 mmol) of Zn powder. The solution was stirred at room temperature for 2 h, producing a green slurry of the divalent vanadium complex $[V_2Cl_3(THF)_6]_2(Zn_2Cl_6)$.[11,31] The slurry was then cooled to −78 °C, and a solution of 0.70 g (2.8 mmol) of $K[1,5\text{-}(Me_3Si)_2C_5H_5]$ in 25 mL of THF was added dropwise with stirring. The mixture was warmed to room temperature slowly and stirred overnight, producing a dark brown solution. After removing the solvent in vacuo, the product was extracted into three 25 mL portions of hexane. The combined brown extracts were filtered under nitrogen and the solution volume reduced in vacuo to approximately 15 mL. Dark brown crystals were isolated by cooling to −86 °C, yielding 0.36 g of product (ca. 57%). Purification of the slightly air-sensitive compound (mp 154−156 °C) was achieved by sublimation in vacuo (ca. 140 °C) or recrystallization from hexane at −86 °C. Anal. Calcd for $C_{22}H_{46}Si_4V$: C, 55.76; H, 9.78. Found: C, 55.82; H, 10.17. IR data (Nujol mull): 3044(mw), 1482(m), 1429(m), 1401(w), 1294(ms), 1254(vs), 1242(vs), 1212(w), 1166(s), 1095(m), 974(s), 950(m), 909(mw), 851(vs), 832(vs), 811(sh), 775(w), 760(w), 744(ms), 687(m), 611(m) cm^{-1}. Mass spectrum: EI, 17 eV; *m*/*e* (relative intensity): 73(12), 187(100), 188(15), 325(20), 397(92), 398(14), 469(16), 473(10). Magnetic susceptibilty (THF, 26.0 °C): $\mu = 1.72\ \mu_B$. EPR data (toluene, ambient): 1.970 ± 0.001, $A(^{51}V) = 81.5 \pm 0.1$ G.

Bis[1,5-bis(trimethylsilyl)pentadienyl]chromium, Cr-[η^5-1,5-$(Me_3Si)_2C_5H_5]_2$. A solution of 0.25 g (0.67 mmol) of $CrCl_3(THF)_3$[32] in 30 mL of THF was reduced with 0.0262 g (0.400 mmol) of Zn dust. Refluxing the purple solution for 1 h produced the light blue "$CrCl_2$" precipitate. The "$CrCl_2$" slurry was cooled to −78 °C, and a solution of 0.35 g (1.4 mmol) of $K[1,5\text{-}(Me_3Si)_2C_5H_5]$ in 20 mL of THF was added dropwise with stirring. Warming to room temperature slowly, followed by overnight stirring, produced a blue-green solution. The solvent was then removed in vacuo and the green residue extracted into four 10 mL portions of hexane, which were filtered under nitrogen. The solution volume was reduced in vacuo to approximately 10 mL, and emerald-green crystals were isolated by cooling to −86 °C, yielding 0.23 g (ca. 72%). The slightly air-sensitive product (mp = 160−162 °C) was purified by sublimation in vacuo (ca. 70 °C) or recrystallization from hexane at −86 °C. Anal. Calcd for $C_{22}H_{46}Si_4Cr$: C, 55.64; H, 9.76. Found: C, 55.15; H, 10.01. IR data (Nujol mull): 3047(w), 3020(sh), 1630(w), 1566(w), 1286(mw), 1254(vs), 1243(vs), 1220(sh), 1165(s), 1096(ms), 992(w), 978(s), 950(m), 906(w), 852(vs), 836(vs), 774(mw), 742(s), 686(m), 661(mw), 610(m) cm^{-1}. Mass spectrum (EI, 17 eV); *m*/*e* (relative intensity): 73(100), 74(10), 108(50), 123(26), 262(55), 475(4).

Bis(1-trimethylsilyl-3-methylpentadienyl)chromium, Cr(1-Me_3Si-3-$MeC_5H_5)_2$. A slurry of $CrCl_3(THF)_3$ (1.46 g, 3.90 mmol) and zinc powder (0.28 g, 4.29 mmol) in 30 mL of THF was refluxed for 1.75 h to give a light blue slurry of "$CrCl_2$". The mixture was cooled to −78 °C, and a solution of $K(1\text{-}Me_3Si\text{-}3\text{-}MeC_5H_5)$[14] (1.50 g, 7.80 mmol) in 30 mL of THF was slowly added. The resulting black-red solution was slowly warmed to room temperature, during which time a dark green solution resulted. After the mixture was stirred overnight, the solvent was removed in vacuo. The crude product was extracted with ca. 80 mL of hexane and then filtered through a Celite pad on a medium frit. The green filtrate was concentrated in vacuo to ca. 5 mL, and the solution was cooled to −60 °C, yielding a dark green crystalline solid (29% isolated yield after two crystallizations). Additional material may be obtained by further concentration and cooling of the solution. Anal. Calcd for $C_{18}H_{34}Si_2Cr$: C, 60.28; H, 9.55. Found: C, 59.96; H, 9.83. Mass spectrum (EI, 20 eV); *m*/*e* (relative intensity): 59(20), 73(100), 75(57), 139(11), 147(17), 306(13), 358(8).

X-ray Diffraction Studies. Single crystals for the X-ray diffraction studies were mounted onto glass fibers using Paratone oil. For both complexes, the determinination of space groups was straightforward based upon systematic absences. The choices of the centrosymmetric space groups *C*2/*c* and

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Table 4. Crystallographic Parameters for $Cr[1,5\text{-}(Me_3Si)_2C_5H_5]_2$ and $Cr(C_5H_5)(2,4\text{-}C_7H_{11})$

formula	$CrSi_4C_{22}H_{46}$	$CrC_{12}H_{16}$
fw	474.95	106.12
temperature (K)	193	200
λ (E)	0.71073	0.71073
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$	*Pnma*
unit cell dimens		
a (Å)	12.057(2)	5.9167(6)
b (Å)	13.377(4)	13.1088(11)
c (Å)	18.090(3)	13.3090(9)
β (deg)	106.64(2)	90
volume (Å^3); *Z*	2795.36; 4	1032.26; 4
density (calc)	1.128	1.366
abs coeff, cm^{-1}	5.74	10.57
θ range	4.0−50.0	4.6−30
limiting indices	+14, +15, ±21	+8, +17, +18
no. of reflns collected	5401	2690
no. of ind reflns; *n*: $I > n\sigma(I)$	3626; 3	1541; 2
$R(F)$	0.035	0.042
$R_w(F)$	0.048	0.090
max. diff Fourier peak (e Å^{-3})	0.38	0.30

Pnma rather than *Cc* and $Pna2_1$ were substantiated by the subsequent successful refinements. The structures were solved by direct methods using the Molen and SHELXS packages, respectively. Hydrogen atoms were placed in positions observed in difference Fourier maps, and in the case of $Cr(C_5H_5)(2,4\text{-}C_7H_{11})$, the hydrogen atoms for the pentadienyl ligand were refined isotropically. The C_5H_5 ligand was observed to adopt two orientations, in an approximate ratio of 0.63:0.37, and each was successfully refined. A summary of pertinent crystallographic information is presented in Table 4.

NMR Studies. The NMR spectra were recorded with a Bruker MSL 300 spectrometer by using concentrated solutions in toluene-d_8 in 5 mm tubes, which were equipped with ground glass and stoppers. The experimental signal shifts, δ^{exp}, were measured relative to the methyl signal of the solvent. Ideally, the paramagnetic signal shifts, δ^{para}, are obtained by subtracting the signal shifts δ^{dia} found for the respective nuclei of isostructural diamagnetic iron derivatives. As these data have not been published for all iron analogues of compounds **1**−**9**, and as the errors of most δ^{exp} values are of the order of δ^{dia}, rounded shift values from representative examples[14,33] were used: *exo*-H 2.7 ppm, *endo*-H 0.2 ppm, H2/4 3.8 ppm, H3 4.4 ppm, Me2/4 and Me3 1.7 ppm, $SiMe_3$ 0.4 ppm, C_5H_5 4.3 ppm, and C_5Me_5 1.8 ppm. To obtain contact shifts, δ^{con}, the dipolar contributions, δ^{dip}, must be eliminated from the δ^{para} values.[34] The largest dipolar shifts are expected for the protons closest to the metal. For an estimate the *g* factors of chromocene ($g_{||} = 2.476$ and $g_{\perp} = 2.049$ [35]), the C−H distance (2.92 Å),[26] and an assumed zero field splitting of 1 cm^{-1} were substituted into eq 41 of ref 11, which yields $\delta^{dip} = -2.2$ ppm. The dipolar proton shifts of compounds **1**−**8** are smaller, because their distances from chromium are greater. These shifts were neglected for the discussion of the data in Table 3. Since the signal shifts are temperature dependent and since the spectra were recorded at different temperatures, the contact shifts were calculated to the standard temperature of 298 K based on the proportionality $\delta^{con} \propto T^{-1}$.

Extended Hückel calculations were carried out by using the program package CACAO, version 4.0.[36] Symmetrized geometrical data based on the crystal structures of compounds **4**[12b,c] and **8**[12d,24] and a standard C−H distance of 1.1 Å were used for the input files.

Acknowledgment. R.D.E. is grateful to the University of Utah and the National Science foundation for partial support of this research.

Supporting Information Available: X-ray structural data, a figure of the NMR spectrum of $V(2,4\text{-}C_7H_{11})_2$, and additional discussion related to spectral line widths. This material is available free of charge via the Internet at http://pubs.acs.org.

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