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Structure and Reactivity of Trimethylsilylmethyl Complexes of Chromium, Including the 13-Electron Alkyl $Cp^*Cr(CH_2SiMe_3)_2$

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Alkylation of $Cp^*Cr(THF)Cl_2$ with 1 or 2 equiv of $LiCH_2SiMe_3$ yielded the paramagnetic chromium alkyls $[Cp^*Cr(\mu\text{-}Cl)(CH_2SiMe_3)]_2$ (**1**), $Cp^*Cr(CH_2SiMe_3)_2$ (**2**), and $Cp^*Cr(L)(CH_2SiMe_3)_2$ (**3a**, L = py; **3b**, L = THF). Compound **2** is a coordinatively unsaturated, pseudo-five-coordinate Cr^{III} complex with a 13-electron configuration, and it catalyzes the polymerization of ethylene. The thermal decomposition of **2** in noncoordinating solvents proceeded via an intermediate, namely the bis(μ-alkylidene) complex $[Cp^*Cr(\mu\text{-}CHSi(CH_3)_3)]_2$ (**4**). Compound **4** suffered reductive elimination to yield the dinuclear Cr^{II} alkyl $Cp^*_2Cr_2(\mu\text{-}CH_2Si(CH_3)_2CH_2\text{-}\mu\text{-}CHSi(CH_3)_3)$ (**5**). In contrast, the decomposition of **2** in THF, i.e., **3b**, yielded the metallacycles $Cp^*Cr(L)(CH_2)_2Si(CH_3)_3)$ (**6a**, L = py; **6b**, L = THF). Compounds **1**, **2**, **3b**, **4**, and **5** have been structurally characterized by X-ray diffraction. The reactions of **2** are rationalized in terms of competing α- and γ-hydrogen elimination processes yielding terminal alkylidene and metallacyclobutane intermediates existing in equilibrium.

Introduction

Our exploration of the organometallic chemistry of the Cp^*Cr^{III} fragment has yielded a plethora of pseudo-octahedral complexes with 15-electron configurations. Three-legged piano stools of the types $[Cp^*CrR_3]^-$, $Cp^*Cr(L)R_2$, and $[Cp^*Cr(L)_2R]^+$ abound.[1−22] To the extent that such molecules are reactive—for example as catalysts for the polymerization of olefins—they exhibit a more or less pronounced tendency to dissociate a ligand, thereby generating coordinatively unsaturated 13-electron alkyls featuring five-coordinate chromium(III).[23] While the evidence for the intervention of such reactive intermediates is compelling, we have sought to prepare and structurally characterize such a species.

The preference of trivalent chromium for six-coordination is illustrated by $[Cp^*Cr(CH_3)(\mu\text{-}CH_3)]_2$,[6] which avoids coordinative unsaturation by means of bridging methyl groups. We reasoned that substituting larger alkyl groups for the methyl ligands might stabilize a mononuclear dialkyl of the constitution Cp^*CrR_2. Herein we report on the success of this strategy and on the ensuing chemistry of trimethylsilylmethyl ligands coordinated to chromium(III).

Results and Discussion

Syntheses and Structures. Addition of 1.0 equiv of trimethylsilylmethyllithium to blue $Cp^*Cr(THF)Cl_2$, formed in situ by reaction of $CrCl_3(THF)_3$ with Cp^*Li in THF, resulted in a rapid color change to violet. Standard workup of the reaction mixture yielded the dinuclear alkyl $[Cp^*Cr(\mu\text{-}Cl)(CH_2SiMe_3)]_2$ (**1**, see Scheme 1), a purple solid that is thermally stable in solution but decomposes upon exposure to air. The molecular structure of **1** has been determined by X-ray diffraction;

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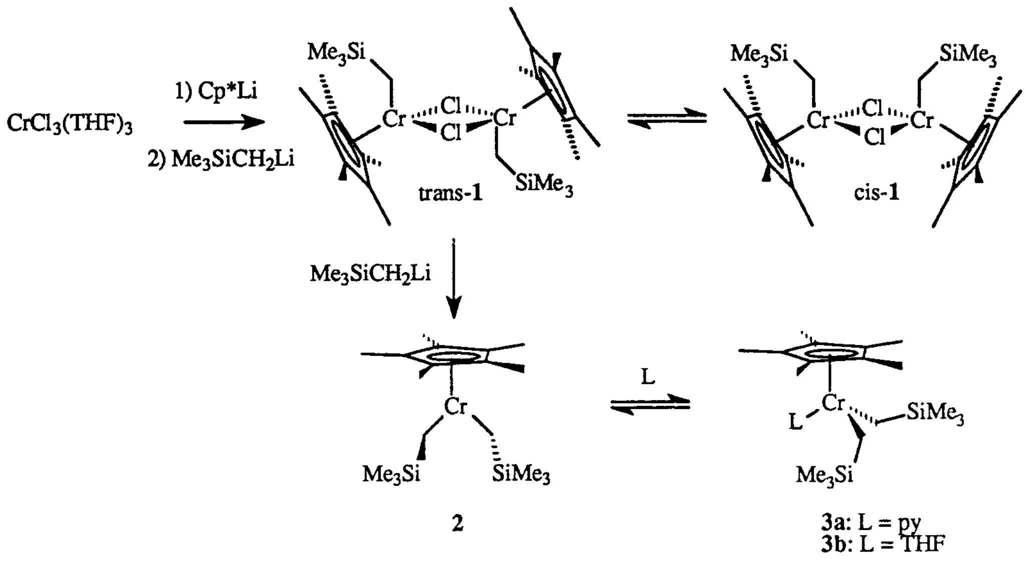
Scheme 1



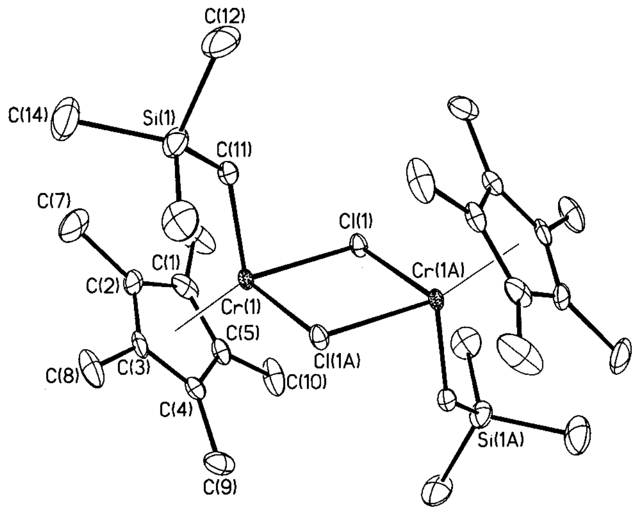


Figure 1. The molecular structure of [Cp*Cr(μ-Cl)(CH$_2$-SiMe$_3$)]$_2$ (**1**). Selected interatomic distances and angles are listed in Table 1.

Table 1. Selected Interatomic Distance and Angles for [Cp*Cr(μ-Cl)(CH$_2$SiMe$_3$)]$_2$ (1)

	Distances (Å)		
Cr(1)−Cr(1A)	3.467(2)	Cr(1)−Cl(1)	2.4085(8)
Cr(1)−Cl(1A)	2.3795(8)	Cr(1)−C(1)	2.225(3)
Cr(1)−C(2)	2.236(3)	Cr(1)−C(3)	2.230(3)
Cr(1)−C(4)	2.288(3)	Cr(1)−C(5)	2.292(3)
Cr(1)−C(11)	2.083(3)	C(11)−Si(1)	1.866(4)
Cr(1)−cent[a]	1.905(3)		
	Angles (deg)		
Cl(1)−Cr(1)−Cl(1A)	87.22(3)	Cr(1)−Cl(1)−Cr(1A)	92.78(3)
Cl(1)−Cr(1)−C(11)	94.63(10)	Cl(1A)−Cr(1)−C(11)	97.00(10)
Cl(1)−Cr(1)−cent[a]	120.4(2)	Cl(1A)−Cr(1)−cent[a]	123.3(2)
C(11)−Cr(1)−cent[a]	125.1(2)	Cr(1)−C(11)−Si(1)	129.7(2)

[a] cent = centroid of Cp* ligand.

it is depicted in Figure 1, and selected interatomic distances and angles are listed in Table 1. The molecule lies on a crystallographic inversion center; it is best described as an edge-sharing bioctahedron (considering the Cp* ring a tridentate ligand occupying one trigonal face of an octahedron). The alkyl groups are positioned trans to each other, and the Cr···Cr distance of 3.47 Å is consistent with the absence of any metal−metal bonding. Indeed, it is significantly longer than the corresponding distances in [CpCr(μ-Cl)CH$_3$]$_2$ (3.29 Å)[1] and [Cp*Cr(μ-Cl)CH$_3$]$_2$ (3.28 Å),[5] presumably indicating steric repulsion between the large alkyl ligands. The Cr−C and Cr−Cl distances of **1** lie within the expected ranges. Thus **1** is but the latest representative of a class of molecules (i.e., [Cp*Cr(μ-Cl)R]$_2$, R = Me, Et, Ph, Bn) that we have described in detail earlier.[10] Its magnetic moment in the solid state (μ_{eff} (295 K) = 4.9(1) μ_B) is on the high end of the range observed for these dimers (i.e., 3.5−4.6 μ_B) and close to that expected for two magnetically independent Cr^{III} ions (5.4 μ_B). Weak antiferromagnetic coupling between the metal centers is responsible for the lower moment.

Contrary to the solid-state structure, solutions of **1** exhibited two sets of isotropically shifted and broadened ^{1}H NMR resonances, consistent with the presence of two isomers, roughly in a 3:2 ratio. The ratio did not change appreciably upon cooling or changing solvent. We surmise that this observation is caused by the presence of cis- and trans-isomers of **1**. The steric demands of the Cp* and Me$_3$SiCH$_2$ ligands are apparently similar enough to preclude a strong structural preference. It is of interest to note that solutions prepared by dissolving crystalline **1**, which consists of the trans-isomer only (see above), at −78 °C exhibited the same set of resonances. The isomerization must therefore be fast on the laboratory time scale even at that low temperature, although it is not fast enough to result in coalescence of the ^{1}H NMR resonances at ambient temperature. The simplest mechanism for the isomerization involves a reversible dissociation of at least one Cr−Cl bond, followed by rotation and reassociation. Despite their structural resemblance of octahedral Cr^{III} coordination compounds, these Cp*Cr alkyls are clearly substitutionally labile.

Addition of 2 equiv of Me$_3$SiCH$_2$Li to Cp*Cr(THF)-Cl$_2$ in THF yielded a purple solution; however, extraction of the solid residue obtained after evaporation of the solvent with pentane produced a brown solution, which, upon cooling to −30 °C, deposited large crystals of Cp*Cr(CH$_2$SiMe$_3$)$_2$ (**2**) in 60% yield. The moderate isolated yield is due to the extreme solubility of **2** in

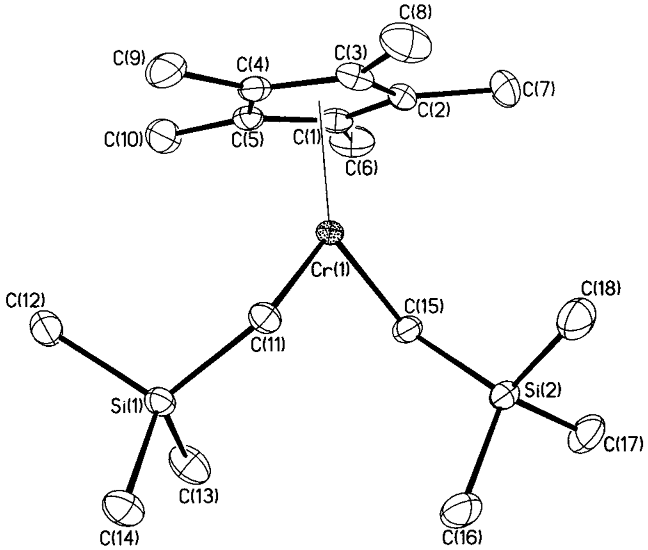


Figure 2. The molecular structure of Cp*Cr(CH_2SiMe_3)$_2$ (**2**). Selected interatomic distances and angles are listed in Table 2.

Table 2. Selected Interatomic Distance and Angles for Cp*Cr(CH_2SiMe_3)$_2$ (2)

Distances (Å)			
Cr(1)−C(1)	2.259(2)	Cr(1)−C(2)	2.246(2)
Cr(1)−C(3)	2.234(2)	Cr(1)−C(4)	2.260(2)
Cr(1)−C(5)	2.240(2)	Cr(1)−cent[a]	1.898(2)
Cr(1)−C(11)	2.073(2)	Cr(1)−C(15)	2.070(2)
C(11)−Si(1)	1.851(2)	C(15)−Si(2)	1.857(2)
Angles (deg)			
C(11)−Cr(1)−C(15)	101.05(11)	C(11)−Cr(1)−cent[a]	130.0(2)
C(15)−Cr(1)−centa	128.9(2)	Cr(1)−C(11)−Si(1)	121.26(12)
Cr(1)−C(15)−Si(2)	118.62(13)		

[a] cent = centroid of Cp* ligand.

hydrocarbons. The 13-electron dialkyl is only marginally stable at ambient temperature, both in solution and in the solid state. Many earlier attempts to grow crystals for a structure determination were thwarted by this combination of high solubility and instability, until the recent advent of a CCD-detector in these laboratories finally enabled the structural characterization of **2**. Its molecular structure is shown in Figure 2, and selected interatomic distances and angles are listed in Table 2. The molecule exhibits no crystallographic symmetry, and it is a mononuclear complex without any chemically significant intermolecular contacts. In keeping with our assignment of Cp* as a tridentate ligand, we consider **2** a pseudo-five-coordinate complex. The two α-carbon atoms (C(11), C(15)) and the Cp* centroid define a plane that contains the Cr atom as well. Despite the coordinative unsaturation of **2**, the solid-state structure provides no hint of agostic interactions between chromium and either the γ-methyl groups (Cr−H ≥ 3.31 Å) or the α-methylene hydrogens (Cr−H ≥ 2.55 Å).[24,25] The magnetic susceptibility of **2** between 4 and 260 K showed Curie behavior, consistent with its mononuclear nature. Its effective magnetic moment (μ_{eff} (250 K) = 3.9(1) μ_B) indicated the presence of three unpaired electrons, as expected for a Cr^{III} (d^3) complex.

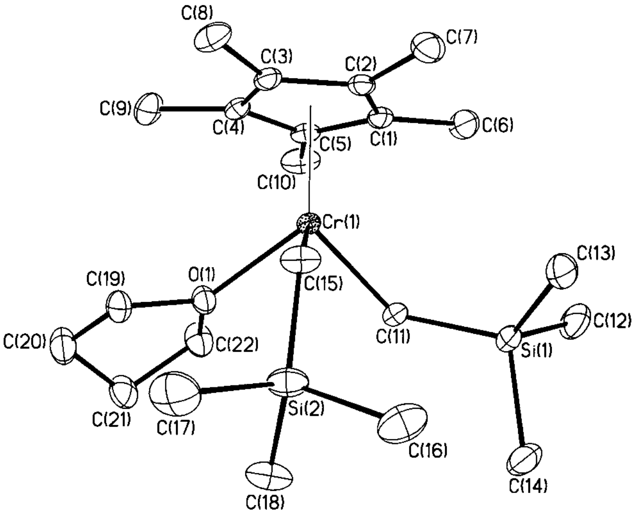


Figure 3. The molecular structure of Cp*Cr(THF)(CH_2SiMe_3)$_2$ (**3b**). Selected interatomic distances and angles are listed in Table 3.

Table 3. Selected Interatomic Distance and Angles for Cp*Cr(THF)(CH_2SiMe_3)$_2$ (3b)

Distances (Å)			
Cr(1)−O(1)	2.122(3)	Cr(1)−C(1)	2.317(5)
Cr(1)−C(2)	2.300(5)	Cr(1)−C(3)	2.339(5)
Cr(1)−C(4)	2.372(4)	Cr(1)−C(5)	2.340(5)
Cr(1)−cent[a]	1.986(5)	Cr(1)−C(11)	2.126(4)
Cr(1)−C(15)	2.125(5)	Si(1)−C(11)	1.882(4)
Si(2)−C(15)	1.879(6)		
Angles (deg)			
O(1)−Cr(1)−C(11)	92.3(2)	O(1)−Cr(1)−C(15)	93.2(2)
C(15)−Cr(1)−C(11)	100.3(2)	O(1)−Cr(1)−cent[a]	118.6(2)
C(11)−Cr(1)−cent[a]	122.9(2)	C(15)−Cr(1)−cent[a]	122.1(2)
Si(1)−C(11)−Cr(1)	129.5(3)	Si(2)−C(15)−Cr(1)	129.1(3)

[a] cent = centroid of Cp* ligand.

Pentacoordination is rather rare for Cr^{III}, due to the significant ligand field stabilization of the d^3 configuration in octahedral coordination.[19,26−29] The large size of the trimethylsilylmethyl ligands combined with the attenuation of the Lewis acidity of the metal by the strong carbanion donors and the absence of any positive charge are presumably responsible for the stability of **2**. When given an opportunity, however, it readily adds external ligands. For example, addition of 1 equiv of pyridine yielded stable Cp*Cr(py)(CH_2SiMe_3)$_2$ (**3a**), a dark green solid. Similarly, dissolution of orange-brown **2** in THF gave a green solution of Cp*Cr(THF)(CH_2SiMe_3)$_2$ (**3b**); the weaker Cr−O bond is formed reversibly, however, and complete evaporation of the THF regenerated **2**. Even minute concentrations of THF in cold pentane solutions (−30 °C) of **2** sufficed to induce crystallization of the THF adduct. Its molecular structure has also been determined and is shown in Figure 3; selected interatomic distances and angles are listed in Table 3. Compound **3b** adopts the familiar geometry of a three-legged piano stool, but the Cr−C distances to the alkyl ligands (Cr−C_{av} 2.13 Å) and the Cp* ring

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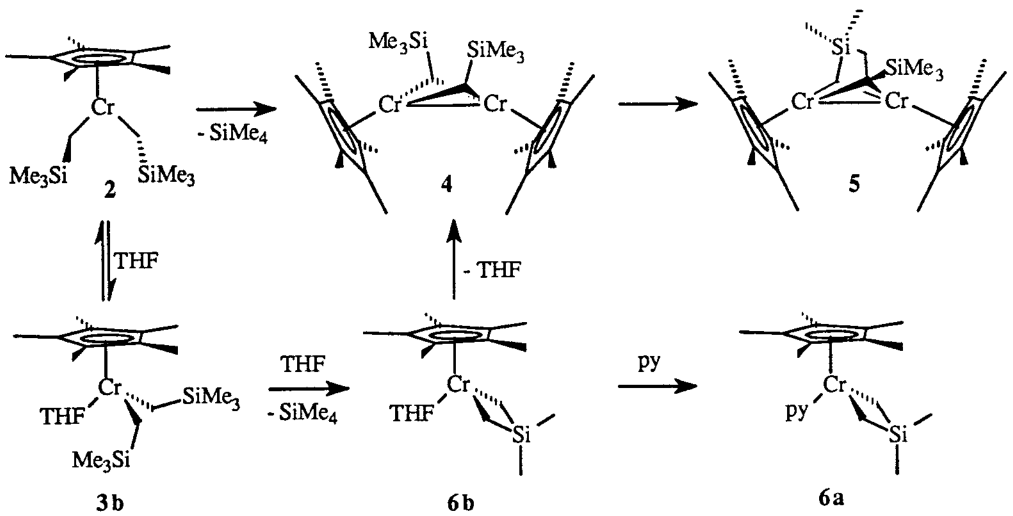
Scheme 2



carbons (Cr$-$C$_{av}$ 2.33 Å) are longer than the typical values, consistent with nonbonded ligand$-$ligand repulsions.

Compound **3b** is a rare example of a six-coordinate Cr^{III} complex that spontaneously loses a ligand upon dissolution. This facile dissociation and the structural characterization of the resulting stable Cr^{III} alkyl **2** establish a secure basis for our earlier claim that related 13-electron species intervene in the stoichiometric and catalytic reactions of paramagnetic Cp*Cr^{III} alkyls. Such dissociative ligand substitution, while entirely in keeping with the known reactivity of Cr^{III} coordination compounds,[30,31] is in contrast to the prevailing associative ligand substitution pathways of organometallic radicals featuring 17-electron configurations.[32,33]

Reactivity. As expected of a coordinatively unsaturated Cp*Cr^{III} alkyl, **2** is a very active catalyst for the polymerization of ethylene under rather mild conditions. Exposure of cold hydrocarbon solutions (pentane or toluene, 0 °C $\geq T \geq -42$ °C) to ethylene (1 atm) resulted in rapid precipitation of polyethylene (M_w = 20 100$-$143 000, M_n 6755$-$20 260, M_w/M_n = 2.98$-$7.06). However, the catalytic activity was short-lived (<20 min), and ultimate productivity was low (ca. 2×10^4 g$_{PE}$ (mol$_{Cr}$ h atm)$^{-1}$). While these observations support our notion that 13-electron alkyls are the catalytically active species in the Cp*Cr system,[23] **2** is not suited in a practical sense for an investigation of the catalysis. Its limited thermal stability, combined with the high exothermicity of the polymerization, puts narrow constraints on the range of possible reaction conditions to be explored (e.g., temperature, pressure).

The cis$-$trans isomerization of **1** already hinted at the possibility of reversible cleavage of the dinuclear chromium complexes. This is further supported by the observation of rapid exchange reactions between **1**, **2**, and [Cp*CrCl(μ-Cl)]$_2$. Thus, a C$_6$D$_6$ solution of an equimolar mixture of **2** and [Cp*CrCl(μ-Cl)]$_2$[10] showed the resonances of **1**, formed in quantitative yield. Similarly, a mixture of **1** and [Cp*CrCl(μ-Cl)]$_2$ exhibited several new resonances (δ $-$26.4, $-$52.3 ppm (Cp*), SiMe$_3$ resonance coincident with that of **1**) attributed to the mixed dinuclear complex Cp*$_2$Cr$_2$(CH$_2$SiMe$_3$)(Cl)(μ-Cl)$_2$.

We turn next to the thermal decomposition of **2**, which is rich in new organometallic molecules and transformations. Compound **2** decomposed slowly at ambient temperature, both in hydrocarbon solution and in the solid state. Monitoring the reaction by ^{1}H NMR (in C$_6$D$_6$) revealed the formation of SiMe$_4$ as well as an organometallic intermediate (**4**, see Scheme 2) of moderate stability, which was eventually transformed into yet another organometallic species (i.e., **5**). At 25 °C, in C$_6$D$_6$, the relative rates of decomposition of **2** (first order in [**2**], $k_2 = 2.5(1) \times 10^{-5}$ s^{-1}) and **4** (first order in [**4**], $k_4 = 9.9(3) \times 10^{-6}$ s^{-1}) were similar enough to prevent isolation of **4**. However, pure **4** could be obtained via a series of transformations of **2** in THF (see below).

The molecular structure of **4** has been determined by X-ray diffraction. There are two crystallographically independent, but chemically similar molecules in the unit cell; one of these is depicted in Figure 4; selected interatomic distances and angles are listed in Table 4. The intermediate is a dinuclear bis(μ-alkylidene) complex, in which each individual chromium maintains the pseudo-five-coordinate configuration of precursor **2**. The four-membered ring at the core of the structure (Cr$_2$C$_2$) is puckered into a butterfly shape with a dihedral angle of 14° between the two CrC$_2$ planes. This deviation from planarity is presumably due to steric interactions between the Cp*-ligands and the trimethylsilyl substituents; despite their large size the latter are positioned cis to each other, to allow an alternating pattern of vicinal substituents around the ring. The Cr$-$Cr distance of 2.69 Å approaches twice the estimated covalent radius of chromium in this system (i.e., 1.32 Å)[11] and is thus short enough to consider metal$-$metal bonding. The CpML$_2$ fragment has low-lying d-orbitals of appropriate symmetry to form M$-$M σ- and π-bonds in edge-shared Cp$_2$M$_2$(μ-L)$_2$,[34] and the effective magnetic moment of **4** (μ_{eff} (295 K) = 2.6(1) μ_B) indicates extensive

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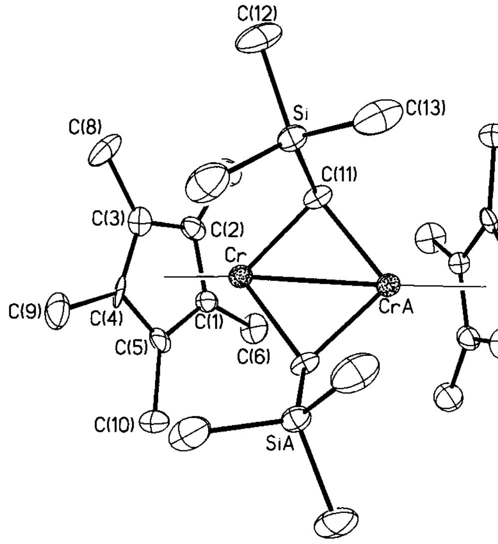

Figure 4. The molecular structure of $[Cp^*Cr(\mu\text{-}CHSiMe_3)]_2$ (**4**); only one of the two crystallographically independent but chemically similar molecules is shown. Selected interatomic distances and angles are listed in Table 4.

Table 4. Selected Interatomic Distance and Angles for $[Cp^*Cr(\mu\text{-}CHSiMe_3)]_2$ (4)

Distances (Å)			
Cr−CrA	2.687(4)	Cr−C(1)	2.213(14)
Cr−C(2)	2.246(14)	Cr−C(3)	2.261(14)
Cr−C(4)	2.260(11)	Cr−C(5)	2.232(11)
Cr(1)−cent[a]	1.891(12)	Cr−C(11)	2.023(10)
Cr−C(11A)	2.003(13)	Si−C(11)	1.843(13)

Angles (deg)			
cent−Cr−C(11)[a]	132.0(5)	cent−Cr−C(11A)[a]	126.7(5)
cent−Cr−CrA[a]	151.5(3)	C(11)−Cr−C(11A)	95.1(5)
Cr−C(11)−CrA	83.7(4)	Cr−C(11)−Si	110.8(6)
Si−C(11)−CrA	120.8(7)		

[a] cent = centroid of Cp* ligand.

spin-pairing. Hence, we assign to **4** a measure of metal−metal bonding, although we do not care to speculate about the exact bond order or bond strength of this interaction.[35] The chromium−carbon distances to the alkylidene carbons differ only marginally; at 2.00−2.02 Å they are significantly shorter than typical Cr^{III}−C σ-bonds (2.09 Å).[11] A similar shortening was also noted in $[(Cp^*Cr)_2(\mu\text{-}CH_3)_2(\mu\text{-}CH_2)]$ and seems to be a general feature for μ-alkylidenes.[12,36]

At ambient temperature, the lifetime of **4** only slightly exceeded that of **2**. Its decomposition yielded yet another paramagnetic organometallic molecule, without the concomitant release of any organic products. The nature of the product was revealed by an X-ray structure determination; the molecular structure of **5** is shown in Figure 5 and selected interatomic distances and angles are listed in Table 5. The molecule is a dinuclear chromium complex as well; however, the formal oxidation state of the metal atoms has been reduced to +II. The organic moiety linking the two metals is best thought of as resulting from a reductive elimination, coupling an alkylidene with a metallacyclobutane to yield a μ,μ-1,4-diyl ligand (i.e., $\mu\text{-}CH_2Si(Me)_2CH_2\text{-}\mu\text{-}CH(SiMe_3)^{2-}$). Compound **5** is an elaborate representative of molecules of the type $[Cp^*Cr(\mu\text{-}R)]_2$, which we have described previously as well.[37]

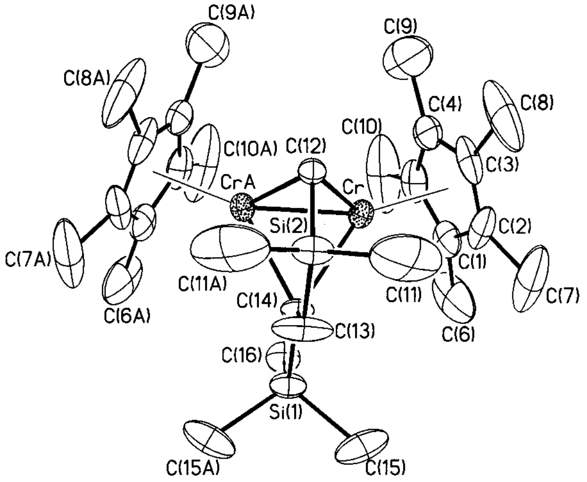

Figure 5. The molecular structure of $Cp_2^*Cr_2(\mu\text{-}CH_2SiMe_2CH_2\text{-}\mu\text{-}CHSiMe_3)$ (**5**). Selected interatomic distances and angles are listed in Table 5.

Table 5. Selected Interatomic Distance and Angles for $Cp_2^*Cr_2(\mu\text{-}CH_2SiMe_2CH_2\text{-}\mu\text{-}CHSiMe_3)$ (5)

Distances (Å)			
Cr−CrA	2.262(2)	Cr−C(1)	2.316(10)
Cr−C(2)	2.345(9)	Cr−C(3)	2.278(12)
Cr−C(4)	2.250(12)	Cr−C(5)	2.270(10)
Cr−cent[a]	1.973(10)	Cr−C(12)	2.181(9)
Cr−C(14)	2.221(9)	Si(1)−C(14)	1.858(11)
Si(2)−C(12)	1.859(11)	Si(2)−C(13)	1.821 (12)
C(13)−C(14)	1.490(15)		

Angles (deg)			
cent−Cr−C(12)[a]	129.9(4)	cent−Cr−C(14)[a]	140.0(4)
cent−Cr−CrA[a]	152.0(3)	C(12)−Cr−C(14)	83.1(3)
C(12)−Cr−CrA	58.8(1)	C(14)−Cr−CrA	59.4(1)
Cr−C(12)−Si(2)	105.8(4)	C(12)−Si(2)−C(13)	101.6(5)
Si(2)−C(13)−C(14)	117.3(8)	Si(1)−C(14)−C(13)	114.3(7)
Cr−C(14)−CrA	61.2(3)	Cr−C(14)−Si(1)	127.0(4)
Cr−C(14)−C(13)	108.2(6)		

[a] cent = centroid of Cp* ligand.

Actually, the crystal structure did not unambiguously establish this assignment, due to the uncertainty in the number of hydrogen atoms attached to the bridging carbon atoms. Indeed, a bis(μ-alkylidene) formed via a dehydrogenative coupling (i.e., $\mu\text{-}CHSi(Me)_2CH_2\text{-}\mu\text{-}C(SiMe_3)^{4-}$) had to be considered and ruled out, especially in light of the apparent crystallographic mirror plane symmetry of the molecule, which leaves no obvious location for a hydrogen atom attached to C(14). Several structural features of **5** are consistent with a bis(μ-alkyl) assignment. The Cr−Cr distance of 2.262(2) Å is much shorter than any we have found in dinuclear Cr^{III} alkyls; on the other hand, it is identical to that of $[Cp^*Cr(\mu\text{-}CH_3)]_2$ (i.e., 2.263(3) Å).[36] The Cr−C distances of **5** (Cr−C(12), 2.181(9) Å and Cr−C(14), 2.221(9) Å), as well, are very similar to those of the latter complex (Cr−C, 2.182(11) and 2.190(11) Å) and do not match the short Cr−C distances of **4** at all. Other physical observables point toward the Cr^{II} formulation as well. The effective magnetic moment of **5** (μ_{eff}(295 K) = 1.1(1) μ_B) is in the range established by other $[Cp^*Cr(\mu\text{-}R)]_2$ derivatives (1.0−1.4 μ_B), and its low value

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is consistent with significant Cr−Cr bonding. Due to its low magnetic moment, the ^{1}H and ^{13}C NMR spectra of **5** were only moderately shifted and broadened. Interestingly, both spectra featured two nonequivalent Cp* resonances as well as two different methyl resonances for the $SiMe_2$ group. This is not consistent with the X-ray diffraction structure, which exhibits crystallographic mirror plane symmetry. We note that the 1,4-diyl assignment actually predicts the spectroscopically observed nonequivalence, because one of the bridging carbon atoms (i.e., C(14)) has three different substituents (beyond the two Cr atoms), and is thus stereogenic. **5** consists of a pair of enantiomers, and its Cp* ligands and two methyl groups are diastereotopic. The apparent mirror symmetry of the crystal structure is caused by positional disorder of the two enantiomers in the crystal. Indeed, several atoms of the alkyl bridge exhibit asymmetric thermal ellipsoids, indicating a disorder that could not be resolved. Interestingly, the positions of the heavy atom substituents of C(14) (i.e., Si(1), C(13)) would seem to force its lone hydrogen atom into a position close to either one of the chromium atoms—the choice of chromium incidentally determining the absolute configuration of the enantiomer. We have no independent spectroscopic evidence for an agostic C−H−Cr interaction, however, and this facet of the structure must remain speculation. Final confirmation of the proposed nature of **5** came from deuterium-labeling studies. Reaction of **5** with excess DCl gas gave $(DCH_2)Si(CH_3)_2CH_2CHDSi(CH_3)_3$, as shown by GC/MS and ^{1}H/^{13}C NMR.

The isolation of pure **4** from the thermal decomposition of **2** in THF invites some scrutiny. Heating a green THF solution of **3b**—prepared by dissolving **2** in THF—to 50 °C for 18 h yielded 1 equiv of $SiMe_4$ and a new organometallic compound (**6b**), which could be isolated by crystallization from a minimum of THF. When dark green **6b** was dissolved in noncoordinating solvents (pentane, toluene), it lost THF irreversibly and produced pure **4**; as noted above, the discovery of this reaction path allowed us to characterize the bis(μ-alkylidene) complex. On the other hand, treatment of **6b** with pyridine gave the pyridine adduct **6a**. However, **6a** and **6b** are not alkylidene complexes, but rather 3-silametallacyclobutanes. Their ^{1}H NMR spectra exhibit two methyl resonances, rather than one large trimethylsilyl resonance expected of an alkylidene. Compound **6a** was also independently prepared by reaction of $Cp^*Cr(py)Cl_2$ with the magnesacycle $Mg(CH_2)_2SiMe_2$. Furthermore, parallel investigations of neopentyl chemistry have yielded the analogous compound $Cp^*Cr(py)(CH_2)_2CMe_2$; the molecular structure of this compound has been determined by X-ray diffraction, and it is a metallacyclobutane.[38]

Mechanism. The thermal decomposition of **2** is surprisingly varied. The molecule relieves steric strain by eliminating 1 equiv of $SiMe_4$, but finding the β-hydrogen elimination pathway blocked, it seems to opt for both α- and/or γ-elimination with equal facility, depending on the circumstances (see Scheme 3). The first-order decomposition of **2** in noncoordinating solvents, yielding **4**, is most simply rationalized as an α-elimination of $SiMe_4$ from monomeric **2**,[39] followed by stabilization of two terminal alkylidenes as bis(μ-alkylidene) **4**. While aggregation of **2** to a bridging alkyl, i.e., $[Cp^*Cr(CH_2SiMe_3)(\mu\text{-}CH_2SiMe_3)]_2$, prior to elimination finds some support in the existence of $[Cp^*Cr(CH_3)(\mu\text{-}CH_3)]_2$,[6] a rate-determining dimerization would presumably result in second-order kinetics. In the presence of potential ligands (e.g., THF, py), the most straightforward mechanism explaining the products (i.e., **6a**,**b**) consists of a γ-elimination from **2**,[40] followed by trapping of the coordinatively unsaturated metallacycle intermediate with a Lewis base. On the basis of the observed inhibition of the decomposition by external ligands—modest for THF and more pronounced for the stronger ligand pyridine—we believe that the γ-elimination proceeds from coordinatively unsaturated **2**, rather than reflecting a different reactivity of the Lewis base adducts **3a** and **3b**. Thus, both a terminal alkylidene as well as a metallacyclobutane are accessible from **2**. Indeed, our observations suggest that these two species must exist in equilibrium and interconvert via a low-barrier pathway. The ultimate fate of the intermediates depends critically on available reaction partners. In the presence of Lewis base, the stability of the trigonal piano stool reasserts itself, yielding **6**. In the absence of such a ligand, the system finds temporary refuge in the form of the μ-alkylidene complex **4**. However, the most stable product is a Cr^{II} alkyl resulting from a reductive elimination of two intermediates, one of each type. A reasonable mechanism for the formation of **5** is shown in Scheme 3 as well. Note that the formulation of the dinuclear intermediate as a mixed valent Cr^{IV},Cr^{II} species is entirely hypothetical; it does, however, motivate the subsequent reductive elimination.

Conclusions

The well-established strategy of employing sterically demanding ligands to stabilize low coordination numbers has allowed the isolation and structural characterization of an electronically (13 valence electrons) and coordinatively (five-coordinate) unsaturated Cr^{III} alkyl. Besides being a rare example of a Cr^{III} coordination compound not adopting octahedral coordination, $Cp^*Cr(CH_2SiMe_3)_2$ (**2**) embodies the postulated active species of our homogeneous model system for the Union Carbide ethylene polymerization catalyst.[41] Remarkably, **2** does not exhibit any ground-state agostic interactions. However, it undergoes facile hydrogen elimination reactions to generate various new organometallic molecules. The mechanism of the decomposition is rationalized in terms of two equilibrating intermediates, namely a metallacyclobutane and a terminal alkylidene. The appearance of these important structural motifs in the organometallic chemistry of Cr^{III} is noteworthy and suggests avenues for further inquiry.

Experimental Section

General Considerations. All manipulations of compounds were carried out by standard Schlenk, vacuum, and glovebox

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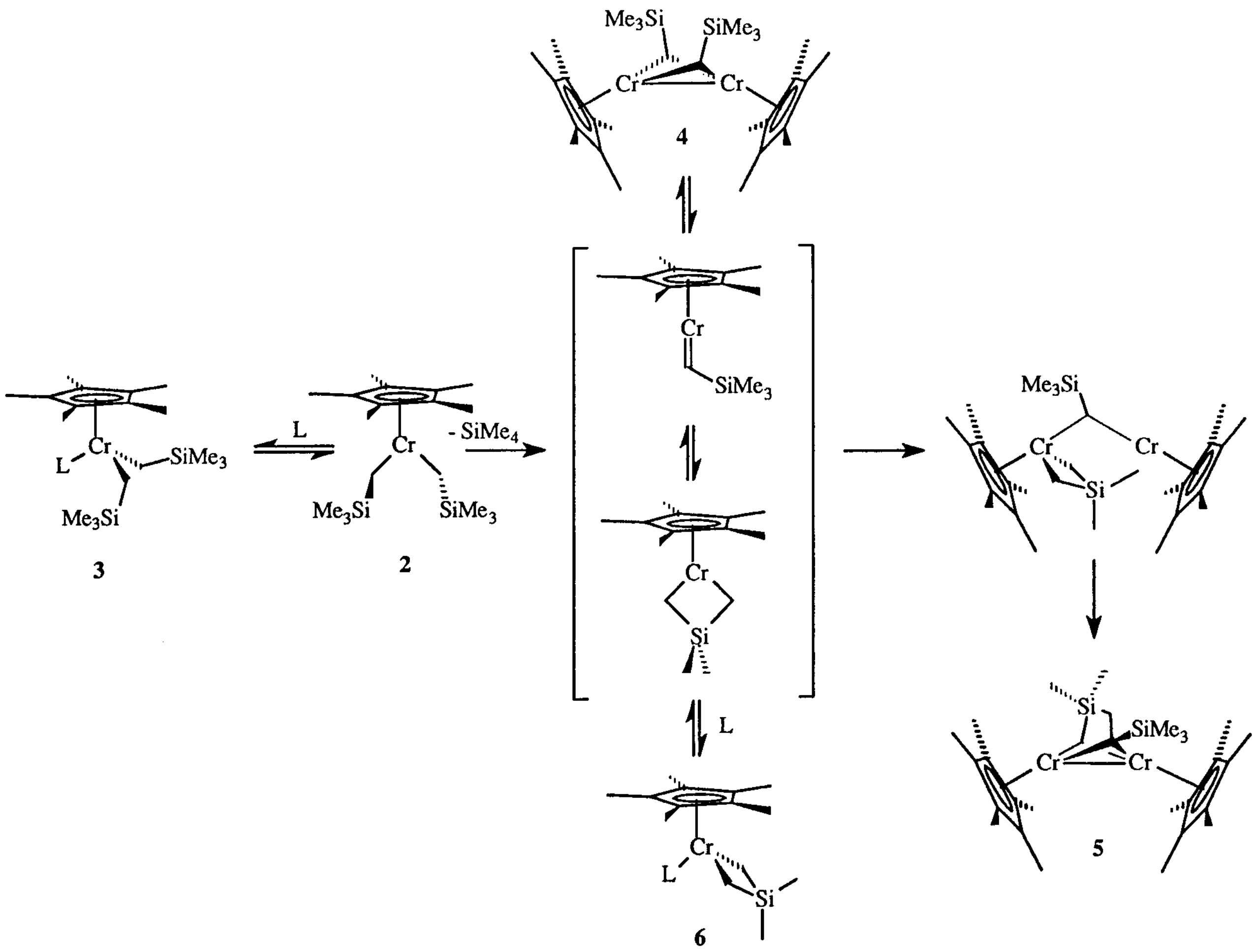
Scheme 3



techniques. Pentane, diethyl ether, tetrahydrofuran, toluene, and hexamethyldisiloxane were distilled from purple Na benzophenone/ketyl solutions. C_6H_6, C_6D_6, C_6D_{12}, and THF-d_8 were all predried with Na and stored under vacuum over Na/K alloy. Pyridine was dried with CaH_2 and vacuum distilled onto 4 Å molecular sieves. CD_2Cl_2 was dried with CaH_2 and stored under vacuum over 4 Å molecular sieves. $CrCl_3$(anhydrous) was purchased from Strem Chemical Co. C_6H_5COCl, D_2O, Li(wire), and CH_3Li were all purchased from Aldrich Chemical Co. and were used as received. Trimethylsilylmethyllithium was purchased from Aldrich as a 1 M solution in pentane and was crystallized from solution at −30 °C and isolated as a white crystalline solid. The solid was dissolved in THF and titrated using a THF solution of diphenylacetic acid. The trimethylsilylmethyllithium was determined to be 99(5)% active. CP grade ethylene was purified with a column of MnO and 4 Å molecular sieves. $CrCl_3(THF)_3$ and LiCp* were synthesized by literature procedures.[42,43] $Mg(CH_2)_2Si(CH_3)_2$ was prepared by a literature procedure, and its activity was determined through a reaction with 1 M HCl and back-titration with 1 M NaOH.[44]

NMR spectra were taken on Bruker AM-250 or WM-250 spectrometers and were referenced to the residual protons of the solvent (C_6D_5H = 7.15 ppm, THF-d_7 = 3.58, 1.73 ppm, $CDHCl_2$ = 5.32 ppm). FTIR spectra were taken on a Mattson Alpha Centauri spectrometer with a resolution of 4 cm^{-1}. UV/vis spectra were taken using a Bruins Instruments Omega 20 spectrophotometer. Mass spectra were obtained by the University of Delaware Mass Spectrometry Facility. Elemental analysis were performed by Oneida Research Services, Whitesboro, NY, 13492. Room-temperature magnetic susceptibilities were determined using a Johnson Matthey magnetic susceptibility balance which utilizes a modification of the Gouy method.

Synthesis of Bis(μ-chloro)bis(trimethylsilylmethyl)-bis(η^5-pentamethylcyclopentadienyl)dichromium(III), $[Cp^*Cr(\mu\text{-}Cl)(CH_2Si(CH_3)_3)]_2$ (1). 0.520 g (5.52 mmol) of trimethylsilylmethyllithium was slowly added to a stirred blue solution of 1.997 g (5.33 mmol) of $CrCl_3THF_3$ and 0.767 g (5.39 mmol) of Cp*Li in 65 mL of THF. The THF was removed by rotoevaporation and trituration with pentane. The solid was extracted with pentane and filtered. The violet pentane solution was concentrated and cooled to −30 °C to give 1.40 g of **1** (84%), mp 140 °C. ^1H NMR (C_6D_6): δ −27.99 (15H), −24.92 (15H), −1.12 (9H), 0.32 (9H) ppm. IR (KBr): 2949 (s), 2911 (s), 2870 (s), 2833 (s), 1431 (w), 1377 (m), 1246 (s), 945 (w), 905 (m), 850 (s), 819(s), 716 (s), 671 (m), 519 (w), 456 (m) cm^{-1}. UV/vis (pentane): λ (ϵ) 290 (22450), 548 (1310) nm. μ_{eff} = 4.9-(1) μ_B (295 K). MS (*m*/*e* (%)): 444 (3.8%), 222 (100%), 186 (14.6%). Anal. Calcd for $C_{28}H_{52}Cr_2Si_2Cl_2$: C, 54.41; H, 8.57. Found: C, 54.26; H, 8.46.

Synthesis of Bis(trimethylsilylmethyl)(η^5-pentamethylcyclopentadienyl)chromium(III), $Cp^*Cr(CH_2Si(CH_3)_3)_2$ (2). Cp*Li (1.000 g, 7.03 mmol) was added to a stirred suspension of 2.642 g of $CrCl_3(THF)_3$ (7.05 mmol) in 60 mL of THF. The resulting blue solution was stirred for 4 h. Trimethylsilylmethyllithium (1.324 g, 14.1 mmol) was slowly added, and the solution turned from blue to dark purple. The THF was then removed by rotoevaporation to give a red brown

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solid. The solid was dissolved in pentane and filtered to remove the LiCl. The pentane solution was concentrated and cooled to −30 °C to give 1.520 g of **2** (4.20 mmol, 60%). ^{1}H NMR (C_6D_6): δ 11.9 (18H), −29.7 (15H) ppm. ^{1}H NMR (THF-d_8, i.e., Cp*Cr((THF-d_8)(CH_2SiMe_3)$_2$, **3b**-d_8): δ −0.61 (18H), −7.23 (15H) ppm. IR (KBr): 2946(s), 2916(s), 2893(s), 2854(m), 1432(m) 1378(m), 1238(s), 971(m), 845(vs), 717(s), 677(m), 516(m), 479(m) cm^{-1}. UV/vis (pentane): λ (ϵ) 462 (650) nm. Elemental analysis was not possible due to the thermal instability of **2**. The magnetic susceptibility of solid **2** in the temperature range of 4−260 K was measured with a Faraday balance. The data (diamagnetic correction = -240×10^{-4} emu/g atom) were fitted with a Curie−Weiss expression: $\chi_m = [C/(T - \theta)]$; $C = 2.454$ emu K mol^{-1}, $\theta = -1.05$ K; μ_{eff} (248 K) = 3.94 μ_B.

Ethylene Polymerization Reactions using 2 as the Catalyst. The polymerizations were carried out in 100 mL Schlenk flasks. The solvent (pentane or toluene) was degassed and then saturated with ethylene. The ethylene was purified by using a column containing 4 Å molecular sieves and MnO. The catalyst was dissolved in a small volume of solvent (~0.5 mL of pentane or toluene) and then injected via syringe into the flask containing the ethylene-saturated solution. The pressure was measured with a mercury manometer. The polymerizations were very rapid, and ethylene uptake stopped after about 20 min. The polyethylene was filtered from solution and was washed with hexane and methanol. The polyethylene was then dried for several hours under vacuum. The samples were then sent to Chevron Chemical Company for GPC and ^{13}C NMR analysis.

Synthesis of Bis(trimethylsilylmethyl)(η^5-pentamethylcyclopentadienyl)pyridinechromium(III), Cp*Cr(py)($CH_2Si(CH_3)_3$)$_2$ (3a). Compound **2** (0.500 g, 1.38 mmol) was dissolved in 30 mL of pentane to produce a red-orange solution. To this stirred solution was added 0.2 mL of pyridine. The solution immediately turned green. The solvent and excess pyridine was removed by rotoevaporation to give a dark green solid. The green solid was dissolved in a minimum of pentane and recrystallized at −30 °C to give 0.453 g (1.03 mmol, 75%) of **3a**. ^{1}H NMR (C_6D_6): δ 21.6 (3H), 0.45 (broad) and 2.0 (shoulder, 24H) ppm. IR (KBr): 2948(s), 2904(s), 2877(s), 2827(s), 1601(m), 1483(m), 1444(s), 1236(s), 1067(w), 1022(w), 903(s), 852(s), 815(s), 751(s), 729(s), 699(m), 673(m) cm^{-1}. UV/vis (pentane): λ (ϵ) 421 (810), 601 (270) nm. μ_{eff} (295 K) = 4.1(1) μ_B. Anal. Calcd for $C_{23}H_{42}NSi_2$: C, 62.28; H, 9.60; N, 3.18. Found: C, 62.57; H, 9.56; N, 3.06.

Synthesis of Bis(μ-trimethylsilylmethylene)bis(η^5-pentamethylcyclopentadienyl)dichromium(III), [Cp*Cr(μ-CHSi(CH$_3$)$_3$)]$_2$ (4). Compound **6b** (0.350 g, 1.01 mmol) was dissolved in 50 mL of pentane. The solution was at first dark green but rapidly changed to brown. The reaction was allowed to stir for 1 h, the pentane was then removed by rotoevaporation, and the resulting brown solid was dissolved in a minimum of pentane and recrystallized at −30 °C to yield 0.146 g (0.27 mmol, 53%) of **4**. ^{1}H NMR (C_6D_6): δ 9.8 (8H), 5.5 (15H) ppm. IR (KBr): 2950(s), 2909(s), 1437(m), 1375(m), 1235(s), 987(m), 934(m), 844(s), 755(m), 671(m) cm^{-1}. μ_{eff} (296 K) = 2.6(1) μ_B. Elemental analysis was precluded by thermal instability.

Kinetic Measurements of the Rates of Disappearance of 2 and 4. Compounds **2** and **4** (0.030 g of each) were placed in separate NMR tubes connected with Pyrex tubing to ground glass joints. C_6D_6 was vacuum distilled into the NMR tubes, and the tubes were flame sealed under vacuum. The tubes were kept frozen in liquid nitrogen until the beginning of the kinetics measurements. The tubes were quickly thawed, and an initial NMR spectrum was taken. NMR spectra were then taken periodically. During the time between NMR measurements the tube were kept in a water bath maintained at 25 °C. The ratios of reactant to product or products were determined by NMR integrations of the Cp* peaks of the compounds involved, and the total concentrations were checked to be constant by comparison to the solvent peak (C_6D_5H).

Synthesis of Cp*$_2$Cr$_2$(μ-CH$_2$Si(CH$_3$)$_2$CH$_2$-μ-CHSi(CH$_3$)$_3$) (5). Compound **2** (0.500 g, 1.38 mmol) was dissolved in 50 mL of pentane and allowed to stir for 2 days at room temperature. During this time the solution turned from red-orange to dark brown. The pentane was evaporated, and the resulting brown solid was dissolved in a minimum of pentane and recrystallized at −30 °C to give 0.253 g (0.46 mmol, 67%) of **5**. ^{1}H NMR (C_6D_6): δ 2.24, 2.20 (30H), 0.62 (3H), 0.57 (3H), 0.46(9H) ppm. ^{13}C NMR (C_6D_6): δ 105.2, 104.7, 15.6, 15.4, 3.1 ppm. IR (KBr): 2944(s), 2905(s), 2859(s), 1437(m), 1375(m), 1240(s), 1022(m), 901(m), 851(s), 828(s), 737(m), 683(m) cm^{-1}. μ_{eff} (294 K) = 1.1(1) μ_B. Anal. Calcd for $C_{28}H_{50}Cr_2Si_2$: C, 61.50; H, 9.22. Found: C, 60.85; H, 9.11.

Reaction of 5 with DCl. Compound **5** (0.100 g, 0.18 mmol) was dissolved in 2 mL of C_6D_6 in a 10 mL round-bottom flask. In a three-necked 100 mL round-bottom flask was placed 40 mL of C_6H_5COCl, and the flask was flushed with Ar gas. The 100 mL round-bottom flask was fitted with a gas inlet valve, a reflux condenser, a septum, and a gas outlet valve on top of the condenser. The outlet was connected to a rubber vacuum hose which was in turn connected to a trap cooled to −78 °C. The outlet of the trap was then connected to a stainless steel needle which was inserted into the flask containing compound **5** dissolved in C_6D_6. An outlet from this last flask led to an oil bubbler and then to a bubbler filled with an aqueous NaOH solution. A slow flow of Ar was established through the apparatus and then 1 mL of D_2O was slowly added dropwise to the benzoyl chloride. The round-bottom flask was then heated to reflux the benzoyl chloride. The DCl produced was flushed through the apparatus, through the −78 °C trap and into the flask containing **5**. The solution turned bright blue with the addition of DCl. After about 1 h the reaction was stopped and the volatiles from the C_6D_6 solution were vacuum transferred into another flask at room temperature. ^{1}H NMR(C_6D_6): δ 0.39 (s, 3H), 0.02 (s, 17H) ppm. ^{13}C NMR (C_6D_6): δ 8.99, 8.69, 8.40, −2.14, −2.43, −2.72 ppm. GC/MS (*m*/*e* (%)): 177(2.3), 176 (M$^+$, 10.8), 175(2.0), 162(3.8), 161(17.4), 160(6.3), 133(2.6), 132(13.5), 131(4.3), 89(2.8), 88(16.6), 87(37.0), 86(21.5), 85(6.6), 84(2.7), 76(3.3), 75(12.7), 74(90.7), 73(100), 60(7.5), 59(16.1), 58(16.1), 57(2.2), 55(2.2).

Synthesis of 2-((Dimethyl)sila)-1,3-propanediyl-(η^5-pentamethylcyclopentadienyl)pyridinechromium(III), Cp*Cr(py)(CH$_2$)$_2$Si(CH$_3$)$_2$, 6a. Method A. LiCp* (0.202 g, 1.42 mmol) was added to a stirred slurry of 0.528 g (1.41 mmol) of CrCl$_3$(THF)$_3$ in 50 mL of THF. The reaction turned blue and was allowed to stir for 3 h. Excess pyridine (1−2 mL) was then added to the solution. The bright blue solution was allowed to stir 15 min, and then 0.281 g of Mg(CH$_2$)$_2$Si(CH$_3$)$_2$ (55% active) (1.40 mmol) was added to the stirring solution. The blue solution turned greenish brown. The THF was then removed by rotoevaporation, and the solid was extracted with pentane and filtered. The pentane solution was concentrated and then cooled to −30 °C to give 0.302 g (0.86 mmol, 61%) of **6a**.

Method B. Compound **2** (0.500 g, 1.38 mmol) was dissolved in 20 mL of THF and this solution of **3b** was heated to 50 °C for 18 h. To this dark green solution was added excess pyridine (1−2 mL), and the solution was allowed to stir for 15 min. The THF and excess pyridine was removed by rotoevaporation to give a dark green solid. This solid was dissolved in pentane and cooled at −30 °C to give 0.330 g (0.94 mmol, 68%) of **6a**. ^{1}H NMR (C_6D_6): δ 29.8 (15H), 22.8 (3H), −20.4 (3H), −27.8 (3H) ppm. IR (KBr): 2937(s), 2890(s), 1601(m), 1481(m), 1443(s), 1238(m), 1063(m), 835(s), 756(m), 701(s), 494(m) cm^{-1}. μ_{eff} (296 K) = 4.0(1) μ_B. Anal. Calcd for $C_{19}H_{30}CrNSi$: C, 64.73; H, 8.58; N, 3.97. Found: C, 64.78; H, 8.62; N, 3.84.

Synthesis of 2-((Dimethyl)sila)-1,3-propanediyl-(η^5-pentamethylcyclopentadienyl)tetrahydrofuranchromium(III), Cp*Cr(THF)(CH$_2$)$_2$Si(CH$_3$)$_2$, 6b. Compound

Table 6. Crystallographic Data for $[Cp^*Cr(\mu\text{-}Cl)(CH_2SiMe_3)]_2$ (1), $Cp^*Cr(CH_2SiMe_3)_2$ (2), $Cp^*Cr(THF)(CH_2SiMe_3)_2$ (3b), $[Cp^*Cr(\mu\text{-}CHSiMe_3)]_2$ (4), and $Cp_2^*Cr_2(\mu\text{-}CH_2SiMe_2CH_2\text{-}\mu\text{-}CHSiMe_3)$ (5)

	1	2	3b	4	5
formula	$C_{28}H_{52}Cl_2Cr_2Si_2$	$C_{18}H_{37}CrSi_2$	$C_{22}H_{45}CrOSi_2$	$C_{28}H_{50}Cr_2Si_2$	$C_{28}H_{50}Cr_2Si_2$
fw	619.78	361.66	433.76	546.9	546.9
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2/c$	$Pnma$
a, Å	7.9644(3)	9.3425(3)	9.9387(2)	17.846(8)	18.207(5)
b, Å	11.0691(4)	10.1774(3)	15.4724(2)	9.456(3)	17.984(4)
c, Å	11.1642(3)	12.4634(4)	17.4294(3)	18.915(8)	9.419(3)
α, deg	105.2073(7)	106.3963(8)			
β, deg	107.8074(4)	102.2484(9)	90.2733(7)	103.810(3)	
γ, deg	105.1991(9)	95.3513(10)			
V, Å^3	839.12(8)	1096.05(10)	2680.18(9)	3099.5(2)	3084.14(14)
Z	1	2	4	4	4
cryst color, habit	brown block	deep amber tablet	brown block	black block	black block
D(calcd), g cm^{-3}	1.226	1.096	1.075	1.172	1.178
μ(Mo Kα), cm^{-1}	8.93	6.26	5.24	7.92	7.95
temp, K	198(2)	198(2)	198(2)	241(2)	29892)
T(max)/T(min)				0.858/0.618	
diffractometer	Siemens P4/CCD	Siemens P4/CCD	Siemens P4/CCD	Siemens P4	Siemens P4
radiation	Mo Kα (λ = 0.71073 Å)				
$R(F)$, %	5.70[a]	5.26[a]	7.51[a]	7.71[a]	5.74[a]
$R(wF)$, %	15.02[a,b]	13.86[a,b]	16.53[a,b]	8.92[c]	6.78[c]

[a] Quantity minimized = $R(wF^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$. [b] $R(wF^2)$, %. [c] Quantity minimized = $\sum\Delta^2$; $R = \sum\Delta/\sum(F_o)$; $R(w) = \sum\Delta w^{1/2}/\sum(F_o w^{1/2})$, $\Delta = |(F_o - F_c)|$.

2 (1.010 g, 2.79 mmol) was placed in a 100 mL flask, and 50 mL of THF was added. The resulting dark green solution was allowed to stir at room temperature for 7 days (heating at 50 °C for 18 h will accomplish the same reaction). The THF was then removed by rotoevaporation, and the resulting dark green solid was dissolved in a minimum of THF and recrystallized at −30 °C to give 0.390 g (1.12 mmol, 40%) of **6b**. ^{1}H NMR (THF-d_8): δ 26.0 (15H), −23.6 (3H), −27.7 (3H) ppm. IR (KBr): 2944(s), 2909(s), 1432(m), 1376(m), 1238(m), 844(s), 680(m), 494(m) cm^{-1}. μ_{eff} (296 K) = 4.0(1) μ_B. Anal. Calcd for $C_{18}H_{33}CrSiO$: C, 62.57; H, 9.63. Found: C, 62.45; H, 9.69.

X-ray Crystallography. Crystal, data collection, and refinement parameters are listed in Table 6. No evidence of symmetry higher than triclinic was observed in the diffraction data of **1** and **2**. The diffraction symmetry and the systematic absences in the diffraction data were uniquely consistent with the reported space group for **3b**. The E-statistics suggested the centrosymmetric space group $P\bar{1}$ for **1** and **2**. The diffraction data and the systematic absences in the data are consistent with the space groups $P2/c$ and $P2$ for **4** and $Pna2_1$ and $Pnma$ for **5**. The E-statistics and the presence of a 2-fold axis in **4** and the presence of a mirror plane in **5** indicated the centrosymmetric space groups, $P2/c$ and $Pnma$, respectively. Solution in these space groups yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. Semiempirical ellipsoid absorption corrections were applied to **4**, but were not required for **1**, **2**, **3b**, and **5**, because there was less than 10% variation in the integrated Ψ-scan intensity data. The molecule of **1** lies on an inversion center; there are two independent, but chemically equivalent half-molecules in the asymmetric unit of **4**, and the molecule **5** lies on a mirror plane. There is irresolvable disorder in Si(2) and C(13) in **5**, which lie on the crystallographic mirror plane. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atom on C(14) could not be located from the difference map and was ignored in the refinement, but included in the intensive unit cell parameters. All other hydrogen atoms were treated as idealized contributions. All software and sources of scattering factors are contained in either the SHELXTL PLUS (4.2) or the SHELXTL (5.1) program libraries (G. Sheldrick, Siemens XRD, Madison, WI). The thermal ellipsoids in Figures 1−5 are drawn at the 30% probability level.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **1**, **2**, **3b**, **4**, and **5** (35 pages). An X-ray crystallographic file, in CIF format, is available through the Internet only. See any current masthead page for ordering information and Web access instructions.

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