

Donor-Ligand-Substituted Cyclopentadienylchromium(III) Complexes: A New Class of Alkene Polymerization Catalyst. 1. Amino-Substituted Systems

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$\text{Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4\text{Li}$ reacts with $\text{Cr}(\text{THF})_3\text{Cl}_3$ to give $(\eta^1:\eta^5\text{-Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{CrCl}_2$, in which the complexation of the N-donor atom to the metal atom has been confirmed by X-ray crystallography. A series of related compounds, e.g. $(\eta^1:\eta^5\text{-cyclo-C}_4\text{H}_8\text{NSiMe}_2\text{OSiMe}_2\text{C}_5\text{H}_4)\text{-CrCl}_2$, has been prepared by varying the substituents on the organic ligand. Further reaction with organomagnesium reagents leads to formation of the corresponding dialkyl–Cr complexes. Related species have been prepared containing imine-, alkoxy-, and alkylthio-substituted cyclopentadienyl groups as well as the C-donor ligand tetramethylimidazol-2-ylidene. Treatment of these compounds with methylalumoxane (MAO) leads to the formation of highly active catalysts for the oligomerization, polymerization, and copolymerization of ethylene.

Introduction

Whereas chromium played a key role in the early development of *heterogeneous* catalysts for the polymerization of alkenes, this metal has been largely ignored in the development of the *homogeneous* methylalumoxane (MAO)-activated systems that have attracted so much attention in the past decade.³ A number of neutral single-component catalysts, e.g. $(\eta^3\text{-C}_3\text{H}_5)_3\text{Cr}$, $\text{Cp}(\eta^3\text{-C}_3\text{H}_5)_2\text{Cr}$, $(\text{Me}_5\text{C}_5)\text{Cr}(\text{CH}_2\text{SiMe}_3)_2$, and $(\text{indenyl})_4\text{Cr}_2$, as well as a few ionic species, e.g. $[(\text{Me}_5\text{C}_5)\text{Cr}(\text{THF})_2\text{Me}]^+\text{-BPh}_4^-$ and $[(t\text{-C}_4\text{H}_9\text{N})_2\text{CrCH}_2\text{Ph}]^+\text{B}(\text{C}_6\text{F}_5)_4^-$, have been reported.⁴ In contrast, the MAO-activated systems are apparently limited to the donor-ligand-substituted cyclopentadienylchromium(III) compounds which we have reported^{5–7} and compounds containing N,O- or N,N-chelate ligands,^{8,9} whereby in the latter case Et_2AlCl has been shown to be a far more effective activator.

In this publication we describe in detail the preparation and properties of the amino-substituted cyclopentadienyl chromium species and a number of related systems. The analogous phosphine-substituted systems will be reported separately.

Results and Discussion

The organochromium compounds described here are members of a relatively large class of amino-substituted cyclopentadienylmetal complexes which are known for many of the transition metals and which have recently been reviewed.¹⁰ The first examples involving chromium were actually prepared by Jonas et al.¹¹ but were not investigated further. Their synthesis is straightforward and involves reacting an alkali-metal salt of the appropriate amino-substituted cyclopentadiene derivative with $\text{Cr}(\text{THF})_3\text{Cl}_3$.

Preparation of the Amino-Substituted Cyclopentadiene Derivatives. The amino-substituted cyclopentadiene derivatives **1a–e** and **2a–c** have been prepared using a standard procedure involving the appropriate (dialkylamino)ethyl or (dialkylamino)propyl chloride (Scheme 1).

The preparation of the corresponding diphenylamino derivatives proved more difficult, and whereas $\text{Ph}_2\text{-NC}_2\text{H}_4\text{Cl}$ could not be obtained pure from the reaction between Ph_2NLi and $\text{ClC}_2\text{H}_4\text{OTos}$ or between LiAlH_4 and $\text{Ph}_2\text{NCOCH}_2\text{Cl}$, $\text{Ph}_2\text{NC}_3\text{H}_6\text{C}_5\text{H}_6$ (**2d**) was prepared

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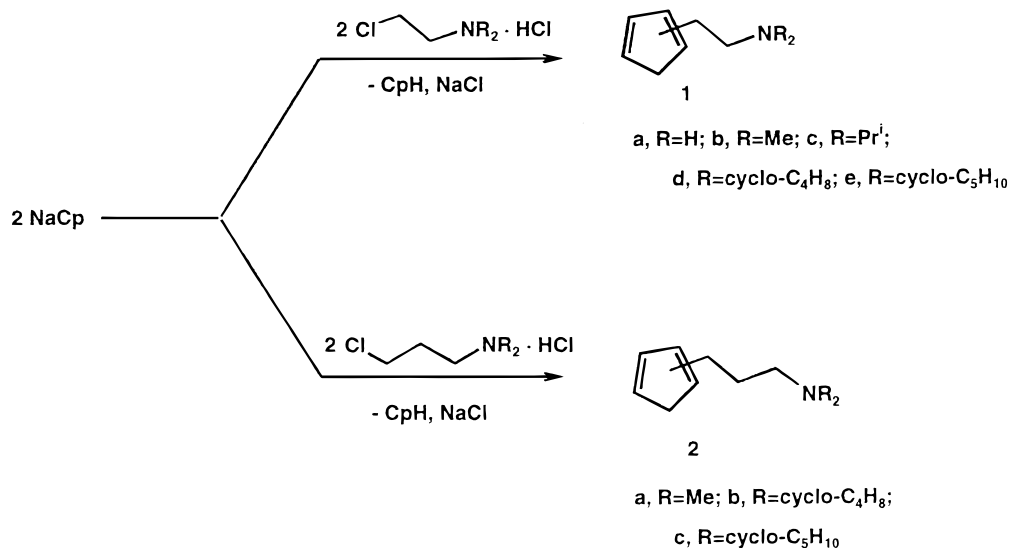
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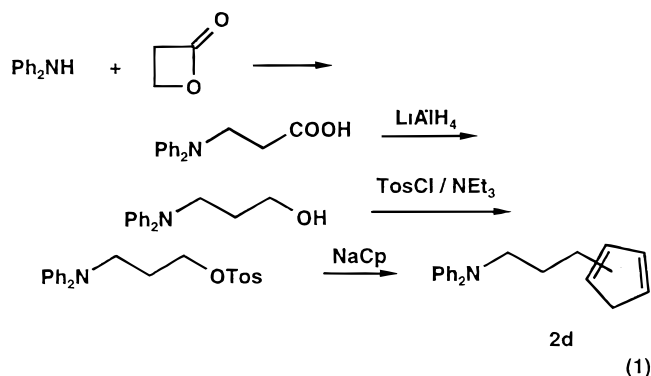
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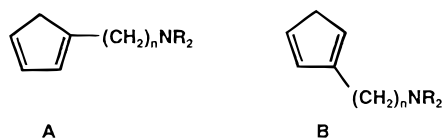
Scheme 1



in modest yield by a multistep synthesis by starting from β -propiolactone (eq 1).¹²



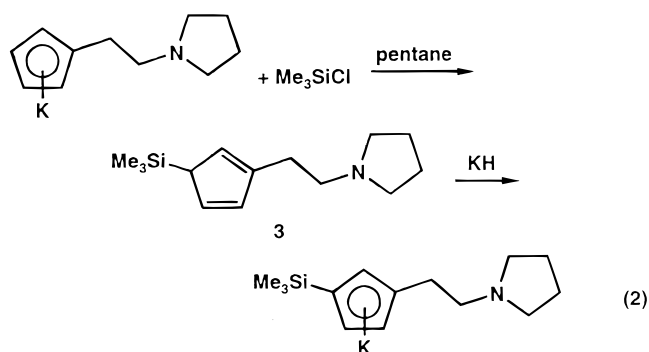
The isolated cyclopentadiene derivatives needed no further purification. The NMR-spectra show that they exist as a mixture of two (**A**, **B**) of three possible isomers in approximately equal amounts.¹³



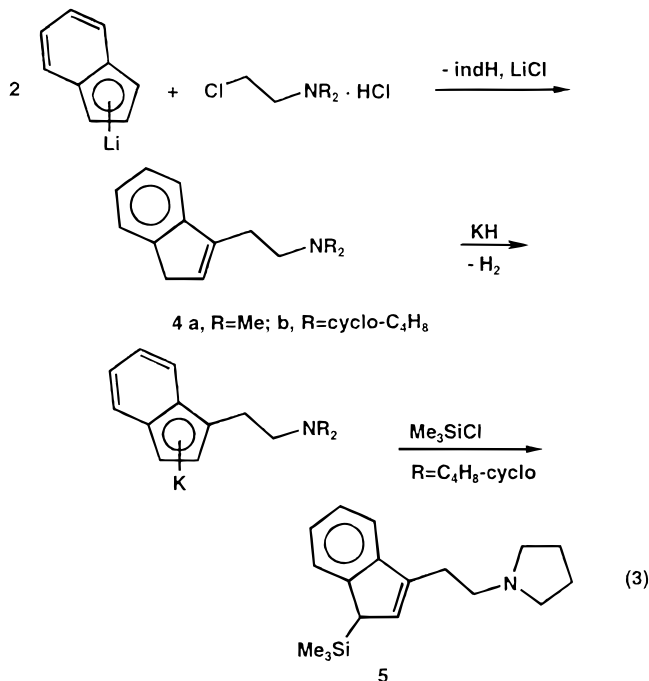
Treatment with NaH or KH in THF or alternatively with BuLi in pentane or diethyl ether leads to the formation of the substituted cyclopentadienylmetal salts as pale pink or white crystalline solids. The reagent of choice is KH, since the resulting product is practically free from complexed THF and the KCl formed in the subsequent reaction with CrCl₃ is more easily removed than either NaCl or LiCl.

Disubstituted cyclopentadiene derivatives are in general prepared by reacting a monosubstituted cyclopentadienyl species with an electrophile, and this procedure has been used to introduce a Me₃Si group to give **3**

(eq 2).¹⁴



A procedure analogous to that presented above has been described by Jonas et al.¹¹ to prepare amino-substituted indenyl ligands. Substitution occurs exclusively in the 2-position of the indenyl group to give **4** and has been extended to a Me₃Si-substituted analogue (**5**) (eq 3).



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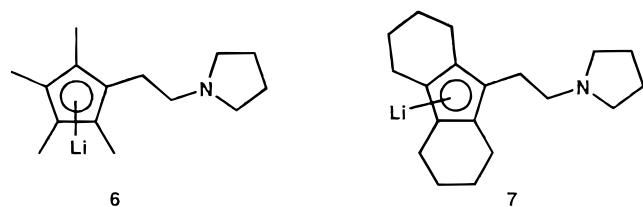
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Table 1. Amino-Substituted Cyclopentadienylchromium Dichloride Compounds

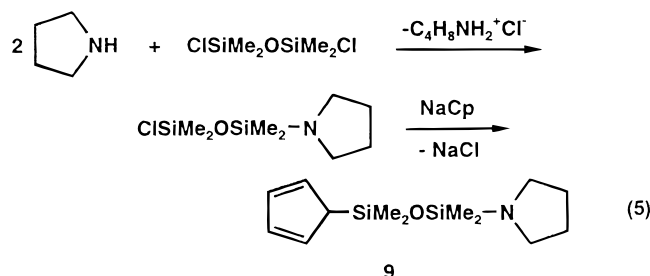
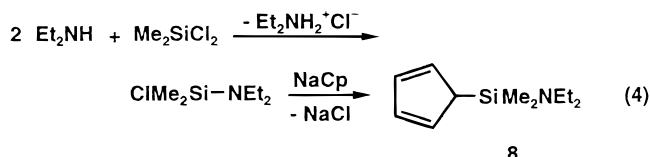
compd	yield (%)	anal. found (calcd)				
		C	H	Cl	Cr	N
(H ₂ NC ₂ H ₄ C ₅ H ₄)CrCl ₂ (10)	63	35.5 (36.4)	4.6 (4.4)	30.9 (30.7)	22.1 (22.5)	5.7 (6.1)
(Me ₂ NC ₂ H ₄ C ₅ H ₄)CrCl ₂ (11) ¹¹	62	41.7 (41.7)	5.3 (5.4)	27.4 (27.4)	20.2 (20.1)	5.4 (5.4)
(cyclo-C ₄ H ₈ NC ₂ H ₄ C ₅ H ₄)CrCl ₂ (12)	95	46.5 (46.3)	5.8 (5.7)	24.8 (24.9)	18.2 (18.2)	4.9 (4.9)
(cyclo-C ₅ H ₁₀ NC ₂ H ₄ C ₅ H ₄)CrCl ₂ (13)	56	48.1 (48.2)	6.1 (6.1)	23.6 (23.7)	17.3 (17.4)	4.6 (4.7)
(Me ₂ NC ₃ H ₆ C ₅ H ₄)CrCl ₂ (14)	66	43.8 (44.0)	5.8 (5.9)	24.6 (26.0)	20.6 (19.1)	5.0 (5.1)
(cyclo-C ₄ H ₈ NC ₃ H ₆ C ₅ H ₄)CrCl ₂ (15)	35	48.0 (48.2)	6.2 (6.1)	23.8 (23.7)	17.3 (17.3)	4.6 (4.7)
(cyclo-C ₅ H ₁₀ NC ₃ H ₆ C ₅ H ₄)CrCl ₂ (16)	73	49.0 (49.9)	6.5 (6.5)	23.1 (22.6)	16.9 (16.6)	4.5 (4.5)
(1,3-cyclo-C ₄ H ₈ NC ₂ H ₄ (Me ₃ Si)C ₅ H ₃)CrCl ₂ (17)	55	47.1 (47.1)	6.8 (6.8)	19.8 (19.8)	14.5 (14.6)	3.9 (3.9) ^a
(1-Me ₂ NC ₂ H ₄ -indenyl)CrCl ₂ (18)	81	50.4 (50.5)	5.3 (5.2)	22.9 (22.9)	16.8 (16.8)	4.5 (4.5)
(1-cyclo-C ₄ H ₈ NC ₂ H ₄ -indenyl)CrCl ₂ (19)	66	53.6 (53.8)	5.4 (5.4)	21.1 (21.2)	15.7 (15.5)	4.1 (4.2)
(1,3-cyclo-C ₄ H ₈ NC ₂ H ₄ (Me ₃ Si)-indenyl)CrCl ₂ (20)	31	53.4 (53.1)	6.2 (6.4)	17.7 (17.4)	12.5 (12.8)	3.7 (3.4) ^b
(Me ₂ NC ₂ H ₄ C ₅ Me ₄)CrCl ₂ (21)	86	49.5 (49.5)	6.9 (7.0)	22.6 (22.5)	16.5 (16.5)	4.4 (4.4)
(cyclo-C ₄ H ₈ NC ₂ H ₄ C ₅ Me ₄)CrCl ₂ (22)	82	52.8 (52.8)	7.0 (7.1)	20.9 (20.8)	15.3 (15.2)	4.1 (4.1)
(cyclo-C ₄ H ₈ NC ₂ H ₄ -fluorenyl[H ₈])CrCl ₂ (23)	70	57.9 (58.0)	7.2 (7.2)	18.1 (18.0)	13.4 (13.2)	3.5 (3.6)
(cyclo-C ₄ H ₈ NSiMe ₂ OSiMe ₂ C ₅ H ₄)CrCl ₂ (24)	79	39.9 (40.1)	6.3 (6.2)	18.2 (18.2)	13.3 (13.4)	3.6 (3.6) ^c

^a% Si: 7.8 (7.9). ^b% Si: 6.7 (6.9). ^c% Si: 14.5 (14.4).

The synthetic procedure for preparing amino-substituted tetraalkylcyclopentadienyl derivatives has been well worked out,^{10,11,15} and we have used it to prepare the lithium salts of 1-(2-(*N*-pyrrolidinyl)ethyl)tetramethylcyclopentadiene (**6**) and of 9-(2-(*N*-pyrrolidinyl)ethyl)octahydrofluorene (**7**).



In addition to the species described above containing C₂H₄ or C₃H₆ fragments bridging the ring and the amino group, we have prepared two examples (**8** and **9**) in which the bridge contains Si-atoms (eqs 4 and 5).¹⁶ The



NMR spectra of **8** and **9** show that at -30°C they have the structures shown, while at higher temperatures the molecules are fluxional. Reaction with BuLi in pentane (**8**) or with NaH in THF (**9**) has been used to convert them into the corresponding cyclopentadienyl salt.

Preparation and Structure of the Organochromium Compounds. Most of the alkali-metal cyclopenten-

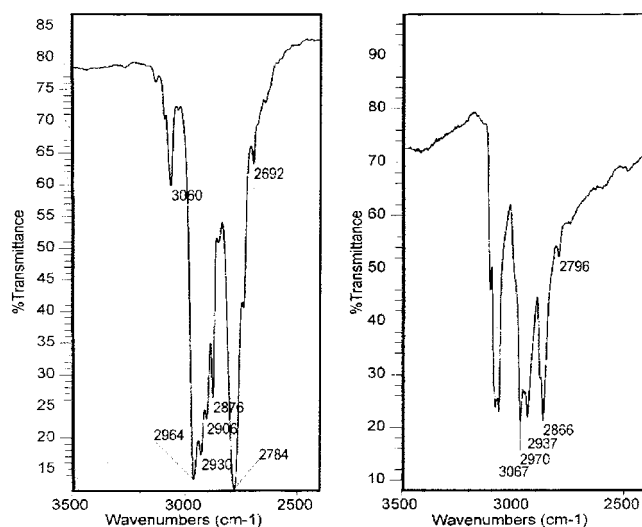
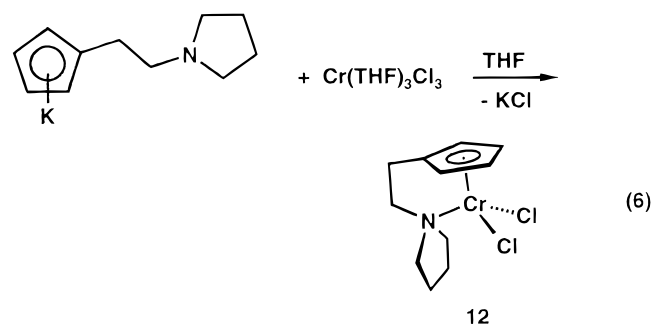


Figure 1. Changes in the stretching frequency pattern upon formation of (cyclo-C₄H₈NC₂H₄C₅H₄)CrCl₂ (**12**).

tadienyl derivatives described in the preceding section react with Cr(THF)₃Cl₃ in THF to give the expected amino-substituted cyclopentadienylchromium dichloride complexes (**10–24**) as blue, crystalline solids (e.g., eq 6), and the isolated compounds are listed in Table 1 along with their analytical data.



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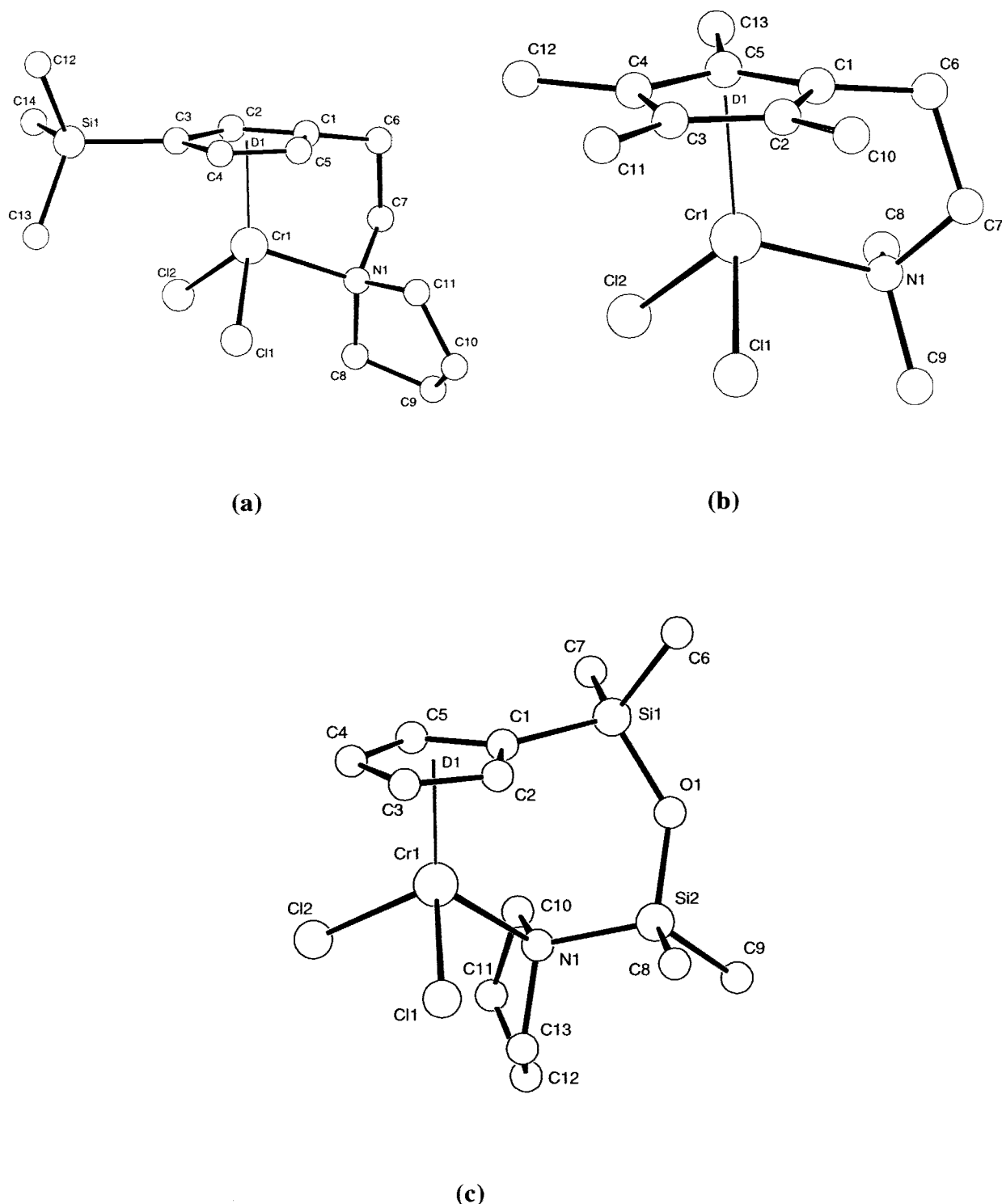


Figure 2. Molecular structures of (a) (1,3-cyclo- $\text{C}_4\text{H}_8\text{NC}_2\text{H}_4(\text{Me}_3\text{Si})\text{C}_5\text{H}_3$) CrCl_2 (**17**), (b) $(\text{Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{CrCl}_2$ (**21**), and (c) $(\text{cyclo-C}_4\text{H}_8\text{NSiMe}_2\text{OSiMe}_2\text{C}_5\text{H}_4)\text{CrCl}_2$ (**24**).

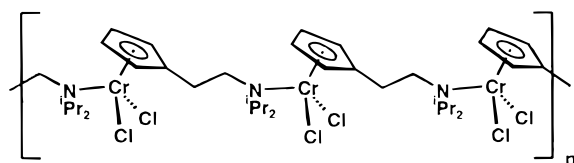
The compounds are paramagnetic, and coordination of the N-donor atom to the metal has been confirmed by X-ray crystallography for selected examples. Support for N-complexation comes from the absence of a strong absorption in the C–H stretching region of the IR spectra which is present in the cyclopentadiene precursor. This is illustrated in Figure 1 for the complex involving cyclo- $\text{C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{H}_4$ complexation and is associated with a shift in the absorption at 2784 cm^{-1} .

The crystal structures of (1,3-cyclo- $\text{C}_4\text{H}_8\text{NC}_2\text{H}_4(\text{Me}_3\text{Si})\text{C}_5\text{H}_3$) CrCl_2 (**17**), $(\text{Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{CrCl}_2$ (**21**), and

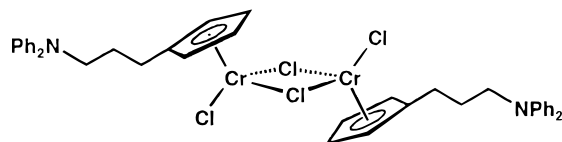
$(\text{cyclo-C}_4\text{H}_8\text{NSiMe}_2\text{OSiMe}_2\text{C}_5\text{H}_4)\text{CrCl}_2$ (**24**) have been determined by X-ray diffraction, and the molecular structures and selected bond parameters are shown in Figure 2 and Table 2. The crystals of both **21** and **24** contain two independent molecules which differ in the arrangement of the fragment bridging the ring and the N-donor atom, and the data shown are for only one molecule. In all three cases the Cr–N distance of 2.1–2.2 Å confirms that the N-donor atom is complexed to the metal and comparison of the data for **24** with those for $\text{Me}_3\text{SiOSiMe}_3$ (Si–O–Si = $148(3)^\circ$, Si–O = $1.631(3)$

Å)¹⁷ suggests that this occurs in a strain-free manner. The pyrrolidine rings in both **24** and **17** are displaced to one side and take up positions opposite the N-bonded SiMe₂ group in **24** and the CH₂ group in **17**. The ring methyl groups in **21** are displaced by an average of 0.10 Å out of the ring plane and away from the metal atom.

In a few cases, the reaction of the amino-substituted cyclopentadienyl salt with CrCl₃ did not lead to the expected product. Although the expected blue solution was obtained upon treating Cr(THF)₃Cl₃ with Prⁱ₂NC₂H₄C₅H₄K in THF, evaporation of the solution gave an insoluble, ill-defined residue which decomposed in the mass spectrometer. The IR spectrum of this material suggests that the amino group is complexed to the metal, while the insolubility suggests that this occurs in an intermolecular rather than an intramolecular manner to give oligomeric or polymeric material (**25**), thereby relieving ring strain associated with the relatively bulky Prⁱ₂N group.

**25**

The product of an analogous reaction with Ph₂NC₃H₆C₅H₄K is green instead of the expected blue. The mass spectrum indicates that this species is dinuclear, while the IR spectrum is similar to that of the substituted cyclopentadiene precursor, suggesting that the compound may well have the dimeric structure **26** with uncomplexed diphenylamino groups.

**26**

Similar behavior is observed in the reaction with Et₂NSiMe₂C₅H₄Li, but in this case the dimeric nature of the product (**27**) has been confirmed by an X-ray diffraction study (Figure 3). The bridging Cl atoms and the Cr atoms lie in the same plane with a nonbonding, intermetallic separation of 3.352(1) Å. Presumably, coordination of the amine to the metal is prevented by excessive strain.

Treatment of the CrCl₂ species with organomagnesium or -lithium reagents results, in most cases, in chloride exchange to give the corresponding dialkyl-Cr species as dark green, air-sensitive compounds which are stable at room temperature in solution or as pure compounds. The isolated compounds (**28–38**) are listed

Table 2. Selected Structural Data for the Amino-Substituted Cyclopentadienylchromium Dichloride Complexes **17, **21**, and **24**^a**

	17		21 ^b		24 ^b
Interatomic Distances (Å, esd)					
Cr–D1 ^c	1.866	Cr–D1	1.882	Cr–D1	1.903
Cr–N1	2.125(3)	Cr–N1	2.175(2)	Cr–N1	2.175(4)
Cr–Cl1	2.286(1)	Cr–Cl1	2.300(1)	Cr–Cl1	2.302(2)
Cr–Cl2	2.284(1)	Cr–Cl2	2.294(1)	Cr–Cl2	2.311(2)
C1–C6	1.498(5)	C1–C6	1.506(4)	C1–Si1	1.863(6)
C6–C7	1.534(5)	C6–C7	1.525(5)	Si1–O1	1.636(4)
C7–N1	1.493(4)	C7–N1	1.492(4)	O1–Si2	1.625(4)
C3–Si1	1.882(3)			Si2–N1	1.804(4)
Bond Angles (deg)					
Cl1–Cr–Cl2	100.6(1)	Cl1–Cr–Cl2	97.4(1)	Cl1–Cr–Cl2	98.3(1)
Cl1–Cr–N1	97.0(1)	Cl1–Cr–N1	98.2(1)	Cl1–Cr–N1	95.4(1)
Cl2–Cr–N1	95.7(1)	Cl2–Cr–N1	95.4(1)	Cl2–Cr–N1	93.4(1)
D1–Cr–Cl1	123.3	D1–Cr–Cl1	121.4	D1–Cr–Cl1	118.6
D1–Cr–N1	112.7	D1–Cr–N1	113.6	D1–Cr–N1	126.1
C1–C6–C7	109.5(3)	C1–C6–C7	109.7(2)	C1–Si1–O1	105.9(2)
C6–C7–N1	110.4(3)	C6–C7–N1	110.6(3)	Si1–O1–Si2	140.7(3)
C7–N1–Cr	105.1(2)	C7–N1–Cr	105.3(2)	O1–Si2–N1	106.8(2)
				Si2–N1–Cr	114.9(2)

^a Esd's are given in parentheses. ^b The data are for one of the two independent molecules present in the unit cell. ^c D1 corresponds to the centroid of the five-membered cyclopentadienyl ring.

in Table 3 along with their analytical data. In addition, we have reported earlier the metallacyclic compounds

(Me₂NC₂H₄C₅Me₄)CrCH₂(CH₂)_nCH₂ (*n* = 2, 4).⁵

The crystal structures of two examples, viz. (cyclo-C₄H₈NC₂H₄C₅Me₄)CrMe₂ (**37**) and (cyclo-C₄H₈NC₂H₄-fluorenyl)[H₈]CrMe₂ (**38**), have been determined, and the molecular structures and selected bonding parameters are shown in Figure 4 and Table 4. Although the π -bonded organic ligands are not identical, the structures can be usefully compared to those of the CrCl₂ compounds **17**, **21**, and **24** (Figure 2). The formation of the CrMe₂ compounds is apparently accompanied by a significant shortening (up to 0.05 Å) of the Cr–N bond, a decrease (up to 7°) in the X–Cr–X angle, and an increase (up to 0.05 Å) of the separation between the metal and C₅ ring (Cr–D1) with respect to the CrCl₂ species. The Cr–Me bond length does not significantly differ from that in other Cr(III)–alkyl complexes.¹⁸ The [H₈]fluorenyl ligand in **38** is essentially planar, with only C15 and C20 lying ca. 0.7 Å out of the C3/C5/C6 plane, and it has a mirror symmetry with respect to the D1/Cr1/C3 plane, whereas related complexes of Ti or Zr have C₂ symmetry.¹⁹

Attempts to prepare CrMe₂ species stabilized by the amino-substituted indenyl group were unsuccessful: treatment of (1-cyclo-C₄H₈NC₂H₄indenyl)CrCl₂ with MeMgCl in THF at –78 °C led to decomposition. The Me group is less electronegative than a Cl atom, and presumably its introduction favors the rearrangement of the η^5 -indenyl group to the less stable η^3 -form, which decomposes.

The product of the reaction between (Me₂NC₂H₄C₅H₄)CrCl₂ and allylmagnesium chloride is unusual in that it is orange (instead of dark green) and less stable than the other dialkylchromium species, decomposing in

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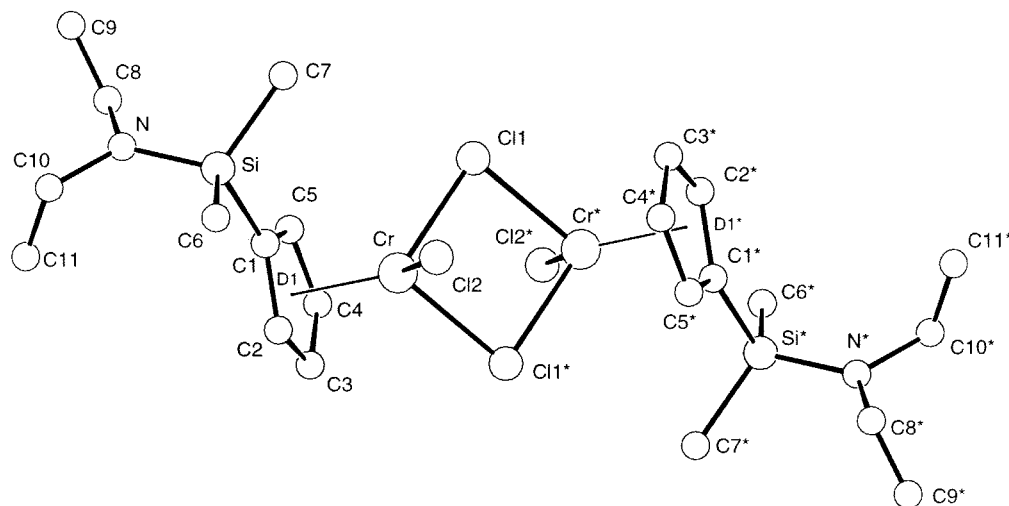


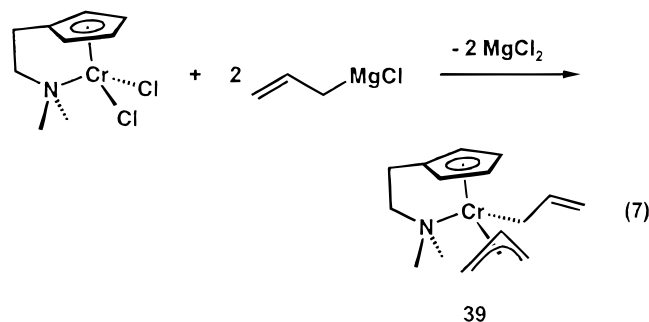
Figure 3. Molecular structure of $[(\text{Et}_2\text{NSiMe}_2\text{C}_5\text{H}_4)\text{CrCl}_2]_2$ (**27**). Selected bond distances (Å) and angles (deg) are as follows: Cr–D1 = 1.862, Cr–Cl1 = 2.365(1), Cr–Cl1* = 2.375(1), Cr–Cl2 = 2.268, Cr–Cr* = 3.352(1); D1–Cr–Cl1 = 121.3, D1–Cr–Cl2 = 126.3, Cl1–Cr–Cl1* = 91.4, Cl1–Cr–Cl2 = 95.1(1)°.

Table 3. Amino-Substituted Cyclopentadienylchromium Dialkyl and Related Compounds

compd	yield (%)	anal. found (calcd)			
		C	H	Cr	N
($\text{Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{H}_4$)CrMe ₂ (28)	84	60.4 (60.5)	9.2 (9.2)	23.9 (23.8)	6.5 (6.4)
($\text{Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{H}_4$)CrEt ₂ (29)	76	63.3 (63.4)	9.8 (9.8)	21.1 (21.1)	5.7 (5.7)
($\text{Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{H}_4$)CrPr ₂ (30)	71	65.8 (65.7)	10.2 (10.3)	18.9 (19.0)	5.0 (5.1)
($\text{Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{H}_4$)Cr(CH ₂ SiMe ₃) ₂ (31)	64	56.1 (56.3)	9.4 (10.0)	14.3 (14.3)	3.9 (3.9)
(cyclo-C ₄ H ₈ NC ₂ H ₄ C ₅ H ₄)CrMe ₂ (32)	46	64.1 (63.9)	9.0 (9.1)	21.2 (21.3)	5.7 (5.7)
(cyclo-C ₅ H ₁₀ NC ₂ H ₄ C ₅ H ₄)CrMe ₂ (33)	33	65.2 (65.1)	9.3 (9.4)	20.0 (20.1)	5.3 (5.4)
($\text{Me}_2\text{NC}_3\text{H}_6\text{C}_5\text{H}_4$)CrMe ₂ (34)	80	61.9 (62.0)	9.4 (9.6)	22.5 (22.4)	6.1 (6.0)
(1,3-cyclo-C ₄ H ₈ NC ₂ H ₄ (Me ₃ Si)C ₅ H ₃)CrMe ₂ (35)	60	60.7 (60.7)	9.7 (9.6)	16.3 (16.4)	4.4 (4.4) ^a
(cyclo-C ₄ H ₈ NC ₂ H ₄ C ₅ Me ₄)Cr(Me)Cl (36)	97	59.8 (59.9)	8.6 (8.5)	16.3 (16.2)	4.4 (4.4) ^b
(cyclo-C ₄ H ₈ NC ₂ H ₄ C ₅ Me ₄)CrMe ₂ (37)	86	68.1 (68.0)	10.1 (10.1)	17.3 (17.3)	4.6 (4.7)
(cyclo-C ₄ H ₈ NC ₂ H ₄ fluorenyl[H ₈])CrMe ₂ (38)	56	71.7 (71.6)	9.7 (9.7)	14.7 (14.8)	4.0 (4.0)

^a % Si: 8.9 (8.9). ^b % Cl: 11.0 (11.1).

solution at -20°C . The presence of absorptions in the IR spectrum at 1640 and 1491 cm^{-1} suggest that this compound has the 17-electron structure **39** and contains both η^3 - and η^1 -allyl groups (eq 7).



Decomposition is also observed upon reacting (cyclo-C₄H₈NC₂H₄C₅Me₄)CrCl₂ (**22**) with (C₄H₆)Mg(THF)₂. However, if the reaction is carried out using active-Mg/butadiene in the presence of PMe₃, an orange, pentane-soluble complex (**40**) is formed. A crystal structure determination (Figure 5) established that **40** contains a cis- η^4 -bonded butadiene molecule bonded in a prone manner and that a PMe₃ molecule has displaced the amino group from the metal atom. Related compounds have been prepared previously by reacting (Me₃C₅)Cr-(PR₃)Cl₂ with (C₄H₆)Mg(THF)₂.²⁰ The displacement of the "hard" N-donor atom by a "soft" P-donor ligand is

Table 4. Selected Structural Data for the Amino-Substituted Cyclopentadienylchromium Dimethyl Complexes **37 and **38**^a**

	37		38
Interatomic Distances (Å)			
Cr–D1	1.920	Cr–D1	1.919
Cr–N1	2.130(2)	Cr–N1	2.128(4)
Cr–C1	2.080(3)	Cr–C1	2.097(8)
Cr–C2	2.079(3)	Cr–C2	2.088(9)
C3–C8	1.509(3)	C3–C8	1.496(8)
C8–C9	1.529(4)	C8–C9	1.516(9)
C9–N1	1.500(3)	C9–N1	1.494(9)
Bond Angles (deg)			
C1–Cr–C2	96.5(1)	C1–Cr–C2	93.3(3)
C1–Cr–N1	97.0(1)	C1–Cr–N1	97.4(2)
C2–Cr–N1	97.9(1)	C2–Cr–N1	97.8(2)
D1–Cr–C1	122.0	D1–Cr–C1	123.3
D1–Cr–N1	113.5	D1–Cr–N1	114.3
C3–C8–C9	110.6(2)	C3–C8–C9	111.2(5)
C8–C9–N1	111.7(2)	C8–C9–N1	111.8(5)
C9–N1–Cr	105.1(1)	C9–N1–Cr	105.8(3)

^a Esd's are given in parentheses.

presumably a result of the formal reduction of the metal from Cr(III) to Cr(I).

As part of an attempt to obtain some insight into the mechanism of the MAO-activated, olefin polymerization catalysts (vide infra), we prepared monomethylchromium compounds as precursors to ionic compounds. We were, however, unable to prepare such species by reacting the appropriate CrCl₂ compounds with 1 equiv

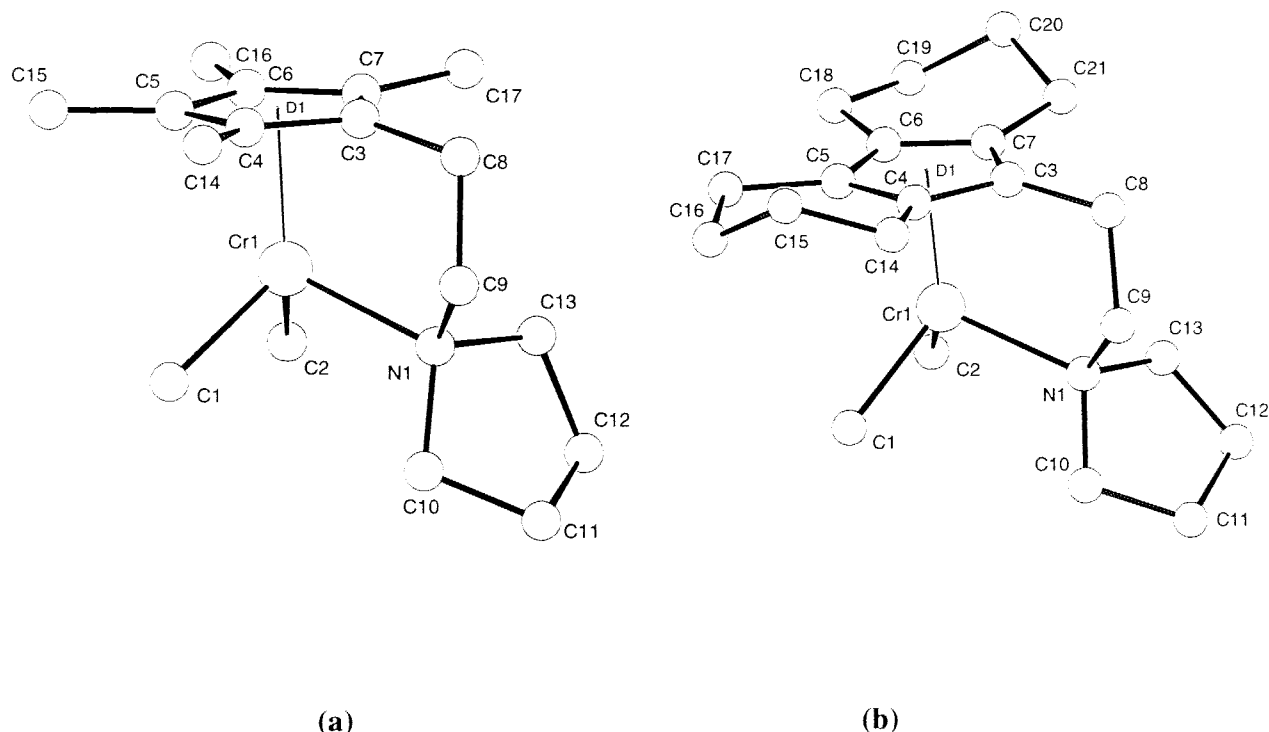
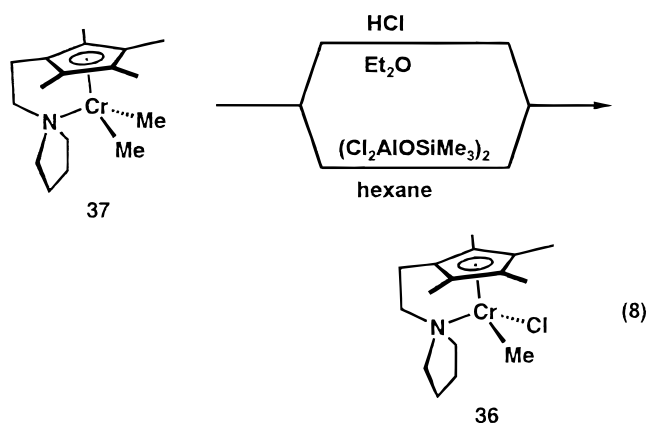


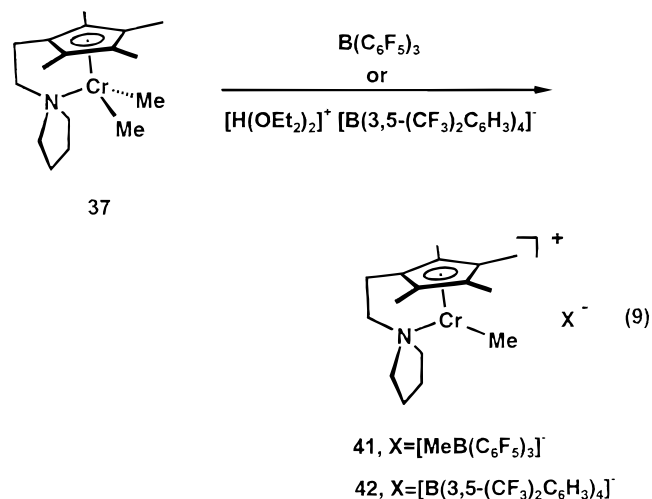
Figure 4. Molecular structures of (a) (cyclo- $\text{C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4$) CrMe_2 (**37**) and (b) (cyclo- $\text{C}_4\text{H}_8\text{NC}_2\text{H}_4$ -fluorenyl)[H_8] CrMe_2 (**38**).

of MeMgCl and had to resort to the partial protolysis of a CrMe_2 system. This was accomplished by treatment either with ethereal HCl or with $(\text{Cl}_2\text{AlOSiMe}_3)_2$ ²¹ in hexane, whereby the latter reagent is preferred since the reagent is more soluble in hexane than the product (eq 8).



Unfortunately, attempts to convert **36** into an ionic species by chloride extraction failed. However, such species could be prepared by reacting **37** with a Lewis

acid. The products (**41**, **42**) of the reaction with $\text{B}(\text{C}_6\text{F}_5)_3$ ²² or the oxonium acid $[\text{H}(\text{OEt}_2)]^+[\text{B}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_4]^-$ ²³ are dark violet solids which are insoluble in toluene and only slightly soluble in diethyl ether or methylene dichloride (eq 9). Although the elemental analyses for



41 and **42** support the suggested formulation, their inactivity for the catalytic polymerization of ethylene suggests that the compounds do not exist as separated ions, and because we have not been able to prepare crystals suitable for an X-ray diffraction study, their true nature remains unknown.

Violet compounds are also formed upon reacting **37** with $(\text{Me}_2\text{AlCl})_2$ or AlMe_3 . In contrast to **41** and **42**, the products **43** and **44** are soluble in toluene and saturated hydrocarbons and these are assumed to be nonionic and

(24) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 11664.

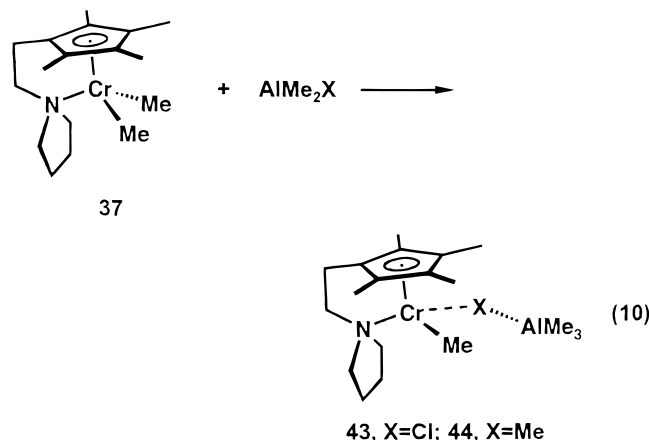
(25) De Kimpe, N.; Verhé, R.; De Buyck, L.; Moëns, L.; Schamp, N. *Synthesis* **1982**, 43.

(26) van der Zeijden, A. A. H.; Mattheis, C.; Fröhlich, R. *Organometallics* **1997**, *16*, 2651.

(27) Qian, C.; Wang, B.; Deng, D.; Sun, J.; Hahn, F. E.; Chen, J.; Zheng, P. *J. Chem. Soc., Dalton Trans.* **1996**, 955.

(28) Draganjac, M.; Ruffing, C. J.; Rauchfuss, T. B. *Organometallics* **1985**, *4*, 1909. Amarasekera, J.; Rauchfuss, T. B. *Inorg. Chem.* **1989**, *28*, 3875.

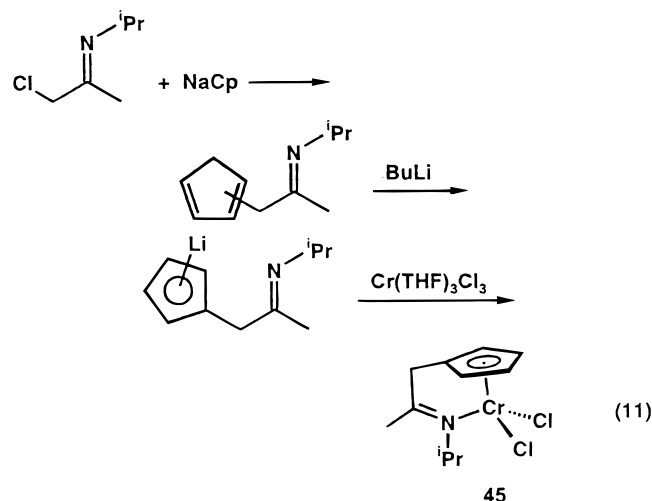
to have structures having groups bridging the two metal atoms (eq 10). A similar reaction is observed between



AlMe_3 and $(\text{cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{CrCl}_2$ (22).

Organochromium Compounds Containing Related Donor Ligands. In addition to the amino-substituted cyclopentadienyl ligands presented above and the phosphino-substituted cyclopentadienyl ligands which will be discussed in a later paper, we have prepared, for comparison purposes, a few related organochromium compounds containing an imine or O-, S-, and C-donor ligands.

Our interest in an imine-substituted cyclopentadienylchromium catalyst stems from the research on the MAO-activated diimine complexes of the late transition metals²⁴ and on the geometrically related amido-substituted cyclopentadienyltitanium(IV) complexes.³ The synthesis of the Pr^i -substituted species (45) is shown in eq 11.²⁵ The blue, air-stable compound 45



dissolves readily in methylene dichloride but is only slightly soluble in toluene. The mass spectrum shows a parent ion, and fragmentation occurs with loss of a Cl atom and the Pr^i group. Complexation of the imine to the metal is accompanied by a shift in the C–N stretching frequency of 45 cm^{-1} to 1603 cm^{-1} . Surprisingly, attempts to convert the compound into the related CrMe_2 species by reaction with MeMgCl were unsuccessful.

An obvious extension is to involve ligands having O or S as the donor atom. Whereas transition-metal

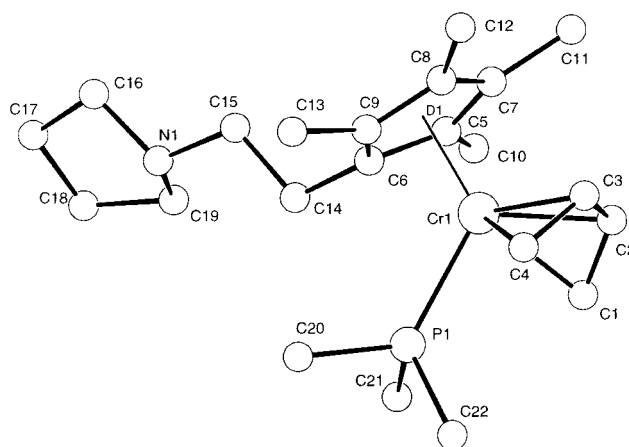
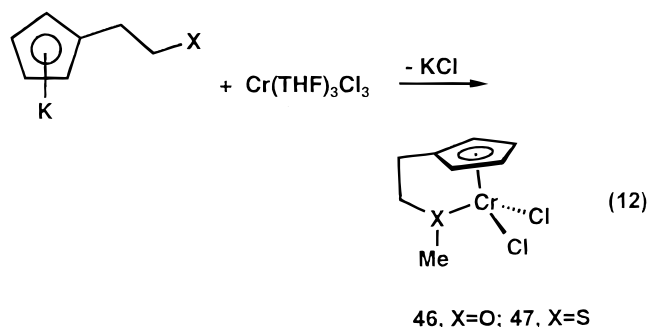


Figure 5. Molecular structure of $(\text{cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)(\eta^4\text{-C}_4\text{H}_6)\text{CrPMe}_3$ (40). Selected bond distances (Å) and angles (deg) are as follows: $\text{Cr1-D1} = 1.865$, $\text{Cr1-P1} = 2.336(1)$, $\text{Cr1-C1} = 2.166(5)$, $\text{Cr1-C2} = 2.079(4)$, $\text{C1-C2} = 1.394(6)$, $\text{C2-C3} = 1.394(6)$, $\text{C3-C4} = 1.433$; $\text{D1-Cr1-P1} = 119.2$, $\text{D1-Cr1-C1} = 137.2$, $\text{D1-Cr1-C2} = 120.8$, $\text{C1-C2-C3} = 121.6(4)$, $\text{C2-C3-C4} = 120.7(3)^\circ$.

compounds containing alkoxy-substituted cyclopentadienyl groups are well-known,^{26,27} examples involving a thio group are far less common.²⁸ Treatment of CrCl_3 with both $\text{MeOC}_2\text{H}_4\text{C}_5\text{H}_4\text{K}$ and $\text{MeSC}_2\text{H}_4\text{C}_5\text{H}_4\text{K}$ led to the expected organochromium compounds (eq 12). Struc-

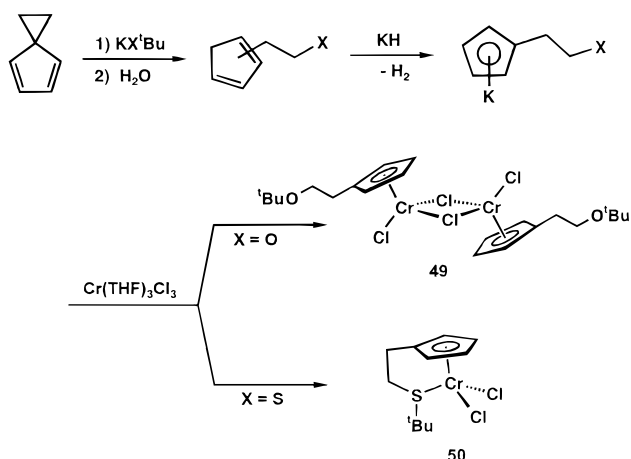


tural characterization of the methoxy compound 46 follows from the mass spectrum (M^+) and the complexation shift of the C–O stretching frequencies from 1119 cm^{-1} in the parent cyclopentadiene derivative to 1039 cm^{-1} in the chromium complex. The methylthio derivative 47 also shows a parent ion in the mass spectrum. Complexation of the S-donor atom to the metal is suggested by the stability in air, but no obvious support can be found in the IR spectrum. The tetramethylcyclopentadienyl analogue of 47, viz. $(\text{MeSC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{-CrCl}_2$ (48), has been prepared analogously by reacting the lithium salt of the organic ligand. The compound is also blue and air-stable, and a parent ion is present in the mass spectrum.

Related ligands containing the *tert*-butoxy and *tert*-butylthio groups have been prepared by reacting spiro-[4.2]hepta-4,6-diene²⁹ with KOtBu^t or KSbt^t in refluxing THF. The structure of the product of the further reaction with CrCl_3 depends, however, upon the nature of the donor atom (Scheme 2). The mass spectra of the product confirm that the *tert*-butylthio derivative (50) is mononuclear whereas the *tert*-butoxy derivative (49) is bi-

(29) Wilcox, C. F.; Craig, R. R. *J. Am. Chem. Soc.* **1961**, *83*, 3866.

Scheme 2



nuclear, while the IR spectrum indicates that the *tert*-butoxy group is not complexed to the metal atom.

We next turned our attention to systems containing C-donor ligands. Whereas numerous chromium compounds containing Fischer carbene ligands have been reported, examples involving the heterocyclic imidazol-2-ylidene ligand were unknown at the time we started our investigations;³⁰ Arduengo³¹ and Herrmann³² had prepared a series of transition-metal complexes containing this ligand and have shown that the metal–donor atom bond is particularly strong. We have concentrated on the 1,3,4,5-tetramethylimidazol-2-ylidene ligand, and the results are summarized in Scheme 3. The carbene ligand was prepared by reacting 1,3,4,5-tetramethylimidazole-2-thione with potassium.³³ Reaction with $\text{CpCr}(\text{THF})\text{Cl}_2$ occurs with displacement of the THF molecule to give **51** as a violet, air-stable compound which is only slightly soluble in THF and precipitates. Subsequent treatment of **51** with excess MeMgCl gives the CrMe_2 derivative **52** in high yield. The product of the analogous reaction with $\text{Cp}^*\text{Cr}(\text{THF})\text{Cl}_2$ is the blue, THF-soluble compound **53**. The mass spectral results indicate that the product of the further reaction with an excess of either MeMgCl or MeLi is a mixture of monomethyl- and dimethyl–Cr species which could not be separated. Characteristic for these chromium–carbene compounds is the presence of an absorption at ca. 1660 cm^{-1} in the infrared spectrum, which is assigned to a C=C stretching frequency of the carbene ligand.

Catalytic Polymerization and Oligomerization of Alkenes. The preparative organochromium chemistry described in detail in the preceding sections was undertaken in part to provide precursors for an investigation of the catalytic polymerization of ethylene in the presence of methylalumoxane (MAO).^{5–7} The product is in most cases a highly linear polyethylene having a melting point (DSC) in the range $128\text{--}132\text{ }^\circ\text{C}$, a crystallinity (IR) of 70–75%, and a molecular weight of $1\text{--}3 \times 10^6$. Our main objective was, however, to

compare the activity of the various organochromium compounds, and we have not investigated the morphology of the polymer in detail.

In view of the high activity of many of the species, the isothermal reaction conditions necessary for a reliable comparison could only be obtained by decreasing the concentration of the Cr component to homeopathic levels, and the values obtained probably represent lower limits. Selected results are shown in Table 5 for reactions carried out with a Cr:MAO ratio of 1:100. Two trends are clearly established in the table: the activity increases considerably upon either substituting the ring H atoms with alkyl groups or the Cl atoms with Me groups. The catalyst $(\text{cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{CrMe}_2$ (**37**)–MAO (Cr:MAO = 1:100) has the remarkable activity of 10 500 kg of PE/(mol of Cr) h at $21\text{ }^\circ\text{C}$ and 2 atm.

The activities of $(\text{Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{H}_4)\text{CrCl}_2$ (**11**), $(\text{Me}_2\text{NC}_3\text{H}_6\text{C}_5\text{H}_4)\text{CrCl}_2$ (**14**), and $(\text{cyclo-C}_4\text{H}_8\text{NSiMe}_2\text{OSiMe}_2\text{C}_5\text{H}_4)\text{CrCl}_2$ (**24**) under the standard conditions are all similar, suggesting that an extension of the chain between the N atom and the ring and the type of linkage have only a minor influence. In contrast, the lower activity (ca. 200 kg of PE/(mol of Cr) h) observed for $[(\text{Et}_2\text{NSiMe}_2\text{C}_5\text{H}_4)\text{CrCl}_2]_2$ (**27**), in which the N atom is not bonded to the Cr atom, suggest that interaction of the donor atom with the metal is probably essential for high activity.

It has already been shown that the activity of the *ansa*-zirconocene–MAO catalysts increases dramatically upon increasing the Zr:Al ratio and that frequently maximum activity is obtained only in the presence of a very large excess of MAO.³⁴ We have also studied the effect of varying the Cr:Al ratio upon the $(\text{cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{CrCl}_2$ (**22**)–catalyzed reaction (Table 6). The results indicate that a ratio of at least 1:100 is necessary while a 4-fold increase in activity is observed up to 1:1000 and that higher concentrations have little effect.

Since any industrial application of these systems would presumably involve more robust reaction conditions, it is noteworthy that the $(\text{cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{CrCl}_2$ (**22**)–MAO catalyst remains highly active at $80\text{ }^\circ\text{C}$ (activity 50 750 kg of PE/(mol of Cr) h); toluene, Al:Cr = 500:1) and, furthermore, the rate of polymerization remained constant for an extended period. Under these conditions, the polyethylene formed remains dissolved and precipitates upon cooling the toluene solution.

The Cr-based catalysts are far less active for the polymerization of alkenes other than ethylene. Both propene and 1-hexene are polymerized by $(\text{cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{CrMe}_2$ (**37**)–MAO, but the activity is low (200–300 kg of polymer/(mol of Cr) h) and the catalyst is quickly deactivated. In both cases an atactic polymer is formed. More promising results are obtained for the copolymerization of 1-alkenes with ethylene. In contrast to propene (which does not copolymerize), ethylene and 1-hexene react together in the presence of $(\text{cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{CrMe}_2$ (**37**)–MAO (Cr:Al = 1:100, $T = 21\text{ }^\circ\text{C}$) in neat 1-hexene as solvent to give a low-molecular-weight elastomer (activity 40 000 kg of polymer/(mol of Cr) h) which is soluble in chloroform or toluene at

(30) While our investigations were in progress, three examples involving the 1,3-dimesitylimidazol-2-ylidene ligand were reported: Voges, M. H.; Rømming, C.; Tilset, M. *Organometallics* **1999**, *18*, 529. See also: Abernethy, C. D.; Clyburne, J. A. C.; Cowley, A. H.; Jones, R. A. *J. Am. Chem. Soc.* **1999**, *121*, 2329.

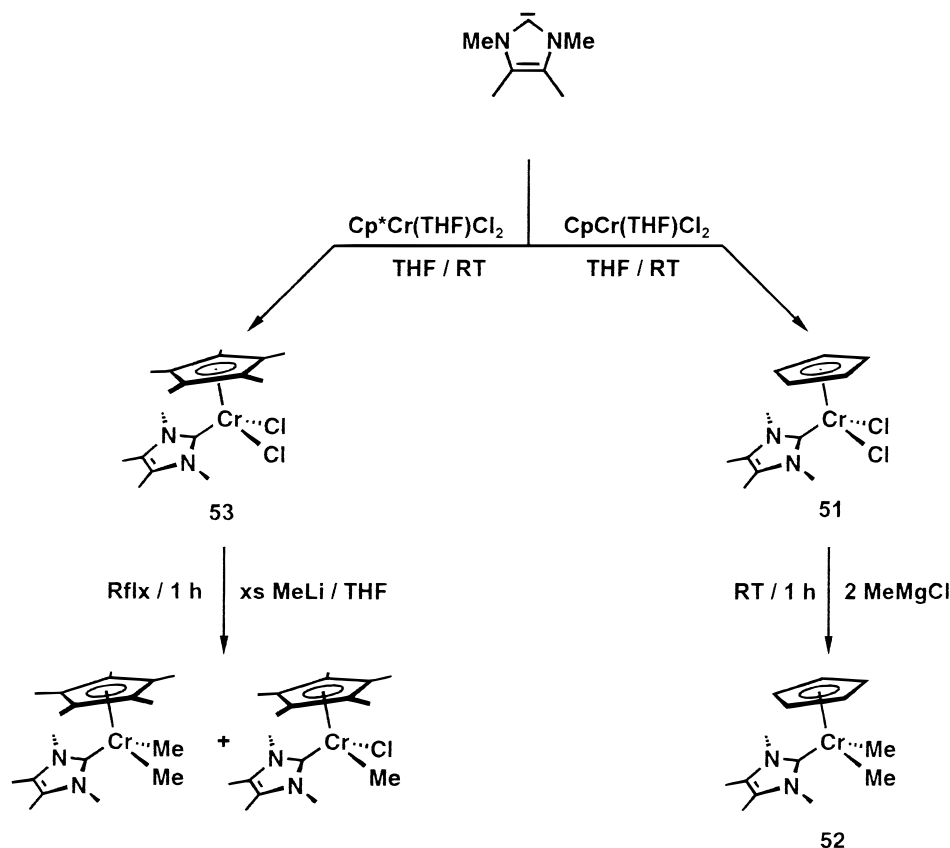
(31) Arduengo, A. J.; Harlow, R. L.; Kline, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 361.

(32) Herrmann, W. A.; Köcher, C. *Angew. Chem.* **1997**, *109*, 2256.

(33) Kuhn, N.; Kratz, T. *Synthesis* **1993**, 561.

(34) Herfert, N.; Fink, G. *Makromol. Chem.* **1992**, *193*, 1359.

Scheme 3

Table 5. Polymerization of Ethylene under Isothermal Conditions^a

compd	amt of Cr (μmol)	$T/\Delta T$ ($^\circ\text{C}$)	amt of PE (g)	activity (kg of PE/ (mol of Cr) h)	$10^{-6}M_w$	M_w/M_n	T_M ($^\circ\text{C}$)	cryst (%)
($\text{Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{H}_4$)CrCl ₂ (11)	5.19	21/2	0.66	1660	2.18	4.05	127	67
(cyclo- $\text{C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{H}_4$)CrCl ₂ (12)	11.22	21/3	1.37	1730	0.90	13.47	127	71
(cyclo- $\text{C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4$)CrCl ₂ (22)	1.71	21/3	0.86	7170	1.91	2.11	131	73
(cyclo- $\text{C}_4\text{H}_8\text{NC}_2\text{H}_4$ -fluorenyl[H_8])CrCl ₂ (23)	5.95	21/4	1.48	3640	0.84	2.73	127	68
($\text{Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{H}_4$)CrMe ₂ (28)	5.27	21/4	1.87	4630	2.50	3.15	129	69
(cyclo- $\text{C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4$)CrMe ₂ (37)	1.05	21/2	0.77	10480	3.14	1.58	129	74
(cyclo- $\text{C}_4\text{H}_8\text{NC}_2\text{H}_4$ -fluorenyl[H_8])CrMe ₂ (38)	1.23	21/4	1.35	10680	1.89	1.56	133	73

^a Conditions: solvent, toluene (250 mL); P_{ethylene} , 2 atm; Cr:MAO = 1:100; t = 4 min.Table 6. (cyclo- $\text{C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4$)CrCl₂ (**22**)–MAO Catalyzed Polymerization of Ethylene^a

Cr:MAO	amt of Cr (μmol)	$T/\Delta T$ ($^\circ\text{C}$)	amt of PE (g)	activity (kg of PE/ (mol of Cr) h)
1:50	3.64	21.0/0	0	0
1:100	3.19	21.0/1.7	1.11	4 550
1:200	2.73	21.0/2.8	1.78	8 860
1:500	0.91	21.0/2.3	1.17	18 320
1:1000	0.68	21.0/2.8	1.15	25 370
1:5000	0.57	21.0/2.8	1.19	28 460
1:10000	0.57	21.0/2.9	1.39	29 540

^a Conditions: solvent, toluene (250 mL); P_{ethylene} , 2 atm; t = 4 min.

room temperature. The ^{13}C NMR spectrum indicates that ca. 15% 1-hexene has been incorporated in a random manner into the polyethylene chain. If the reaction is carried out in 80% toluene/20% 1-hexene as solvent, an insoluble polymer is formed at a reduced rate (6900 kg of polymer/(mol of Cr) h). Although this material has not been investigated further, the low melting point (112 $^\circ\text{C}$) indicates that some 1-hexene incorporation has occurred. Similar behavior in the copolymerization of 1-hexene and ethylene is observed

with (cyclo- $\text{C}_4\text{H}_8\text{NC}_2\text{H}_4$ fluorenyl[H_8])CrMe₂ (**38**)–MAO. This system can also copolymerize norbornene with ethylene under mild conditions (21 $^\circ\text{C}$; 2 bar of ethylene; Cr:Al = 1:3800). The product of the reaction when it is carried out in 74% toluene/26% norbornene as solvent is a low-melting-point amorphous solid. Its ^{13}C NMR spectrum indicates that ca. 25% norbornene has been incorporated in an exo manner.³⁵

The imino-substituted cyclopentadienylchromium complex ($\text{Pr}^i\text{N}=\text{CMeCH}_2\text{C}_5\text{H}_4$)CrCl₂ (**45**) in the presence of MAO gives a system having an activity similar to that of the ($\text{Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{H}_4$)CrCl₂ (**11**)–MAO system for the polymerization of ethylene. The methylthio-substituted system ($\text{MeSC}_2\text{H}_4\text{C}_5\text{H}_4$)CrCl₂ (**47**)–MAO has a moderate activity (activity 4025 kg of polymer/(mol of Cr) h; P = 2 atm; $T/\Delta T$ = 27/36 $^\circ\text{C}$; Cr:Al = 1:100) to give a product which consists of a 1:1 mixture of polyethylene and oligomers (C_4 – C_{36} ; GC). The corresponding methoxy-substituted compound ($\text{MeOC}_2\text{H}_4\text{C}_5\text{H}_4$)CrCl₂ (**46**) reacts with MAO in the absence of ethylene to give an

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insoluble product which is not catalytically active. However, if the compound is treated with MAO in the presence of ethylene, normal polymerization behavior is observed (activity 2870 kg of PE/(mol of Cr) h); $P = 2$ atm; $T/\Delta T = 26/34$ °C) to give a high-molecular-weight polyethylene (MW 4.7×10^6). The behavior of the Cr-carbene complex CpCr(tetramethylimidazol-2-ylidene)-Cl₂ (**51**) was disappointing: the low solubility necessitated the use of a toluene/CH₂Cl₂ solvent mixture, and the activity, after treatment with MAO, was low. The polymer formed, however, was unusual in that it is highly branched and melts in two steps (89/120 °C), while the GPC measurement indicates the presence of low- and high-molecular-weight fractions, suggesting that more than one active species is involved.

Mechanistic Considerations. Because we have no direct evidence of mechanistic relevance—the ionic species [(cyclo-C₄H₈NC₂H₄C₅Me₄)CrMe]⁺X[−] (X = B(C₆H₃(CF₃)₂-3,5)₄ (**42**), MeB(C₆F₅)₃ (**41**)) were, unfortunately, inactive—we can only assume that the Cr-catalyzed reaction occurs in a manner analogous to that suggested for the *ansa*-zirconocene–MAO systems and involves ethylene complexation to a cationic Cr–Me species followed by multiple insertion with agostic-H–Cr stabilization with chain termination proceeding through β -H-transfer from the growing alkyl chain to a complexed ethylene molecule. Details of a theoretical treatment which support this concept are presented in a separate publication.³⁶

We have also no original contribution to make on the role of the MAO in the chromium-catalyzed reactions and assume that, as previously suggested,³⁷ the active component is AlMe₃, which is present at a level of 10–20% in MAO and which acts both as an alkylating agent and as a Lewis acid to produce the active cationic Cr–Me species. One or more of the components in the oligomethylalumoxane may well encapsulate the resulting AlMe₄[−] or AlMe₃Cl[−] anion and act as a spacer to separate the ions.

In keeping with this suggestion is the observation that, for the (cyclo-C₄H₈NC₂H₄C₅Me₄)CrCl₂ (**22**)–MAO system, the addition of 20 equiv of AlMe₃ to 100 equiv of MAO results in a significant increase in activity (Cr:MAO:AlMe₃ = 1:100:0, activity 4550 kg PE/(mol of Cr) h); Cr:MAO:AlMe₃ = 1:100:20, activity 7730 kg of PE/(mol of Cr) h), while 80% of the aluminum in MAO can be replaced by AlMe₃ without a significant decrease in activity.

The significantly higher activity of the dimethylchromium compounds compared to the dichlorochromium compounds (Table 5) is perhaps a consequence of the relatively low Cr:MAO concentration (1:100) used in the standard reactions and suggests that anions such as AlMe₄[−] and AlMe₃Cl[−] might be involved whereby the separation from the chromium–methyl cation of the former might be expected to be more complete. At higher MAO concentrations complete alkylation of the chromium will occur, and as expected, the difference becomes less significant. The increase in activity upon

methyl substitution of the five-membered ring (Table 5) could have a steric origin: the separation of the cation and anion (**54**) is enhanced, and hence, the reacting ethylene molecule has more facile access to the metal. The fluorenyl-substituted system (Table 5) is less congested, and as expected the activity is lower. In addition, methyl substitution of the five-membered ring will strengthen the bond between the ring and the metal atom, which may be expected to facilitate the transfer of an Me or Cl group to the aluminum.

Experimental Section

All experiments and manipulations were carried out under argon. The organochromium compounds have been characterized by a combination of infrared spectroscopy (Nicolet 7199 and 750 FI/IR), mass spectroscopy (Finnigan MAT 8200) and elemental analyses as well as by crystal structure determinations of selected examples. (η^1 : η^5 -Me₂NC₂H₄C₅H₄)CrCl₂ and (η^1 : η^5 -Me₂NC₃H₆C₅H₄)CrCl₂ were prepared according to the literature.¹¹ The substituted cyclopentadiene derivative were prepared by modification of published procedures¹⁰ and typical examples are described below.

cyclo-C₄H₈NC₂H₄C₅H₅ (1d**).** A solution of NaC₅H₅(THF)_{0.27} (7.04 g, 65.5 mmol) in THF (200 mL) was cooled to −10 °C and solid (2-chloroethyl)pyrrolidine hydrochloride (5.06 g, 29.75 mmol) added slowly. The reaction mixture was stirred for 16 h at room temperature and evaporated to dryness. The red-brown residue was then treated with pentane (200 mL) and distilled water (100 mL). The organic material was extracted with pentane and the combined extract dried with MgSO₄ and evaporated to dryness to give the product as a yellow liquid. Yield: 4.29 g (88%). Anal. Calcd for C₁₁H₁₇N: C, 80.9; H, 10.5; N, 8.6. Found: C, 80.5; H, 10.4; N, 8.7. IR (KBr): ν 2964 s, 2784 s cm^{−1}. MS: *m/e* 163 (M⁺), 84, 42. ¹H NMR (CDCl₃): δ 6.43/6.25/6.19/6.04 (=CH), 2.94/2.90 (CH₂), 2.64 (C₂H₄), 2.54/1.79 (NC₂H₄). ¹³C NMR (CDCl₃): δ 147.4/145.0, 134.5/133.5/132.3/130.5/126.7/126.3 (=CH), 56.4/55.8/54.1/54.0 (NCH₂), 43.1/41.1/30.4/29.6/23.3 (CH₂).

Treatment of this compound with KH or NaH in THF or BuLi in pentane or diethyl ether led to formation of the corresponding cyclopentadienyl derivative.

cyclo-C₄H₈NC₃H₆C₅H₅ (**2b**) and cyclo-C₅H₁₀NC₃H₆C₅H₅ (**2c**) were prepared similarly.

1-(cyclo-C₄H₈NC₂H₄)C₉H₇ (4b**)** was prepared as a yellowish liquid by adding (2-chloroethyl)pyrrolidine hydrochloride (9.56 g, 56 mmol) portionwise to a solution of lithium indenide (20.76 g, 170 mmol) in THF (200 mL) at −10 °C. The reaction mixture was stirred at room temperature for 16 h and at 50 °C for 2 h and evaporated to dryness under high vacuum. The red-brown residue was taken up in pentane (200 mL) and treated with distilled water (100 mL). The aqueous phase was washed with pentane (2 × 100 mL) and the combined organic phases dried with MgSO₄ and evaporated under oil-pump vacuum. The resulting yellowish oil was heated at 50 °C under a high vacuum for 3 h to remove traces of indene. Yield: 11.2 g (94%). Anal. Calcd for C₁₅H₁₉N: C, 84.5; H, 9.0; N, 6.6. Found: C, 84.3; H, 9.1; N, 6.6. MS: *m/e* 213 (M⁺), 128, 115. IR (liquid): ν 2962 s, 2783 s, 769 s cm^{−1}. ¹H NMR (CDCl₃): δ 7.39/7.27/7.16/6.20/3.28 (indene), 2.77/2.57/1.79 (CH₂). ¹³C NMR (CDCl₃): δ 145.1/144.1/142.4/128.0/126.1/124.3/123.5/118.7/37.6 (indene), 55.0/54.1/27.4/23.3 (CH₂).

The compound was converted into the cyclopentadienyl derivative 1-(cyclo-C₄H₈NC₂H₄)C₉H₆K by treatment with KH in THF at 50 °C.

Et₂NSiMe₂C₅H₅ (8**)** was prepared as a yellow oil by adding a solution of Et₂NSiMe₂Cl¹⁶ (27.68 g, 0.17 mol) in pentane (300 mL) to NaC₅H₅(THF)_{0.27} (19.76 g, 0.18 mol) in THF (100 mL) at −30 °C over 4 h. The reaction mixture was stirred for a further 4 h at room temperature and evaporated to dryness.

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The residue was dissolved in pentane (150 mL), the solution filtered, and the solvent removed under oil-pump vacuum. Yield: 27.1 g (83%). IR (liquid): ν 2964 s, 1204 s, 1173 s, 1029 s, 1251 s, 805 s cm^{-1} . ^1H NMR (CDCl_3 , -30°C): δ 6.63/6.53 (t, =CH), 3.59 (s, CH), 2.81 (q, NCH_2), 0.98 (t, Me), -0.06 (s, Me_2Si). ^{13}C NMR (CDCl_3 , -70°C): δ 132.8/129.5 (=CH), 55.8 (CH), 38.9 (NCH_2), 15.2 (Me), -3.9 (SiMe_2).

Treatment with BuLi in pentane led to the formation of the cyclopentadienyl derivative $\text{Et}_2\text{NSiMe}_2\text{C}_5\text{H}_4\text{Li}$.

cyclo- $\text{C}_4\text{H}_8\text{SiMe}_2\text{OSiMe}_2\text{C}_5\text{H}_5$ (9) was prepared as a pale yellow oil by adding a solution of $\text{NaC}_5\text{H}_5(\text{THF})_{0.27}$ (10.9 g, 101.2 mmol) in THF (70 mL) dropwise to a solution of cyclo- $\text{C}_4\text{H}_8\text{SiMe}_2\text{OSiMe}_2\text{Cl}$ (23.3 g, 98.0 mmol) in pentane (250 mL) at -30°C . The reaction mixture was stirred at room temperature for 4 h and the solvent removed under oil-pump vacuum. The residue was taken up in pentane (100 mL), the solution filtered, and the solvent distilled off. Yield: 23.1 g (88%). IR (liquid): ν 2960 s, 1256 s, 795 s, 1058 s cm^{-1} . MS: m/e 267 (M^+), 252, 202. ^1H NMR (CDCl_3): δ 6.62/6.51 (=CH), 3.50 (CH), 2.99 (NCH_2), 1.71 (CH_2), 0.12/ -0.08 (Me_2Si). ^{13}C NMR (CD_2Cl_2): δ 132.8/130.7 (=CH), 54.6 (CH), 46.4 (NCH_2), 27.0 (CH_2), $-1.0/-1.4$ (SiMe_2).

Treatment with NaH in THF led to the formation of the cyclopentadienyl derivative cyclo- $\text{C}_4\text{H}_8\text{NSiMe}_2\text{OSiMe}_2\text{C}_5\text{H}_4\text{Na}$.

cyclo- $\text{C}_4\text{H}_8\text{SiMe}_2\text{OSiMe}_2\text{Cl}$ was prepared as a colorless oil by adding a solution of pyrrolidine (36 mL, 0.43 mol) in pentane (70 mL) to a solution of $\text{ClSiMe}_2\text{OSiMe}_2\text{Cl}$ (43.7 g, 0.22 mol) in pentane at -50°C . The reaction mixture was stirred for 4 h at room temperature, filtered and the solvent removed under oil-pump vacuum. Yield: 48.2 g (94%). IR (liquid): ν 2964 s, 1204 s, 1173 s, 1029 s, 1251 s, 805 s cm^{-1} . ^1H NMR (CDCl_3 , -30°C): δ 6.63/6.53 (t, =CH), 3.59 (s, CH), 2.81 (q, NCH_2), 0.98 (t, Me), -0.06 (s, Me_2Si). ^{13}C NMR (CDCl_3 , -70°C): δ 132.8/129.5 (=CH), 55.8 (CH), 38.9 (NCH_2), 15.2 (Me), -3.9 (SiMe_2).

$\text{Pr}^i\text{N}=\text{C}(\text{Me})\text{CH}_2\text{C}_5\text{H}_5$ was prepared as a red-brown, sensitive liquid by adding a solution of $\text{NaC}_5\text{H}_5(\text{THF})_{0.27}$ in THF (100 mL) to a solution of $\text{Pr}^i\text{N}=\text{C}(\text{Me})\text{CH}_2\text{Cl}$ (14.7 g, 0.11 mol)²⁵ in diethyl ether (100 mL) at -10°C . The reaction mixture was stirred at room temperature for 12 h. The solvent was removed under oil-pump vacuum and the red-brown residue taken up in pentane (200 mL) and treated with distilled water (100 mL). The aqueous phase was separated and extracted with pentane (2×100 mL) and the combined pentane solution dried with MgSO_4 and evaporated under an oil-pump vacuum. Yield: 15.2 g (82%). Anal. Calcd for $\text{C}_{11}\text{H}_{17}\text{N}$: C, 80.9; H, 10.5; N, 8.6. Found: C, 78.6; H, 10.7; N, 8.9. MS: m/e 163 (M^+), 148, 120, 106. IR (liquid): ν 2966 s, 1658 s cm^{-1} . ^1H NMR (CDCl_3 , -30°C): δ 6.44/6.32–6.08 (=CH), 3.73/3.60 (CMe_2), 3.33/3.29 ($\text{CH}_2\text{C}=\text{C}$), 3.00/2.88 (CH_2), 1.80 ($\text{MeC}=\text{C}$), 1.17 (CH).

$\text{MeSeC}_2\text{H}_4\text{C}_5\text{H}_5$ was prepared by adding a solution of $\text{NaC}_5\text{H}_5(\text{THF})_{0.27}$ (12.2 g, 108 mmol) in THF (100 mL) to 2-chloroethyl methyl sulfide (11.9 g, 108 mmol) in pentane (80 mL) at room temperature. The reaction mixture was stirred for 12 h and evaporated to dryness. The residue was taken up in pentane (100 mL), and water (100 mL) was added. The aqueous phase was extracted with pentane (2×50 mL) and the combined extract dried over MgSO_4 and evaporated to dryness to give the compound as a yellowish oil. Yield: 12.8 g (84%). ^1H NMR (CDCl_3): δ 6.45–6.40/6.26/6.21/6.06 (=CH), 2.95/2.90 (CH_2), 2.68 (C_2H_4), 2.11/2.10 (Me). ^{13}C NMR (CDCl_3): δ 147.2/145.0/134.0/133.6/132.1/130.7/127.2/126.6 (=CH), 43.0/41.0 (CH_2), 34.0/33.2 (SCH_2), 30.3/29.7 (CH_2), 15.3/15.2 (Me).

$\text{Bu}^i\text{SC}_2\text{H}_4\text{C}_5\text{H}_5$ was prepared by adding spiro[4.2]heptane-4,6-diene (30.3 g, 0.33 mol) to a suspension of NaSBu^i (33.2 g, 0.3 mol) in THF (250 mL) and heating under reflux for 5 days. The resulting red solution was evaporated to dryness and the product treated with pentane (250 mL) and distilled water (250 mL). The aqueous phase was extracted with pentane (2×50 mL) and the combined extract dried over MgSO_4 and evaporated to dryness under a vacuum. The resulting yellow oil was

distilled under an oil-pump vacuum at 62°C . Yield: 33.9 g (62%). IR (liquid): ν 1522 w, 1472 m, 1458 m, 1363 m, 677 s cm^{-1} . MS: m/e 182 (M^+), 126, 103. ^1H NMR (CDCl_3): δ 6.42/6.24/6.07 (=CH), 2.95/2.91 (CH_2), 2.69 (C_2H_4), 1.33 (Me). ^{13}C NMR (CDCl_3): δ 147.7/145.3, 133.8/133.3/132.2/130.8/127.2/126.6 (=CH), 45.9/45.4 (SC), 43.1/40.2 (CH_2), 30.9 (Me), 31.1/30.4 (SCH_2), 28.2/27.5 (CH_2).

($\eta^1:\eta^5\text{-H}_2\text{NC}_2\text{H}_4\text{C}_5\text{H}_4$) CrCl_2 (10) was prepared by adding a solution of $\text{KC}_5\text{H}_4\text{C}_2\text{H}_4\text{NH}_2$ (0.32 g, 2.16 mmol) in THF (20 mL) to a stirred suspension of $\text{Cr}(\text{THF})_3\text{Cl}_3$ (0.90 g, 2.4 mmol) in THF (50 mL) at -78°C . The suspension was stirred for 2 h at -78°C and then for 12 h at room temperature. The resulting cloudy blue solution was evaporated to dryness under vacuum and the blue residue washed with hot toluene and dried under high vacuum for 24 h at 100°C . Yield: 0.32 g (63%). IR (KBr): ν 3197 s, 3098 s, 2919 s, 1570 s, 1481 s, 1460 s, 822 s cm^{-1} . MS: m/e 230 (M^+), 194, 165, 108.

($\eta^1:\eta^5\text{-cyclo-}\text{C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{H}_4$) CrCl_2 (12) was prepared by adding ether–HCl (3.8 mL of a 1.1 M solution in diethyl ether; 4.2 mmol) to a green solution of ($\eta^1:\eta^5\text{-cyclo-}\text{C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{H}_4$)– CrMe_2 (0.46 g, 1.88 mmol) in diethyl ether (60 mL) at -70°C . The resulting violet suspension was stirred at -30°C for 1 h, and the blue precipitate was isolated and dried at room temperature under high vacuum. Yield: 0.51 g (95%). IR (KBr): ν 3067 s, 2970 s, 2937 s, 2866 s, 1442 s, 842 s cm^{-1} (see Figure 1). MS: m/e 284 (M^+), 248, 212, 162.

($\eta^1:\eta^5\text{-cyclo-}\text{C}_5\text{H}_{10}\text{NC}_2\text{H}_4\text{C}_5\text{H}_4$) CrCl_2 (13) was prepared by adding a solution of $\text{KC}_5\text{H}_4\text{C}_2\text{H}_4\text{NC}_5\text{H}_{10}\text{-cyclo}$ (1.28 g, 5.97 mmol) in THF (20 mL) to a stirred suspension of $\text{Cr}(\text{THF})_3\text{Cl}_3$ (1.31 g, 3.5 mmol) in THF (50 mL) at room temperature. The solution was stirred for 2 h and evaporated to dryness under high vacuum and the resulting blue residue extracted with CH_2Cl_2 (70 mL). The extract was evaporated to dryness and the residue extracted with hot toluene (80 mL). The extract was cooled to -50°C , and the compound precipitated as blue needles, which were washed with pentane at room temperature and dried under high vacuum. Yield: 0.99 g (56%). IR (KBr): ν 3070 m, 2935 s, 2857 s, 2800 m, 1467 s, 1445 s, 860 s, 841 s, 817 s cm^{-1} . MS: m/e 298 (M^+), 262, 226, 176.

($\eta^1:\eta^5\text{-cyclo-}\text{C}_4\text{H}_8\text{NC}_3\text{H}_6\text{C}_5\text{H}_4$) CrCl_2 (15) was prepared as described above as blue crystals by reacting $\text{NaC}_5\text{H}_4\text{C}_3\text{H}_6\text{-NC}_4\text{H}_8\text{-cyclo}$ with $\text{Cr}(\text{THF})_3\text{Cl}_3$ in THF. Yield: 35%. IR (KBr): ν 2959 s, 2878 s, 1440 s, 816 s cm^{-1} . MS: m/e 298 (M^+), 263, 176.

($\eta^1:\eta^5\text{-cyclo-}\text{C}_5\text{H}_{10}\text{NC}_3\text{H}_6\text{C}_5\text{H}_4$) CrCl_2 (16) was prepared as described above as blue crystals by reacting $\text{NaC}_5\text{H}_4\text{C}_3\text{H}_6\text{-NC}_5\text{H}_{10}\text{-cyclo}$ with $\text{Cr}(\text{THF})_3\text{Cl}_3$ in THF. Yield: 73%. IR (KBr): ν 2928 s, 2855 s, 835 s cm^{-1} . MS: m/e 312 (M^+), 277, 240, 190.

($\eta^1:\eta^5\text{-1,3-cyclo-}\text{C}_4\text{H}_8\text{NC}_2\text{H}_4(\text{Me}_3\text{Si})\text{C}_5\text{H}_3$) CrCl_2 (17) was prepared by reacting a solution of 1,3-cyclo- $\text{C}_4\text{H}_8\text{NC}_2\text{H}_4(\text{Me}_3\text{Si})\text{C}_5\text{H}_4$ (1.75 g, 7.45 mmol) in THF (20 mL) with a solution of n -butyllithium in hexane (4.5 mL of a 1.66 M solution; 7.45 mmol) at -10°C . The resulting yellow solution was stirred at room temperature for 1 h and added to a suspension of $\text{Cr}(\text{THF})_3\text{Cl}_3$ (2.79 g, 7.46 mmol) in THF (50 mL). The resulting blue solution was stirred for 2 h and evaporated to dryness and the residue extracted with toluene (150 mL). The extract was concentrated and cooled to give the compound as blue needles, which were washed with pentane and dried under vacuum. Yield: 1.46 g (55%). IR (KBr): ν 3063 m, 2964 m, 2878 m, 1244 s, 845 s, 758 s cm^{-1} . MS: m/e 356 (M^+), 341, 320, 234. Crystal structure determination: see Figure 2.

($\eta^1:\eta^5\text{-1-Me}_2\text{NC}_2\text{H}_4\text{C}_9\text{H}_6$) CrCl_2 (18) was prepared as described above as a green crystalline solid by reacting (1-Me₂-NC₂H₄-indenyl)K with $\text{Cr}(\text{THF})_3\text{Cl}_3$ in THF. Yield: 81%. IR (KBr): ν 816 s, 760 s, 734 s cm^{-1} . MS: m/e 308 (M^+), 272, 186.

($\eta^1:\eta^5\text{-1-cyclo-}\text{C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_9\text{H}_6$) CrCl_2 (19) was prepared as described above as a green crystalline solid by reacting (1-cyclo- $\text{C}_4\text{H}_8\text{NC}_2\text{H}_4$ -indenyl)K with $\text{Cr}(\text{THF})_3\text{Cl}_3$ in THF. Yield:

66%. IR (KBr): ν 3075 m, 3051 m, 2963 s, 2948 s, 2877 s, 1454 s, 1439 s, 823 s, 805 s, 753 s, 745 s cm^{-1} . MS: m/e 334 (M^+), 299, 212.

($\eta^1\text{:}\eta^5\text{-1,3-cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4(\text{Me}_3\text{Si})\text{C}_9\text{H}_5\text{)CrCl}_2$ (**20**) was prepared as described above as a green crystalline solid by reacting (1,3-cyclo- $\text{C}_4\text{H}_8\text{NC}_2\text{H}_4(\text{Me}_3\text{Si})$ -indenyl)K with $\text{Cr}(\text{THF})_3\text{Cl}_3$ in THF. Yield: 31%. IR (KBr): ν 3054 m, 2961 s, 2883 s, 1450 s, 1244 s, 841 s, 756 s cm^{-1} . MS: m/e 406 (M^+), 391, 370, 284.

($\eta^1\text{:}\eta^5\text{-Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4\text{)CrCl}_2$ (**21**) was prepared by adding a solution of $\text{Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4\text{Li}$ (1.25 g, 6.3 mmol) in THF (20 mL) to a suspension of $\text{Cr}(\text{THF})_3\text{Cl}_3$ (2.36 g, 6.3 mmol) in THF (50 mL) at room temperature. The reaction mixture was stirred for 15 h and evaporated to dryness and the residue extracted with boiling toluene. The extract was cooled to -70°C to give the product as dark blue needles, which were isolated, washed with diethyl ether, and dried under high vacuum. Yield: 1.70 g (86%). IR (KBr): ν 2922 s, 1473 s, 1457 s, 1437 s, 1379 s, 1015 s, 1004 s, 915 s, 769 s cm^{-1} . MS: m/e 314 (M^+), 278. Crystal structure determination: see Figure 2.

($\eta^1\text{:}\eta^5\text{-cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4\text{)CrCl}_2$ (**22**) was prepared by adding cyclo- $\text{C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4\text{Li}$ (2.20 g, 9.77 mmol) dissolved in THF (150 mL) to a suspension of $\text{Cr}(\text{THF})_3\text{Cl}_3$ (3.66 g, 9.77 mmol) in THF (150 mL) at room temperature and stirring for 2 h. The resulting solution was evaporated to dryness and the residue extracted with toluene (100 mL). The extract was concentrated and cooled to -40°C to give the compound as blue needles, which were isolated, washed at room temperature with a small amount of pentane, and dried under high vacuum. Yield: 2.72 g (82%). IR (KBr): ν 2958 s, 2925 s, 2884 s, 1453 s, 1378 s cm^{-1} . MS: m/e 340 (M^+), 304, 218.

($\eta^1\text{:}\eta^5\text{-9-cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_{13}\text{H}_{16}\text{)CrCl}_2$ (**23**) was prepared as described above as blue needles by reacting (9-cyclo- $\text{C}_4\text{H}_8\text{NC}_2\text{H}_4$ -octahydrofluorenyl)Li with $\text{Cr}(\text{THF})_3\text{Cl}_3$ in THF. Yield: 70%. IR (KBr): ν 2940 s, 2868 s, 1452 s, 1427 s cm^{-1} . MS: m/e 392 (M^+), 356, 270.

($\eta^1\text{:}\eta^5\text{-cyclo-C}_4\text{H}_8\text{NSiMe}_2\text{OSiMe}_2\text{C}_5\text{H}_4\text{)CrCl}_2$ (**24**) was prepared as described above (see **13**) by reacting $\text{NaC}_5\text{H}_4\text{SiMe}_2\text{OSiMe}_2\text{NC}_4\text{H}_8\text{-cyclo}$ with $\text{Cr}(\text{THF})_3\text{Cl}_3$ in THF at room temperature and isolated as blue needles by extracting the evaporated residue with diethyl ether. Yield: 79%. IR (KBr): ν 3105 m, 3078 m, 2957 m, 2886 m, 1259 s, 1038 s, 828 s cm^{-1} . MS: decomposes. Crystal structure determination: see Figure 2.

($\eta^1\text{:}\eta^5\text{-Et}_2\text{NSiMe}_2\text{C}_5\text{H}_4\text{)CrCl}_2$ (**27**). A solution of $\text{Et}_2\text{NSiMe}_2\text{C}_5\text{H}_4\text{Li}$ (3.47 g, 17.24 mmol) in THF (50 mL) was added at room temperature to a suspension of $\text{Cr}(\text{THF})_3\text{Cl}_3$ (6.60 g, 17.62 mmol) in THF (100 mL). The resulting deep blue solution was evaporated to dryness and the oily residue extracted with pentane (200 mL). Cooling the extract to 0°C give the compound as a black crystalline solid. Yield: 3.07 g (56%). Anal. Calcd for $\text{C}_{22}\text{H}_{40}\text{Cl}_4\text{Cr}_2\text{N}_2\text{Si}_2$: C, 41.6; H, 6.4; Cl, 22.4; Cr, 16.4; N, 4.4; Si, 8.9. Found: C, 41.6; H, 6.3; Cl, 22.6; Cr, 16.5; N, 4.4; Si, 8.7. IR (KBr): ν 2962 s, 2924 s, 2866 s, 1166 s, 1251 s, 831 s, 815 s, 785 s cm^{-1} . MS: decomposes. Crystal structure determination: see Figure 3.

($\eta^1\text{:}\eta^5\text{-Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{H}_4\text{)CrMe}_2$ (**28**) was prepared by adding MeMgCl (3.5 mL of a 2.82 M solution in THF, 9.85 mmol) in THF (10 mL) dropwise into a suspension of $(\text{Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{H}_4)\text{-CrCl}_2$ in THF (40 mL) at -20°C . The resulting dark green solution was stirred for 1 h at room temperature and then evaporated to dryness. The residue was extracted with pentane (total 100 mL) and the extract cooled to give the compound as dark green crystals. Yield: 0.81 g (84%). IR (KBr): ν 2946 s, 2884 s, 2817 s, 2768 s, 1461 s, 815 s, 799 s cm^{-1} . MS: m/e 219 ($\text{M}^+ + \text{H}$), 204.

($\eta^1\text{:}\eta^5\text{-Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{H}_4\text{)CrEt}_2$ (**29**) was prepared as described above as dark green crystals by reacting EtMgBr with $(\text{Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{H}_4)\text{CrCl}_2$ in diethyl ether/THF at -80°C to room temperature. Yield: 76%. IR (KBr): ν 2914 s, 2870 s, 2839 s, 2776 s, 792 s, 773 s cm^{-1} . MS: m/e 217 ($\text{M}^+ - \text{Et}$), 187.

($\eta^1\text{:}\eta^5\text{-Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{H}_4\text{)CrPr}^i_2$ (**30**) was prepared as described above as dark green crystals by reacting Pr^iMgBr with $(\text{Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{H}_4)\text{CrCl}_2$ in diethyl ether/THF at -80°C to room temperature. Yield: 71%. IR (KBr): ν 2943 s, 2908 s, 2828 s, 794 s, 771 s cm^{-1} . MS: m/e 231 ($\text{M}^+ - \text{Pr}^i$), 187.

($\eta^1\text{:}\eta^5\text{-Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{H}_4\text{)Cr}(\text{CH}_2\text{SiMe}_3)_2$ (**31**) was prepared as dark green needles by reacting $\text{LiCH}_2\text{SiMe}_3$ with $(\text{Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{H}_4)\text{CrCl}_2$ in pentane/THF at -20°C to room temperature. Yield: 64%. IR (KBr): ν 2943 s, 2877 s, 2828 s, 1250 s, 1236 s, 855 s, 845 s, 796 s cm^{-1} . MS: m/e 362 (M^+), 347, 275, 187.

($\eta^1\text{:}\eta^5\text{-cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{H}_4\text{)CrMe}_2$ (**32**) was prepared as described below (see **34**), as dark green crystals, by reacting $\text{Cr}(\text{THF})_3\text{Cl}_3$ successively with cyclo- $\text{C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{H}_4\text{Li}$ and MeMgCl in THF at -20°C to room temperature. Yield: 46%. IR (KBr): ν 2958 s, 2903 s, 2856 s, 2781 s, 797 s, 785 s cm^{-1} . MS: m/e 244 (M^+), 229, 143, 131.

($\eta^1\text{:}\eta^5\text{-cyclo-C}_5\text{H}_{10}\text{NC}_2\text{H}_4\text{C}_5\text{H}_4\text{)CrMe}_2$ (**33**) was prepared as olive green crystals by reacting MeMgCl with (cyclo- $\text{C}_5\text{H}_{10}\text{-NC}_2\text{H}_4\text{C}_5\text{H}_4\text{)CrCl}_2$ in THF at -20°C to room temperature. The compound decomposes slowly at room temperature. Yield: 33%. IR (KBr): ν 2973 s, 2910 s, 2861 s, 786 s cm^{-1} . MS: m/e 257 (M^+), 172, 157, 131.

($\eta^1\text{:}\eta^5\text{-Me}_2\text{NC}_3\text{H}_6\text{C}_5\text{H}_4\text{)CrMe}_2$ (**34**) was prepared by adding $\text{Me}_2\text{NC}_3\text{H}_6\text{C}_5\text{H}_4\text{Na}$ (3.12 g, 18.01 mmol) dissolved in THF (100 mL) to a suspension of $\text{Cr}(\text{THF})_3\text{Cl}_3$ (7.92 g, 21.15 mmol) in THF (60 mL) at room temperature. The resulting dark blue solution was cooled to -20°C , and MeMgCl (15 mL of a 2.82 M solution in THF, 43 mmol) in THF (15 mL) was added slowly over 1 h. The resulting green-blue solution was stirred for 2 h at room temperature and evaporated to dryness and the residue extracted with pentane (total 300 mL). The extract was cooled to give the compound as dark blue crystals. Yield: 3.4 g (80%). IR (KBr): ν 2908 s, 2861 s, 2787 s, 779 s cm^{-1} . MS: m/e 233 ($\text{M}^+ - \text{H}$), 218, 174, 131.

($\eta^1\text{:}\eta^5\text{-1,3-cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4(\text{Me}_3\text{Si})\text{C}_5\text{H}_3\text{)CrMe}_2$ (**35**) was prepared as a dark green oil by reacting MeMgCl with (1,3-cyclo- $\text{C}_4\text{H}_8\text{NC}_2\text{H}_4(\text{Me}_3\text{Si})\text{C}_5\text{H}_3\text{)CrCl}_2$ in THF at -20°C to room temperature. Yield: 60%. IR (KBr): ν 2952 s, 2918 s, 2859 s, 1247 s, 836 s, 756 s cm^{-1} . MS: m/e 316 (M^+), 301.

($\eta^1\text{:}\eta^5\text{-cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4\text{)Cr}(\text{Me})\text{Cl}$ (**36**) was prepared by reacting (cyclo- $\text{C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4\text{)CrMe}_2$ (0.97 g, 3.21 mmol) with a solution of $(\text{Cl}_2\text{AlOSiMe}_3)_2$ (0.33 g, 1.77 mmol) in hexane (60 mL) at room temperature. The compound precipitates out as violet crystals, which were isolated and dried under high vacuum. Yield: 1.0 g (97%). IR (KBr): ν 2961 s, 2916 s, 2865 s cm^{-1} . MS: decomposes.

The compound can also be prepared (yield 90%) by reacting (cyclo- $\text{C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4\text{)CrMe}_2$ with 1 equiv of HCl in diethyl ether at -70°C .

($\eta^1\text{:}\eta^5\text{-Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4\text{)CrC}_4\text{H}_8\text{-cyclo}^5$ was prepared by adding slowly a solution of 1,4-dilithiobutane (16.0 mL of a 0.32 M solution in diethyl ether, 5.1 mmol) in THF (20 mL) to $(\text{Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{CrCl}_2$ (1.43 g, 4.5 mmol) in THF (50 mL) at -20°C . The reaction mixture was stirred at -10°C for 15 h and evaporated to dryness at -10°C . The residue was extracted with pentane at 0°C and the extract cooled to -70°C to give the compound as dark green needles, which were recrystallized from pentane at -30°C . Yield: 1.04 g (77%). Anal. Calcd for $\text{C}_{17}\text{H}_{30}\text{CrN}$: C, 68.0; H, 10.1; Cr, 17.3; N, 4.7. Found: C, 67.9; H, 10.0; Cr, 17.4; N, 4.6. IR (KBr): ν 2912 s, 2817 s, 1461 s cm^{-1} . MS: m/e 272 ($\text{M}^+ - \text{C}_2\text{H}_4$), 244, 187. Crystal structure determination: see ref 5.

The compound has also been prepared by reacting $(\text{Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{CrCl}_2$ (0.55 g, 1.7 mmol) with PMe_3 (0.4 mL, 3.8 mmol) in THF (50 mL). The solution was cooled to -80°C and saturated with ethylene for 15 min. Active Mg^{38} (0.09 g, 3.7 mmol) was added and the solution stirred under an atmosphere of ethylene for 15 h at -30°C . The dark green reaction

mixture was filtered and evaporated to dryness at $-30\text{ }^{\circ}\text{C}$ and the residue extracted with pentane at $-10\text{ }^{\circ}\text{C}$. The extract was cooled to $-70\text{ }^{\circ}\text{C}$ to give the compound as dark green needles. Yield: 0.47 g (90%).

$(\eta^1:\eta^5\text{-Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{CrC}_6\text{H}_{10}\text{-cyclo}^5$ was prepared by adding slowly a solution of 1,6- $\text{C}_6\text{H}_{12}(\text{MgCl})_2$ (15.0 mL of a 0.30 M solution in THF, 4.5 mmol) in THF (50 mL) to $(\text{Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{-Me}_4)\text{CrCl}_2$ (1.41 g, 4.5 mmol) in THF (100 mL) at $-30\text{ }^{\circ}\text{C}$. The reaction mixture was stirred for 15 h at $-10\text{ }^{\circ}\text{C}$ and evaporated to dryness and the residue extracted with pentane at $-10\text{ }^{\circ}\text{C}$. The extract was concentrated to 20 mL and cooled to $-70\text{ }^{\circ}\text{C}$ to give the compound as dark green prisms. Yield: 0.73 g (49%). Anal. Calcd for $\text{C}_{19}\text{H}_{34}\text{CrN}$: C, 69.5; H, 10.4; Cr, 15.8; N, 4.3. Found: C, 65.7; H, 10.0; Cr, 15.4; N, 4.2. IR (KBr): ν 2907 s, 2840 s, 1463 s, 1435 s cm^{-1} . MS: m/e 328 (M^+), 242, 187. Crystal structure determination: see ref 5.

$(\eta^1:\eta^5\text{-cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{CrMe}_2$ (**37**) was prepared as described above (see **34**), as dark green crystals, by reacting $\text{Cr}(\text{THF})_3\text{Cl}_3$ successively with $\text{cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4\text{Li}$ and MeMgCl in THF at $-20\text{ }^{\circ}\text{C}$ to room temperature. Yield: 86%. IR (KBr): ν 2963 s, 2900 s, 2849 s, 2778 s cm^{-1} . MS: m/e 301 ($\text{M}^+ + \text{H}$), 285, 199. Crystal structure determination: see Figure 4.

$(\eta^1:\eta^5\text{-9-cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_{13}\text{H}_{16})\text{CrMe}_2$ (**38**) was prepared as described above (see **34**), as dark green needles, by reacting $\text{Cr}(\text{THF})_3\text{Cl}_3$ successively with (9-cyclo- $\text{C}_4\text{H}_8\text{NC}_2\text{H}_4$ -octahydrofluorenyl)Li and MeMgCl in THF at $-20\text{ }^{\circ}\text{C}$ to room temperature. Yield: 56%. IR (KBr): ν 2930 s, 2854 s, 1437 s cm^{-1} . MS: m/e 337 ($\text{M}^+ - \text{Me}$), 268. Crystal structure determination: see Figure 4.

$(\eta^1:\eta^5\text{-Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{H}_4)\text{Cr}(\eta^3\text{-C}_3\text{H}_5)_2$ (**39**) was prepared as an orange crystalline solid by reacting $\text{C}_3\text{H}_5\text{MgCl}$ with $(\text{Me}_2\text{-NC}_2\text{H}_4\text{C}_5\text{H}_4)\text{CrCl}_2$ in diethyl ether/THF at -80 to $-30\text{ }^{\circ}\text{C}$. Yield: 80%. Anal. Calcd for $\text{C}_{15}\text{H}_{24}\text{CrN}$: C, 66.6; H, 9.0; Cr, 19.2; N, 5.2. Found: C, 66.7; H, 9.1; Cr, 19.2; N, 5.2. IR (KBr): ν 2940 s, 2815 s, 2765 s, 1640 w ($\eta^1\text{-C}_3\text{H}_5$), 1462 s, 800 s cm^{-1} . MS: m/e 270 (M^+), 229, 187.

$(\eta^5\text{-cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)(\eta^4\text{-C}_4\text{H}_6)\text{CrPMe}_3$ (**40**). A suspension of $\text{Cr}(\text{THF})_3\text{Cl}_3$ (1.95 g, 5.21 mmol) in THF (50 mL) was treated at room temperature with $\text{cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4\text{-Li}$ (1.11 g, 4.95 mmol) in THF (50 mL). The resulting dark blue solution was stirred for 2 h, cooled to $-70\text{ }^{\circ}\text{C}$, and treated successively with PMe_3 (1.2 mL, 11 mmol), butadiene (20 mL), and active Mg^{38} (0.29 g, 11.7 mmol). The resulting red solution was stirred for 12 h at $-30\text{ }^{\circ}\text{C}$ and filtered and then evaporated to dryness. The red-brown residue was extracted with pentane. Cooling the extract gave the compound as dark red cubes. Yield: 1.87 g (94%). Anal. Calcd for $\text{C}_{20}\text{H}_{39}\text{CrNP}$: C, 66.0; H, 9.8; Cr, 13.0; N, 3.5; P, 7.7. Found: C, 65.9; H, 9.9; Cr, 12.9; N, 3.6; P, 7.8. IR (KBr): ν 2927, 2805, 1456, 1429, 1374, 1348 cm^{-1} . MS: m/e 324 ($\text{M}^+ - \text{PMe}_3$), 270, 266. Crystal structure determination: see Figure 5.

$[(\eta^1:\eta^5\text{-cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{CrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (**41**) was prepared as a violet solid by reacting a solution of $(\text{cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{CrMe}_2$ (0.30 g, 1.0 mmol) in toluene (20 mL) with a solution of $\text{B}(\text{C}_6\text{F}_5)_3$ (0.52 g, 1.0 mmol) in toluene (20 mL) at $-10\text{ }^{\circ}\text{C}$. The solution was separated from a small amount of an oily residue and evaporated to dryness. Yield: 0.57 g (69%). Anal. Calcd for $\text{C}_{35}\text{H}_{30}\text{BCrF}_{15}\text{N}$: C, 51.7; H, 3.7; B, 1.3; Cr, 6.4; F, 35.1; N, 1.7. Found: C, 51.8; H, 3.8; B, 1.5; Cr, 6.4; F, 34.9; N, 1.8. IR (KBr): ν 1511 s, 1457 s, 1087 s, 949 s cm^{-1} . MS: m/e 797 ($\text{M}^+ - \text{Me}$), 630.

$[(\eta^1:\eta^5\text{-cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{CrMe}]^+[\text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2\text{-3,5})_4\text{-0.5Et}_2\text{O}]^-$ (**42**) was prepared by reacting a solution of $(\text{cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{CrMe}_2$ (0.09 g, 0.3 mmol) in diethyl ether (50 mL) with a solution of $\text{HB}(\text{C}_6\text{H}_3(\text{CF}_3)_2\text{-3,5})_4\text{-2Et}_2\text{O}^{23}$ at $-10\text{ }^{\circ}\text{C}$. The reaction mixture was stirred at room temperature for 1 h and the resulting violet precipitate isolated, washed with diethyl ether (10 mL), and dried under high vacuum. Yield: 0.28 g (78%). Anal. Calcd for $\text{C}_{50}\text{H}_{44}\text{BCrF}_{24}\text{-NO}$: C, 50.6; H, 3.8; B, 0.9; Cr, 4.4; F, 38.5; N, 1.2. Found: C,

50.8; H, 3.8; B, 0.9; Cr, 4.4; F, 37.3; N, 1.1. IR (KBr): ν 1355 s, 1278 s, 1162 s, 1124 s cm^{-1} .

$(\eta^1:\eta^5\text{-cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{Cr}(\text{Me})\text{Cl}\cdot\text{AlMe}_3$ (**43**) was prepared by adding AlMe_2Cl (3.65 mL of a 0.18 M solution in toluene, 0.65 mmol) to $(\text{cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{CrMe}_2$ (0.20 g, 0.65 mmol) dissolved in toluene (20 mL) at room temperature. The resulting violet solution was filtered and evaporated to dryness and the residue washed with pentane. The residue was dissolved in toluene and the solution cooled to $-40\text{ }^{\circ}\text{C}$ to give the compound as violet quadratic crystals. Yield: 0.44 g (92%). Anal. Calcd for $\text{C}_{19}\text{H}_{36}\text{AlClCrN}$: C, 58.1; H, 9.3; Al, 6.9; Cl, 9.0; Cr, 13.2; N, 3.6. Found: C, 58.0; H, 9.0; Al, 7.1; Cl, 9.2; Cr, 13.1; N, 3.4. IR (KBr): ν 2921 s, 2880 s, 1185 s, 696 s cm^{-1} . MS: decomposes.

$(\eta^1:\eta^5\text{-cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{CrMe}_2\cdot\text{AlMe}_3$ (**44**) was prepared by reacting a solution of $(\text{cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{CrMe}_2$ (0.37 g, 1.2 mmol) in toluene (30 mL) with AlMe_3 (1.26 mL of a 0.97 M solution in toluene, 1.30 mmol). The color of the solution changed immediately from green to violet. The solution was filtered and evaporated to dryness and the residue dissolved in hexane (20 mL). Cooling the solution to $-40\text{ }^{\circ}\text{C}$ gave the compound as violet needles. Yield: 0.40 g (88%). Anal. Calcd for $\text{C}_{20}\text{H}_{39}\text{AlCrN}$: C, 64.5; H, 10.6; Al, 7.2; Cr, 14.0; N, 3.8. Found: C, 64.6; H, 10.5; Al, 7.2; Cr, 14.1; N, 3.7. IR (KBr): ν 2959 s, 2916 s, 2886 s, 1185 s, 704 s cm^{-1} . MS: decomposes.

$(\eta^1:\eta^5\text{-cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{Cr}(\text{Me})\text{Cl}\cdot\text{AlMe}_2\text{Cl}$ was prepared by reacting a solution of $(\text{cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{CrCl}_2$ (0.56 g, 1.63 mmol) in toluene (70 mL) with AlMe_3 (8 mL of a 0.41 M solution in toluene, 3.3 mmol) at room temperature. The resulting violet solution was evaporated to dryness and the residue washed with pentane and dried under high vacuum. The residue was dissolved in toluene and the solution cooled to $-30\text{ }^{\circ}\text{C}$ to give the compound as a violet solid. Yield: 0.47 g (70%). Anal. Calcd for $\text{C}_{18}\text{H}_{33}\text{AlCl}_2\text{CrN}$: C, 52.3; H, 8.1; Al, 6.5; Cl, 17.2; Cr, 12.6; N, 3.4. Found: C, 52.2; H, 8.1; Al, 6.4; Cl, 17.0; Cr, 12.7; N, 3.4. IR (KBr): ν 2924 s, 2868 s, 682 s cm^{-1} . MS: decomposes.

$(\eta^1:\eta^5\text{-Pr}^i\text{N}=\text{C}(\text{Me})\text{CH}_2\text{C}_5\text{H}_4)\text{CrCl}_2$ (**45**). A solution of $\text{Pr}^i\text{N}=\text{C}(\text{Me})\text{CH}_2\text{C}_5\text{H}_4\text{Li}$ (0.92 g, 5.63 mmol) in THF (30 mL) was added to a suspension of $\text{Cr}(\text{THF})_3\text{Cl}_3$ (2.23 g, 5.96 mmol) in THF (50 mL) at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was stirred at room temperature for 3 h and evaporated to dryness and the residue extracted with CH_2Cl_2 (50 mL). The extract was cooled to $-70\text{ }^{\circ}\text{C}$ to give the compound as a microcrystalline blue solid. Yield: 1.12 g (70%). Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{Cl}_2\text{CrN}$: C, 46.3; H, 5.7; Cl, 24.9; Cr, 18.2; N, 4.9. Found: C, 46.4; H, 5.7; Cl, 25.0; Cr, 18.2; N, 4.8. IR (KBr): ν 2971 s, 2928 s, 2870 s, 1604 s, 1379 s, 1365 s, 809 s cm^{-1} . MS: m/e 284 (M^+), 249, 212, 206.

$(\eta^1:\eta^5\text{-MeOC}_2\text{H}_4\text{C}_5\text{H}_4)\text{CrCl}_2$ (**46**) was prepared by adding a solution of $\text{LiC}_5\text{H}_4\text{C}_2\text{H}_4\text{OMe}$ (1.23 g, 9.5 mmol) in THF (50 mL) to a suspension of $\text{Cr}(\text{THF})_3\text{Cl}_3$ (3.68 g, 9.8 mmol) in THF (70 mL) at room temperature. The reaction mixture was stirred for 2 h and evaporated to dryness and the blue residue extracted with boiling toluene (250 mL). The extract was evaporated to dryness and the residue taken up in CH_2Cl_2 (20 mL). The extract was filtered and cooled to $-70\text{ }^{\circ}\text{C}$ to give the compound as blue needles, which were washed with pentane at room temperature and dried under vacuum. Yield: 1.7 g (71%). Anal. Calcd for $\text{C}_8\text{H}_{11}\text{Cl}_2\text{CrO}$: C, 39.1; H, 4.5; Cl, 28.8; Cr, 21.1. Found: C, 38.9; H, 4.6; Cl, 28.7; Cr, 21.3. IR (KBr): ν 1054 s, 1039 s, 833 s, 814 s cm^{-1} . MS: m/e 245 (M^+), 210, 143.

$(\eta^1:\eta^5\text{-MeSC}_2\text{H}_4\text{C}_5\text{H}_4)\text{CrCl}_2$ (**47**) was prepared as blue needles as described above by reacting $\text{NaC}_5\text{H}_4\text{C}_2\text{H}_4\text{SMe}$ with $\text{Cr}(\text{THF})_3\text{Cl}_3$ in THF at room temperature. Yield: 75%. Anal. Calcd for $\text{C}_8\text{H}_{11}\text{Cl}_2\text{CrS}$: C, 36.7; H, 4.2; Cl, 27.1; Cr, 19.8; S, 12.1. Found: C, 36.8; H, 4.3; Cl, 27.0; Cr, 19.7; S, 12.6. IR (KBr): ν 1477 m, 1418 m, 832 s cm^{-1} . MS: m/e 261 (M^+), 225, 190, 178.

Table 7. Crystallographic Data

	24	17	21	37	38	27	40
formula	C ₁₃ H ₂₄ Cl ₂ CrNOSi ₂	C ₁₄ H ₂₄ Cl ₂ CrNSi	C ₁₃ H ₂₂ Cl ₂ CrN	C ₁₇ H ₃₀ CrN	C ₂₁ H ₃₄ CrN	C ₁₁ H ₂₀ Cl ₂ CrNSi	C ₂₂ H ₃₉ CrNP
mol wt	389.41	357.33	315.23	300.42	352.49	317.27	400.51
cryst size, mm	0.42 × 0.49 × 0.49	0.48 × 0.32 × 0.18	0.63 × 0.42 × 0.25	0.39 × 0.46 × 0.60	0.28 × 0.53 × 0.81	0.32 × 0.53 × 0.56	0.46 × 0.49 × 0.63
<i>V</i> (Å ³)	7287.5(11)	1737.5(2)	2967.5(7)	1638.2(2)	3858.9(13)	792.8(2)	2222.7(2)
ρ_{calcd} (g/cm ³)	1.419	1.366	1.411	1.218	1.213	1.329	1.197
<i>T</i> _{Messung} (°C)	20	20	20	−173	20	20	20
λ (Mo K α) (Å)	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69
<i>Z</i>	16	4	8	4	8	2	4
μ_{abs} (mm ^{−1})	1.034	1.023	1.110	0.687	0.593	1.111	0.592
no. of rflns measd	7373	4129	6756	2699	4630	3213	2864
no. of obsd rflns	3016	3948	5294	2509	2773	2076	2518
no. of variables	361	172	334	169	415	145	250
space group (No.)	<i>Pbca</i> (16)	<i>P2₁/a</i> (14)	<i>P2₁/a</i> (14)	<i>P2₁2₁2₁</i> (19)	<i>Pna2₁</i> (33)	<i>P1</i> (2)	<i>P2₁2₁2₁</i> (19)
<i>a</i> (Å)	14.3798(13)	12.4723(8)	14.957(3)	10.8358(9)	22.5207(8)	7.6250(11)	9.6215(4)
<i>b</i> (Å)	27.6664(10)	11.6609(7)	11.7539(18)	11.3905(9)	15.451(5)	7.821(2)	12.9841(5)
<i>c</i> (Å)	18.318(2)	12.5696(12)	18.3102(16)	13.2727(8)	11.0900(12)	14.054(2)	17.792(2)
α (deg)	90	90	90	90	90	75.982(11)	90
β (deg)	90	108.118(6)	112.796(9)	90	90	83.044(14)	90
γ (deg)	90	90	90	90	90	77.86(2)	90
<i>R</i>	0.0515	0.0432	0.0376	0.0433	0.0482	0.0539	0.0396
<i>R</i> _w	0.1301	0.1259	0.1092	0.1251	0.1291	0.1635	0.1059
resid electron density (e Å ^{−3})	0.447	0.614	0.380	0.508	0.348	0.680	0.314

(η^1 : η^5 -MeSC₂H₄C₅Me₄)CrCl₂ (**48**) was prepared as blue needles as described above by reacting LiC₅Me₄C₂H₄SMe with Cr(THF)₃Cl₃ in THF at room temperature. Yield: 75%. Anal. Calcd for C₁₂H₁₉Cl₂CrS: C, 43.3; H, 6.0; Cl, 22.3; Cr, 16.3; S, 10.1. Found: C, 45.4; H, 5.9; Cl, 22.4; Cr, 16.3; S, 10.0. IR (KBr): ν 1421 s, 1377 s cm^{−1}. MS: *m/e* 317 (M⁺), 281, 266, 235.

(η^1 : η^5 -Bu^tSC₂H₄C₅H₄)CrCl₂ (**50**) was prepared as a blue solid as described above by reacting KC₅H₄C₂H₄SBu^t with Cr(THF)₃Cl₃ in THF at room temperature. Yield: 78%. Anal. Calcd for C₁₁H₁₇Cl₂CrS: C, 43.4; H, 5.6; Cl, 23.3; Cr, 17.1; S, 10.5. Found: C, 43.3; H, 5.6; Cl, 23.2; Cr, 17.5; S, 10.5. IR (KBr): ν 1476 s, 1462 s, 1429 s, 1365 s, 827 s cm^{−1}. MS: *m/e* 303 (M⁺), 268, 247, 211, 165.

CpCr(1,3,4,5-tetramethylimidazol-2-ylidene)Cl₂ (**51**) was prepared by adding a solution of 1,3,4,5-tetramethylimidazol-2-ylidene (0.33 g, 2.7 mmol) in THF (25 mL) to a suspension of CpCr(THF)Cl₂ (0.69 g, 2.7 mmol) in THF (25 mL) at room temperature. The resulting violet precipitate was isolated, washed with THF, and dried under high vacuum. Yield: 0.78 g (94%). Anal. Calcd for C₁₂H₁₇Cl₂CrN₂: C, 46.2; H, 5.5; Cl, 22.7; Cr, 16.7; N, 9.0. Found: C, 46.0; H, 5.5; Cl, 22.8; Cr, 16.6; N, 8.9. IR (KBr): ν 1653 m, 1432 s, 1374 s, 804 s cm^{−1}. MS: *m/e* 311 (M⁺), 276, 246, 211.

CpCr(1,3,4,5-tetramethylimidazol-2-ylidene)Me₂ (**52**) was prepared by adding a solution of MeMgCl (0.6 mL of a 1.07 M solution in THF; 0.63 mmol) in THF (20 mL) to a suspension of CpCr(1,3,4,5-tetramethylimidazol-2-ylidene)Cl₂ (0.09 g, 0.3 mmol) in THF (20 mL) at room temperature, whereupon the color of the solution changed from blue to red. The solution was evaporated to dryness and the residue extracted with diethyl ether (40 mL). The compound crystallized as red needles upon cooling the extract to 0 °C. Yield: 0.07 g (83%). Anal. Calcd for C₁₄H₂₃CrN₂: C, 62.0; H, 8.6; Cr, 19.2; N, 10.3. Found: C, 62.2; H, 8.5; Cr, 19.1; N, 10.2. IR (KBr): ν 2919 s, 2866 s, 1657 m, 1430 s, 1373 s, 795 s, 776 s. MS: *m/e* 271 (M⁺), 256, 241, 176, 117.

(Me₅C₅)Cr(1,3,4,5-tetramethylimidazol-2-ylidene)Cl₂ (**53**) was prepared as described above (see **51**) as a violet solid by reacting the carbene with (Me₅C₅)CrCl₂ in THF at room temperature. Yield: 90%. Anal. Calcd for C₁₇H₂₇Cl₂CrN₂: C, 53.4; H, 7.1; Cl, 18.6; Cr, 13.6; N, 7.3. Found: C, 53.6; H, 7.2; Cl, 18.6; Cr, 13.6; N, 7.3. IR (KBr): ν 1660 m, 1569 m, 1433 s, 1371 s cm^{−1}. MS: *m/e* 381 (M⁺), 346, 257, 222.

Catalytic Reactions. The polymerization reactions were carried out in a thermostated glass autoclave (Büchi, BEP 280) and stirred with a glass paddle stirrer (1000 rotations/min) coupled to an external magnet. The gas flow and reactor temperature were recorded automatically. The autoclave was filled with toluene (240 mL) and the solvent saturated with ethylene at 2 atm. The catalyst solution was prepared externally by dissolving the chromium compound in toluene and treating it with a known concentration of a toluene solution of MAO. The required solution was then diluted to 10 mL and injected into the stirred reaction solution. The reaction was terminated by simultaneously closing the ethylene valve and injecting methanol (10 mL) into the reactor. The contents of the reactor were treated with dilute HCl/MeOH, and the toluene fraction was tested (GC) for the presence of oligomers. The polymer suspension was stirred overnight and the PE collected and washed with methanol. The procedure was repeated and the polymer dried under high vacuum. The melting point and crystallinity of the polymer was determined by standard methods (DSC, du Pont, 912/9900; IR, Nicolet 7199/750). The average molecular weight and distribution were determined by gel-permeation chromatography (GPC).

Crystal Structure Determinations. The crystal structure analysis of compounds **17**, **21**, **24**, **27**, **37**, **38**, and **40** were carried out using a CAD-4 single-crystal diffractometer (Enraf-Nonius). Crystallographic data and details of the refinement are listed in Table 7. Final coordinates and equivalent isotropic thermal parameters are included in the Supporting Information.

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Supporting Information Available: Detailed information on the crystal structure determinations, including tables of data collection parameters, final atomic positional and thermal parameters, and interatomic distances and angles as well as ORTEP diagrams. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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