Chromium Complexes with Me_2Si-Bridged Cyclopentadienyl-imidazolin-2-imine Ligands: Synthesis, Structure, and Use in Ethylene Polymerization Catalysis

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Imidazolin-2-imino-functionalized tetramethylcyclopentadienes **3**-H have been prepared in high yields by the reaction of 2 equiv of 1,3,4,5-tetramethylimidazolin-2-imine (**1a**), 1,3-diisopropyl-4,5-dimethylimidazolin-2-imine (**1b**), and 1,3-di-*tert*-butylimidazolin-2-imine (**1c**) with 5-(chlorodimethylsilyl)-1,2,3,4-tetramethyl-1,3-cyclopentadiene (**2**), whereas the corresponding indene **6**-H has been obtained from the reaction of **1b** with 1-(chlordimethylsilyl)indene (**5**). Deprotonation of **3**-H and **6**-H with the Schlosser base (KO*t*Bu/*n*BuLi) affords the highly reactive potassium salts (**3**)K and (**6**)K, which are useful precursors for the coordination of these ligands to transition metals. The chromium complexes **4a**, **4b**, **4c**, and **7** have been prepared by salt metathesis reactions of (**3**)K and (**6**)K with $[CrCl_3(THF)_3]$, and the molecular structures of all four paramagnetic complexes have been established by X-ray diffraction analyses. In the case of **4a**, **4b**, and **7**, the formation of constrained-geometry complexes with chelating Me_2Si-bridged cyclopentadienyl-imidazolin-2-imine ligands is observed. The presence of short Cr−N bonds is indicative of the strong electron-donating capacity of the imidazoline-2-imino-nitrogen atom, which is based on the ability of the imidazolium ring to effectively stabilize a positive charge. In contrast, the steric bulk of the *tert*-butyl groups in **4c** prevents coordination of the imine moiety. Activation of the chromium complexes **4** and **7** with methylaluminoxane (MAO) affords catalysts for the polymerization of ethylene at ambient temperature and under normal pressure.

Introduction

Since the 1950s, heterogeneous chromium-based systems such as the silica-supported Phillips[1] and Union Carbide[2] catalysts have been among the most important catalysts for the production of polyolefins.[3] In contrast, homogeneous chromium systems have been ignored for a long time.[4,5] During the past decade, however, the development of homogeneous chromium-based catalysts for olefin polymerization has attracted particular attention,[4–7] since significant advances have been made in this area by the use of cyclopentadienyl chromium(III) precatalysts bearing an additional neutral donor, either bridged or unbridged to the Cp unit.[8–22] Theoretical studies have shown that a high donor concentration in the vicinity of the metal atom is essential for high activities and, thus, that a bridge linking the donor group and the cyclopentadienyl moiety is favorable.[11,23] Furthermore, a large number of non-Cp chromium-based catalysts have been developed in recent years, which are able to match the polymerization activities and properties described for systems containing Cp ligands.[6,7,24–30] A selection of chromium complexes with nitrogen-donor-functionalized cyclopentadienyl

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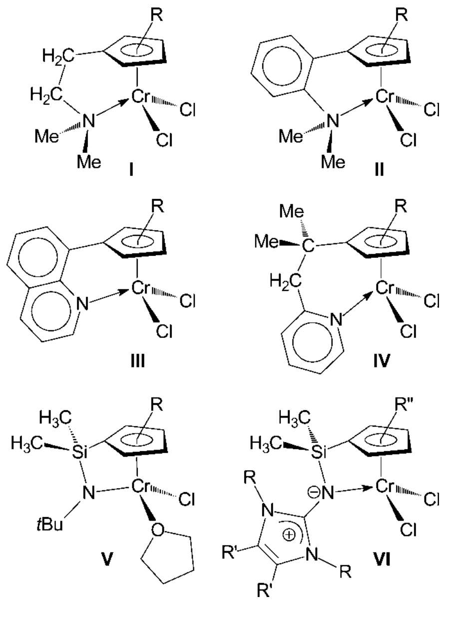
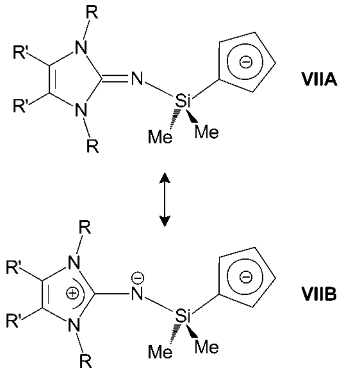


Figure 1. Selected half-sandwich cyclopentadienyl chromium complexes with pendant N-donor groups; arrows indicate bonds between chromium and neutral donor moieties.

ligands is shown in Figure 1. Apart from complexes with neutral N-donor groups such as aminoethyl (**I**),[10] anilinyl (**II**),[14] quinolinyl (**III**),[18] and pyridylethyl (**IV**),[19] the silicon-bridged *ansa*-cyclopentadienyl-amido complex **V** (R = tetramethyl) is one of the most important systems that have been studied as homogeneous model systems for industrially applied heterogeneous catalysts.[4,31] Monoalkylation of **V** leads to neutral single-site catalysts of the type [(η^5-C_5Me_4-$SiMe_2$-N*t*Bu)CrR] (R = alkyl), which are isostructural with the cationic active sites generated from prototypical "contrained-geometry" half-sandwich group 4 catalysts,[32,33] e.g., from [η^5-C_5Me_4-$SiMe_2$-NR)MCl_2] (M = Ti, Zr, Hf), by addition of an appropriate cocatalyst.

Recently, we have introduced a novel and versatile method for the preparation of imidazolin-2-imines by a Staudinger-type reaction of Arduengo-carbenes of the imidazolin-2-ylidene type with trimethylsilyl azide, followed by protolytic cleavage of the N−Si bond in the intermediate 2-trimethylsilyliminoimidazolines.[34] The resulting imines are valuable ligand precursors in their own right[35] and are also useful building blocks for the design and preparation of novel multidentate poly(imidazolin-2-imine) ligands.[36] These ligands attain their unique properties from the ability to effectively delocalize a positive charge over the imidazole moiety, producing compounds with considerably enhanced basicity and N-nucleophilicity.[34,37] In a similar fashion, tethering of an imidazolin-2-imine moiety to a cyclopentadienyl ring via a Me_2Si bridge leads to ligands of type **VII**, which can be described by the two limiting resonance structures **VIIA** and **VIIB** (Scheme 1). Upon metal complexation, the contribution of the mesomeric form **VIIB** becomes even more pronounced, and the resulting chromium complexes **VI** (Figure 1) can be expected to behave as true "constrained-geometry" *ansa*-cyclopentadienyl-amido complexes despite the overall neutral charge of the donor moiety. Accordingly, compensation of the positive chromium(III) charges requires an additional negatively charged ligand, and the dichlorides **VII** can be regarded as structural analogues to well-established and commercialized group 4 *ansa*-cyclopentadienyl-amido complexes.[32] In this contribution, we wish to present the synthesis and structural characterization of the first chromium(III) complexes of type **VI** containing imino-functionalized tetramethylcyclopentadienyl and indenyl ligands, together with a preliminary investigation of their use as precatalysts for ethylene polymerization.

Scheme 1. Mesomeric Structures for Cyclopentadienyl-imidazolin-2-imine Ligands



Results and Discussion

Ligand Syntheses. The synthesis of the imidazoline-2-imino-tetramethylcyclopentadienes **3**-H is accomplished by the reaction of 5-(chlorodimethylsilyl)-1,2,3,4-tetramethyl-1,3-cyclopentadiene (**2**) with 2 equiv of the appropriate 2-iminoimidazoline **1**, whereby 1 equiv of the imine **1** scavenges the hydrochloric

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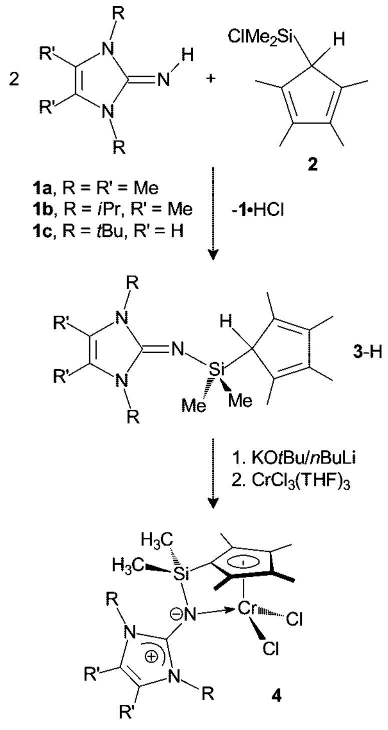
Scheme 2. Syntheses of Tetramethylcyclopentadienyl-imidazolin-2-imine Chromium Complexes



acid with the formation and precipitation of the corresponding 2-aminoimidazolium chloride **1**•HCl from the reaction mixture (Scheme 2). After filtration and evaporation of the solvent, **3a**-H (R = Me, R′ = Me), **3b**-H (R = iPr, R′ = Me), and **3c**-H (R = *t*Bu, R′ = H) are obtained as pale yellow oils. The formation of the cyclopentadienes **3**-H from the corresponding imines **1** can easily be followed by ^{1}H NMR spectroscopy, since four additional resonances are observed for the (tetramethylcyclopentadienyl)dimethylsilyl moiety, while the imine NH resonance disappears. The resonances of the imidazolin-2-imine moieties are only slightly shifted in comparison to the imines **1** and are almost identical with those reported for the corresponding 2-(trimethylsilylimino)imidazolines.[34,35b,c] No fluxional behavior is observed for the cyclopentadiene moieties, and the ^{1}H NMR spectra exhibit singlets at 3.20 ppm (**3a**-H, **3b**-H) and 3.48 ppm (**3c**-H) for the CH hydrogen atom together with two signals at about 2.22 and 1.96 ppm for the 2,4- and 3,5-methyl groups, respectively, revealing that the compounds **3**-H adopt C_s-symmetry with the silyl bridge in the allylic position. In the ^{13}C NMR spectra, product formation is indicated by characteristic high-field shifts of about 10 ppm for the imidazoline C2 resonances. The cyclopentadiene CH carbon resonances are observed at ca. 60 ppm, whereas the resonances for the carbon atoms in the 2,5- and 3,4-positions appear in the range 133−135 ppm.

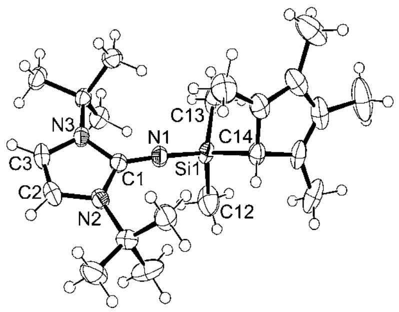


Figure 2. ORTEP drawing of one of the two independent molecules **3c**-H with thermal displacement parameters at 50% probability. Selected bond lengths [Å] and angles [deg]: C1−N1 1.274(2), C1−N2 1.400(2), C1−N3 1.399(2), N1−Si1 1.659(2), Si1−C14 1.922(2); C1−N1−Si1 164.87(13), N1−Si1−C14 109.48(8), N1−C1−N2 127.38(14), 128.30(17), N2−C1−N3 104.31(15).

Colorless tablet-shaped single crystals of **3c**-H obtained at room temperature from the crude oil were subjected to an X-ray diffraction analysis, and the molecular structure of one of the two independent molecules in the asymmetric unit is shown in Figure 2. Since the second molecule, which is not shown, suffers from disorder of the tetramethylcyclopentadienyl ring over two positions, its structural parameters are not discussed. In agreement with the molecular structure of the corresponding 1,3-di-*tert*-butyl-2-(trimethylsilylimino)imidazoline,[35c] a short exocyclic C1−N1 bond distance of 1.274(2) Å is observed, a value that is expected for a typical N−C$_{sp2}$ double bond (1.28 Å).[38] Because of the steric bulk of the *tert*-butyl substituents, **3c**-H exhibits a large C1−N1−Si1 angle of 164.9(1)° and a long Si1−C14 bond distance of 1.922(2) Å, which is significantly longer than the corresponding Si1−C$_{methyl}$ bond lengths [1.863(2)/1.871(2) Å]. In agreement with the ^{1}H NMR spectroscopic data, the cyclopentadiene CH hydrogen atom is located at the carbon atom C14, unequivocally confirming the allylic position of the silyl moiety.

The reaction of the cyclopentadienes **3**-H with a mixture of KO*t*Bu/*n*BuLi (Schlosser base)[39] in hexane at ambient temperature furnished the potassium cyclopentadienides (**3**)K in high yields as off-white solids (Scheme 2). The air- and moisture-sensitive potassium salts (**3**)K represent important precursors for further complexation reactions. In each case, deprotonation is accompanied by disappearance of the cyclopentadiene CH resonance in the ^{1}H NMR spectra and by a marked low-field shift of the corresponding ^{13}C NMR resonance. The corresponding indenyl derivative (**6**)K can be isolated as a white crystalline solid from the reaction of 1-(chlorodimethylsilyl)indene (**2**) with 2 equiv of the imine **1b** (R = *i*Pr, R′ = Me), followed by instantaneous deprotonation of the intermediate **6**-H, which is unstable under ambient conditions (Scheme 3). Apart from the fact that different ^{1}H and ^{13}C NMR resonances are observed for the indenyl moiety, the spectroscopic characteristics are very similar to those observed for the potassium tetramethylcyclopentadienide (**3b**)K.

Synthesis and Characterization of Chromium(III) Complexes. The reactions of the potassium salts (**3**)K and (**6**)K with [CrCl$_3$(THF)$_3$] in THF at ambient temperature were accompanied by color changes from deep purple to deep blue or deep green, respectively, and the chromium tetramethylcyclopentadienyl complexes **4** and the indenyl complex **7** are isolated in moderate to high yields (Schemes 2 and 3). These compounds were characterized by means of elemental analysis and mass spectrometry, and the molecular structures of all complexes (**4a**, **4b**, **4c**, and **7**) have been established by X-ray diffraction analyses in order to compare the structural changes upon variation of the substitution patterns. The structural parameters are summarized in Table 1, and ORTEP presentations are depicted in Figures 3, 4, and 5, respectively. For **4a** and **4b** (Figure 3), coordination of the nitrogen atom is clearly confirmed, and both complexes

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Scheme 3. Syntheses of Indenyl-imidazolin-2-imine Chromium Complexes

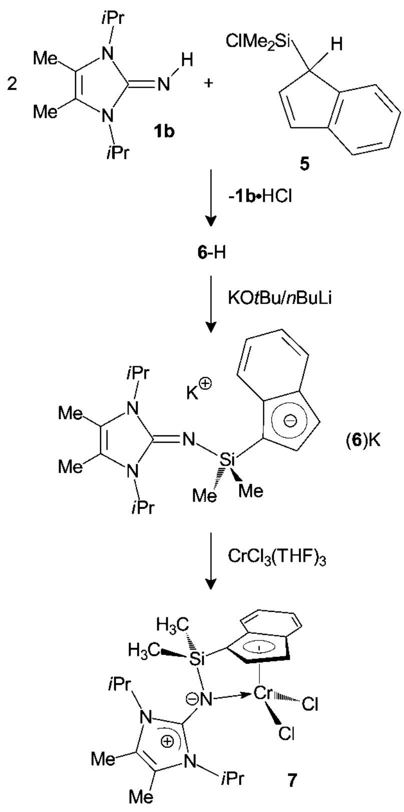

exhibit a three-legged piano-stool geometry with a distorted pseudotetrahedral environment around the chromium atoms. **4a** is almost perfectly C_s symmetric with the idealized mirror plane containing the *ipso*-carbon atom C10, Si, N1, C1, and the chromium atom. The imidazole moiety in **4a** adopts a perpendicular orientation toward this mirror plane [interplanar angle 87.8(1)°], ruling out any significant π-interaction between the exocyclic nitrogen atom and the imidazole system. In comparison to the molecular structure of **3c**-H (Figure 2) and other silylated imidazolin-2-imines,[34] this orientation leads to a pronounced elongation of the C1−N1 bond [1.274(2) Å in **3c**-H versus 1.344(3) Å in **4a**] and to a more obtuse N2−C1−N3 angle [104.3(2)° in **3c**-H versus 106.3(2)° in **4a**], indicating an increase of the imidazolium-amide character, as indicated by the mesomeric form **VIIB** in Scheme 1.[40] As a consequence, a short Cr−N1 bond distance of 2.041(2) Å is observed, which confirms the strong donating capability of the planar, three-coordinate nitrogen atom N1 (sum of angles = 360°). This bond length is shorter than the corresponding Cr−N distances found in the complexes **I**−**IV** (Figure 1), containing neutral N-donor groups, e.g., Cr−N = 2.175(2) Å in **I** (R = Me$_4$),[10] 2.251(3) Å in **II** (R = Me$_4$),[14] 2.088(2) Å in **III** (R = Me$_4$),[14] and 2.108(2) Å in **IV** (R = H$_4$).[19] It should be noted, however, that the Cr−N distance of 1.920(4) Å in the most closely related and structurally characterized complex [(η^5-C$_5$Me$_4$-SiMe$_2$-N*t*Bu)Cr(CH$_2$SiMe$_3$)], which features a dianionic cyclopentadienyl-amido ligand, is significantly shorter.[31]

The molecular structure of the diisopropyl derivative **4b** deviates more strongly from C_s symmetry than **4a**, and a pronounced twisting of the imidazole ring is observed, which is presumably a result of minimizing the steric interaction between the isopropyl groups and the tetramethylcyclopentadienyl and chloride ligands. As a consequence, a pronounced elongation of the Cr−N1 bond distance [2.086(1) Å] is observed, and the angles around N1 differ significantly from those observed in **4a** (Table 1), although the planarity of this nitrogen atom is retained (sum of angles = 359.9°). In contrast, the most sterically encumbered complex **4c**, containing *tert*-butyl substituents, does not display a coordinated imino group in the solid state (Figure 4). Instead, the formation of a centrosymmetric dimer is observed, with one terminal and two bridging chlorine ligands completing the coordination sphere of each chromium atom. Similar structures have been observed several times for related complexes of the type [(η^5-C$_5$R$_5$)CrCl$_2$]$_2$.[10,41] The structural parameters of the imidazolin-2-imine moiety fall in the range of those previously determined for related systems,[34] and they are also almost identical to those in **3c**-H (*vide supra*).

Attachment of the imine-donor group to the 1-position of the indenyl ring leads to a racemic mixture of chiral indenyl complexes **7**. Compound **7** crystallizes in the achiral space group $P2_1/c$, and the asymmetric unit contains two independent molecules with almost identical structural features (Figure 5). In analogy with the tetramethylcyclopentadienyl complexes **4a** and **4b**, the indenyl rings are pentahapto-bound to the chromium atom, albeit in a distorted manner because of the constrained geometry imposed by coordination of the imino-nitrogen atom N1 (Table 1). The Cr−N1 distances in both independent molecules are identical (2.070 Å) and adopt an intermediate position with respect to the values found for **4a** and **4b**. Similar to **4b**, the 1,3-diisopropylimidazole moiety adopts a twisted orientation with one of the isopropyl groups leaning toward the annulated six-membered ring, resulting in short Me$_2$CH···C contacts of 2.70 and 2.72 Å, respectively, which could be interpreted as weak hydrogen bonds.[42]

Ethylene Polymerization. To estimate the potential of the dichloro chromium complexes **4** and **7** as precatalysts for olefin polymerization, all four complexes were screened for the polymerization of ethylene (p = 1 bar) in toluene at 25 °C in the presence of methylaluminoxane (MAO); the results are summarized in Table 2. The catalysts derived from the tetramethylcyclopentadienyl complexes **4a**−**4c** exhibit moderate activities and produce polyethylene (PE) of low molecular weight. The large polydispersities and multimodal distribution of the molecular weights of the PE obtained by use of these catalytic systems reveal the presence of more than one active site and suggest decomposition of the complexes after a relatively short active period. In contrast, the indenyl complex **7**, on activation with MAO, shows high activities up to 2125 g (PE) mmol^{-1} (precat.) bar^{-1} h^{-1}, comparable to that observed for the metallocene Cp$_2$ZrCl$_2$, which was also tested as a reference system. However, if the reaction time is extended, the catalytic performance decreases noticeably, while the

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Table 1. Selected Bond Lengths [Å] and Angles [deg]

	4a	4b	4c	7[a]
Cr−Cp$_{\mathrm{av}}$	2.254	2.250	2.235	2.285/2.281
Cr−Cp$_{\mathrm{ct}}$	1.899	1.893	1.880	1.937/1.932
Cr−Cp$_{\mathrm{range}}$	2.187(2)−2.311(2)	2.179(1)−2.312(1)	2.219(7)−2.269(7)	2.187(4)−2.399(3)/2.181(3)−2.397(3)
Cr−Cl1	2.307(1)	2.323(1)	2.283(2)	2.294(1)/2.291(1)
Cr−Cl2	2.300(1)	2.294(1)	2.396(2)	2.292(1)/2.284(1)
Cr−N1	2.041(2)	2.086(1)		2.070(2)/2.070(3)
N1−Si	1.718(2)	1.722(1)	1.657(6)	1.726(3)/1.715(3)
Si−C$_{ipso}$	1.896(2)	1.882(1)	1.899(7)	1.876(3)/1.870(3)
N1−C1	1.344(3)	1.343(2)	1.266(9)	1.338(4)/1.347(4)
C1−N2	1.357(3)	1.365(2)	1.387(9)	1.358(4)/1.366(4)
C1−N3	1.351(3)	1.364(2)	1.408(10)	1.364(4)/1.351(4)
N1−Si−C$_{ipso}$	92.0(1)	93.0(1)	105.2(3)	92.8(1)/92.9(1)
Cr−N1−C1	128.9(2)	126.6(1)		127.6(2)/128.6(2)
Cr−N1−Si	101.3(1)	99.3(1)		97.8(1)
C1−N1−Si	129.8(2)	133.9(1)	167.6(6)	134.2(2)/133.1(2)
N2−C1−N3	106.3(2)	106.6(1)	104.6(6)	106.2(3)/106.7(3)
N1−C1−N2	126.6(2)	126.1(1)	129.0(7)	127.8(3)/126.8(3)
N1−C1−N3	127.2(2)	127.3(1)	126.4(7)	125.9(3)/126.6(3)

[a] Values given for two independent molecules in the asymmetric unit.

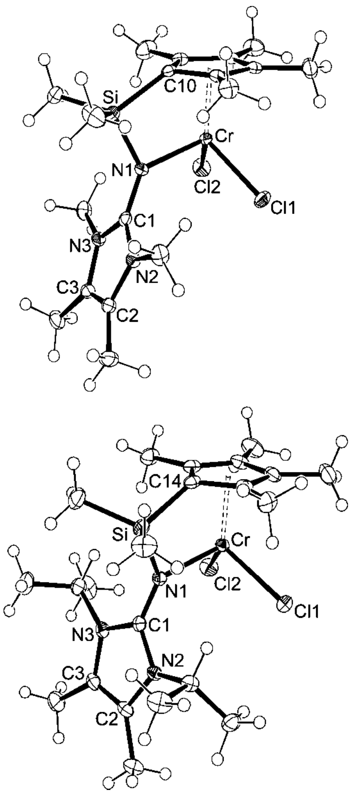

Figure 3. ORTEP drawings of **4a** (top) and **4b** (bottom) with thermal displacement parameters at 50% probability.

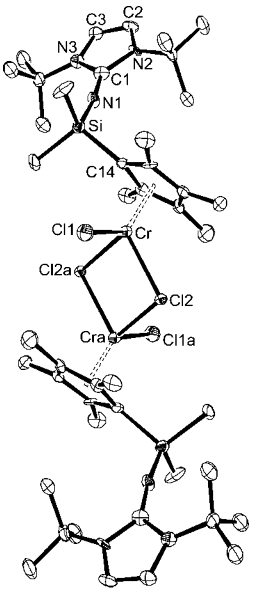

Figure 4. ORTEP drawing of dimeric **4c** with thermal displacement parameters at 50% probability; hydrogen atoms are omitted for clarity.

polydispersity of the PE increases. Such behavior might again be attributed to decomposition of the initial catalyst and to the operation of more than one active site. It should be noted that the results obtained for ethylene polymerization with the precatalysts **I**−**IV** (Figure 1) and derivatives thereof are more clear-cut, since relatively narrow polydispersities have been observed in most cases,[10,14,19] suggesting that the imine-donor moiety in complexes **4** and **7** suffers faster degradation than the amine and N-heterocyclic donor groups in **I**−**IV**. In contrast, very low activities and bimodal product distributions have been reported for the single-site catalyst [(η^5-C_5Me_4-$SiMe_2$-N*t*Bu)Cr(CH_2SiMe_3)], which has been obtained from **V** (Figure 1) by reaction with $LiCH_2SiMe_3$.[31] Further studies are in progress to elaborate alkylation reactions of complexes **4** and **7** and to study the possibility to generate catalytically active species by alkyl abstraction from the resulting dialkyl complexes.

Conclusions

With this contribution, we have presented the synthesis of new imidazoline-2-imino-functionalized cyclopentadienyl and indenyl ligands. The ligand precursors **3**-H and **6**-H can be easily transformed into the corresponding potassium salts (**3**)K and (**6**)K, which are, in the case of an appropriate choice of the imidazole substituents, useful precursors for the preparation of constrained geometry chromium(III) complexes. The complexes **4a**−**4c** and **7** can be used as precatalysts for ethylene polymerization at room temperature; however, the broad and bimodal molecular weight distributions observed in the presence of MAO imply that activation results in the formation of more than one active catalyst site.

The extraordinary electron-donating capacity of the tethered nitrogen donor atom stems from the ability of the imidazole ring to effectively stabilize a positive charge, resulting in the

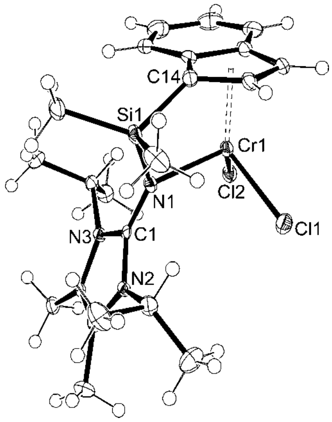

Figure 5. ORTEP drawing of one of two independent molecules **7** with thermal displacement parameters at 50% probability.

formation of short Cr−N bond distances, which are among the shortest bond lengths established for N-donor-functionalized Cp-chromium dichloride complexes. These cyclopentadienyl-imidazolin-2-imine ligands represent monoanionic analogues of dianionic cyclopentadienyl-amido ligands and as such form chromium(III) complexes that are structurally closely related to well-established *ansa*-cyclopentadienyl-amido complexes containing tetravalent group 4 metals.[32] In the same way, it should be possible to obtain isostructural complexes by introduction of other trivalent metal atoms such as rare earth elements (group 3 and lanthanides),[43] and the resulting cyclopentadienyl-imidazolin-2-imine complexes require two monoanionic ligands to attain an overall neutral charge, whereas conventional *ansa*-cyclopentadienyl-amido complexes of the type $[(\eta^5\text{-Cp-SiMe}_2\text{-NR})\text{LnX}]$ (Ln = rare earth metal) contain only one additional anionic ligand X.[44]

Experimental Section

All operations were performed in a glovebox under a dry argon atmosphere (MBraun 200B) or on a high-vacuum line using Schlenk techniques. All solvents were dried by a solvent purification system (MBraun) and stored over molecular sieve (4 Å) prior to use. The 2-iminoimidazolines **1**,[34] 1-(chlordimethylsilyl)indene (**5**)[45] and $[\text{CrCl}_3(\text{THF})_3]$[46] were prepared according to published procedures. 5-(Chlorodimethylsilyl)-1,2,3,4-tetramethyl-1,3-cyclopentadiene (**2**) was purchased from Boulder Scientific Company and distilled prior to use. Cp_2ZrCl_2 was obtained from Aldrich and used as received. Elemental analyses (C, H, N) were performed on a Elementar Vario EL III and a Vario Micro Cube elemental analyzer. ^{1}H and ^{13}C NMR spectra were measured on Bruker DPX 200, Bruker AV 300, and Bruker DRX 400 spectrometers using the solvent as internal standard. The assignment of all resonances was supported by two-dimensional NMR spectroscopy (COSY, HMBC, and HSQC experiments). Mass spectrometry (EI) has been performed on a Finnigan MAT 90 device.

General Procedure for the Synthesis of the Tetramethylcyclopentadienes 3-H. A solution of the 2-iminoimidazoline **1** (2 equiv) in hexane was treated with 1 equiv of **2** at ambient temperature and was stirred for 90 min. The solution was separated from the cloudy precipitate of **1**·HCl by filtration over a glass frit, and the solvent of the filtrate was removed *in vacuo*. The tetramethylcyclopentadienes **3**-H were obtained as pale yellow oils, which can be purified from excess **2** by heating under vacuum for several hours at 70 °C. The hydrochlorides **1**·HCl can be recycled, and their reaction with an equivalent amount of potassium hydride in THF affords the imines **1** in quantitative yield.

3a-H. Yield: 85%. Anal. Calcd for $\text{C}_{18}\text{H}_{31}\text{N}_3\text{Si}$: C, 68.08; H, 9.84; N 13.23. Found: C, 65.58; H, 9.29; N, 13.42. ^{1}H NMR (200 MHz, C_6D_6): 3.21 (1H, s, *ipso*-CH), 2.80 (6H, s, NCH_3), 2.22 (6H, s, *o*-CCH_3), 1.95 (6H, s, *m*-CCH_3), 1.46 (6H, s, NCCH_3), 0.39 (6H, s, SiCH_3). ^{13}C{H} NMR (50.33 MHz, C_6D_6): 145.9 (NCN), 134.3 (*m*-C), 134.0 (*o*-C), 113.3 (N*C*CH_3), 60.4 (*ipso*-C), 28.4 (NCH_3), 15.1 (*o*-C*C*H_3), 11.6 (*m*-C*C*H_3), 8.6 (NC*C*H_3), 2.8 (SiCH_3).

3b-H. Yield: 98%. Anal. Calcd for $\text{C}_{22}\text{H}_{39}\text{N}_3\text{Si}$: C, 70.72; H, 10.52; N, 11.25. Found: C, 69.80; H, 10.59; N, 11.60. ^{1}H NMR (400 MHz, C_6D_6): 4.63 (2H, sept, C*H*CH_3), 3.20 (1H, s, *ipso*-CH), 2.22 (6H, s, *o*-CCH_3), 1.97 (6H, s, *m*-CCH_3), 1.71 (6H, s, NCCH_3), 1.17 (12H, d, CHC*H*$_3$), 0.34 (6H, s, SiCH_3). ^{13}C {H} NMR (100.62 MHz, C_6D_6): 144.2 (NCN), 134.5 (*m*-C), 133.9 (*o*-C), 114.0 (N*C*CH_3), 59.8 (*ipso*-C), 44.9 (*C*HCH_3), 21.5 (CH*C*H$_3$), 15.0 (*o*-C*C*H$_3$), 11.6 (*m*-C*C*H$_3$), 10.0 (NC*C*H$_3$), 1.7 (SiCH_3).

3c-H. Yield: 94%. Anal. Calcd for $\text{C}_{22}\text{H}_{39}\text{N}_3\text{Si}$: C, 70.72; H, 10.52; N, 11.25. Found: C, 69.68; H, 10.18; N, 11.13. ^{1}H NMR (400 MHz, C_6D_6): 6.04 (2H, s, NCH), 3.48 (1H, s, *ipso*-CH), 2.22 (6H, s, *o*-CCH_3), 1.97 (6H, s, *m*-CCH_3), 1.37 (18H, s, NCCH_3), 0.37 (6H, s, SiCH_3). ^{13}C{H} NMR (50.33 MHz, C_6D_6): 140.7 (NCN), 135.4 (*m*-C), 134.6 (*o*-C), 107.8 (NCH), 59.0 (*ipso*-C), 54.9 (N*C*CH_3), 28.9 (NC*C*H$_3$), 15.4 (*o*-C*C*H$_3$), 12.1 (*m*-C*C*H$_3$), 2.2 (SiCH_3).

General Procedure for the Synthesis of the Potassium Tetramethylcyclopentadienides (3)K. To a suspension of potassium *tert*-butoxide (1 equiv) in hexane at 0 °C was added dropwise a 1.6 M solution of *n*-BuLi in hexane (1.1 equiv), and the mixture was stirred for 20 min. A solution of **3**-H (1 equiv) in hexane was added to the resulting cloudy suspension, and the slurry was allowed to reach ambient temperature overnight. After filtration the white solid was washed several times with hexane and dried *in vacuo*.

(**3a**)K. Yield: 83%. ^{1}H NMR (200 MHz, C_6D_6/THF-d_8, 1:1): 2.96 (6H, s, NCH_3), 2.15 (6H, s, *o*-CCH_3), 1.99 (6H, s, *m*-CCH_3), 1.74 (6H, s, NCCH_3), 0.32 (12H, s, SiCH_3). ^{13}C{H} NMR (50.33 MHz, C_6D_6/THF-d_8, 1:1) 119.8 (*m*-C), 116.9 (*o*-C), 115.5 (N*C*CH_3), 32.0 (NCH_3), 17.5 (*o*-C*C*H$_3$), 14.6 (*m*-C*C*H$_3$), 12.0 (NC*C*H$_3$), 11.2 (SiCH_3). The NCN and the *ipso*-C resonances could not be detected.

(**3b**)K. Yield: 63%. ^{1}H NMR (200 MHz, THF-d_8): 4.69 (2H, sept, C*H*CH_3), 2.09 (6H, s, *o*-CCH_3), 1.99 (6H, s, NCCH_3), 1.90 (6H, s, *m*-CCH_3), 1.17 (12H, d, CHC*H*$_3$), 0.19 (6H, s, SiCH_3). ^{13}C{H} NMR (50.33 MHz, THF-d_8): 145.1 (NCN), 116.5 (*m*-C), 114.1 (N*C*CH_3), 111.8 (*o*-C), 107.8 (*ipso*-C), 45.2 (*C*HCH_3), 21.9 (CH*C*H$_3$), 14.8 (*o*-C*C*H$_3$), 11.9 (*m*-C*C*H$_3$), 10.3 (NC*C*H$_3$), 7.2 (SiCH_3).

(**3c**)K. Yield: 86%. ^{1}H NMR (200 MHz, THF-d_8): 6.20 (2H, s, NCH), 2.11 (6H, s, *o*-CCH_3), 1.93 (6H, s, *m*-CCH_3), 1.38 (18H, s, NCCH_3), 0.28 (6H, s, SiCH_3). Due to the poor solubility of **3c**, no satisfactory ^{13}C NMR spectrum could be recorded.

Synthesis of the Potassium Indenide (6)K. To a suspension of 126 mg (1.13 mmol) of potassium *tert*-butoxide (1 equiv) in 20 mL of hexane at 0 °C was added dropwise 0.72 mL (1.15 mmol) of a 1.6 M solution of *n*-BuLi in hexane (1.1 equiv), and the mixture was stirred for 20 min. In the meantime, a solution of 235 mg (1.13 mmol) of 1-(chlorodimethylsilyl)indene (**5**) in 5 mL of hexane was added at −20 °C to a solution of 440 mg (2.25 mmol) of **1b** in 15 mL of hexane. The reaction mixture was stirred for 5 min, and the solution was separated by filtration. The filtrate was directly added to the freshly prepared Schlosser

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Table 2. Ethylene Polymerization Data[a]

catalyst	m [mg]; *n* [μmol]	reaction time [min]	yield PE [mg]	activity[b]	M_w	PDI [M_w/M_n]
4a	2.7; 6.14	30	100	32	51 000	16.87
4b	2.2; 4.44	30	117	53	87 000	18.94
4c	2.6; 5.25	30	96	37	457 000/6800[c]	4.07/2.90[c]
7	1.9; 3.88	5	687	2125	78 000	4.11
7	2.8; 5.72	15	915	640	446 000	14.02
7	2.4; 4.90	30	1800	734	717 000	20.00
Cp_2ZrCl_2	2.1;7.18	15	2250	1253		

[a] Activation with MAO (Al:Cr 1000), 1 atm pressure of ethylene, $T = 25$ °C, toluene (40 mL). [b] Activity = g(PE) mmol(precat.)$^{-1}$ bar(ethylene)$^{-1}$ h^{-1}. [c] Bimodal distribution with two distinct maxima.

Table 3. Crystallographic Data for Compounds 3c-H, 4a, 4b, 4c, and 7

	3c-H	**4a**	**4b**	**4c**	**7**
formula	$C_{22}H_{39}N_3Si$	$C_{18}H_{30}Cl_2CrN_3Si$	$C_{22}H_{38}Cl_2CrN_3Si$	$C_{44}H_{76}Cl_4Cr_2N_6Si_2$	$C_{22}H_{32}Cl_2CrN_3Si$
molecular weight [g/mol]	373.65	439.44	495.54	991.08	489.50
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$
cryst dimens [mm^3]	0.49 × 0.42 × 0.35	0.29 × 0.23 × 0.09	0.48 × 0.37 × 0.25	0.33 × 0.17 × 0.09	0.35 × 0.15 × 0.02
a [Å]	12.956(1)	11.255(1)	17.112(2)	12.377(2)	9.6270(4)
b [Å]	14.538(2)	12.359(1)	8.925(1)	12.957(1)	27.148(1)
c [Å]	15.102(2)	15.035(2)	16.633(2)	16.870(2)	18.324(1)
α [deg]	97.509(3)				
β [deg]	106.363(3)	93.670(3)	96.069(3)	109.259(4)	91.220(3)
γ [deg]	115.410(3)				
V [Å^3]	2359.0(4)	2087.0(4)	2525.9(5)	2553.9(5)	4787.9(4)
Z	4	4	4	2	8
D_{calc} [g/cm^3]	1.052	1.399	1.303	1.289	1.358
μ [mm^{-1}]	0.110	0.868	0.726	0.718	0.765
T [K]	133	133	133	133	100
θ range [deg]	1.47−30.51	1.81−28.28	1.20−30.53	1.79−25.59	2.25−26.37
no. of rflns collected	28 156	37 221	50 767	5212	102 684
no. of unique rflns	14 129	5173	7710	5292	9771
$R1$ ($I_o > 2\sigma(I_o)$)	5.42%	4.37%	2.98%	7.08%	4.27%
$wR2$ (all data)	14.89%	11.56%	8.03%	16.22%	10.16%
GOF	0.91	1.09	1.05	0.99	1.06
largest hole and peak (e·Å^{-3})	−0.40/0.38	−0.42/0.62	−0.29/0.42	−0.66/0.47	−0.58/0.93

base. The suspension was allowed to reach ambient temperature overnight. Filtration, washing with several portions of hexane, and removal of all volatiles afforded 377 mg (0.93 mmol, 83%) of (**6**)K as a white solid.

Anal. Calcd for $C_{22}H_{32}KN_3Si$: C, 65.13; H, 7.95; N, 10.36. Found: C, 63.98; H, 7.57; N, 9.76. ^1H NMR (400 MHz, THF-d_8): 7.59 (1H, m, IndC5), 7.27 (1H, m, IndC7), 6.76 (1H, d, IndC2), 6.40 (2H, m, IndC8/9), 6.02 (1H, dd, IndC3), 4.73 (2H, sept, C*H*CH$_3$), 1.96 (6H, s, NCCH$_3$), 1.11 (12 H, d, CHC*H*$_3$), 0.32 (6 H, s, SiCH$_3$). $^{13}C\{H\}$ NMR (100.62 MHz, THF-d_8): 145.5 (NCN), 136.0 (C8), 134.0 (C9), 126.4 (C2), 120.9 (C4), 118.8 (C7), 114.2 (N*C*CH$_3$), 113.5, 113.2 (C5/6), 104.3 (C1), 96.7 (C3) 45.3 (*C*HCH$_3$), 21.7 (CH*C*H$_3$), 10.2 (NC*C*H$_3$), 5.0 (SiCH$_3$).

General Procedure for the Synthesis of the Chromium Tetramethylcyclopentadienyl Complexes 4. A solution of [CrCl$_3$(THF)$_3$] (1 equiv) in THF was treated with 1 equiv of (**3**)K at ambient temperature and was stirred for 30 min. The solvent was removed *in vacuo*, and the resulting oily product was washed with hexane and extracted with toluene. Filtration and removal of the solvent afforded the complexes **4** as blue (**4a**, **4b**) and green (**4c**) solids, respectively. Analytically pure crystals were obtained by diffusion of hexane into a saturated dichloromethane solution (**4a**) and by cooling (−35 °C) of a saturated toluene solution (**4b**) or a saturated diethyl ether solution (**4c**), respectively.

4a. Yield: 71%. Anal. Calcd for $C_{18}H_{30}Cl_2CrN_3Si$: C, 49.20; H, 6.88; N, 9.56. Found: C, 47.78; H, 6.57; N, 8.91. MS(EI): 438 (100) [M$^+$], 316 (96) [M$^+$ − CrCl$_2$], 196 (52) [M$^+$ − CrCl$_2$ − C$_5$Me$_4$].

4b. Yield: 43%. Anal. Calcd for $C_{22}H_{38}Cl_2CrN_3Si$: C, 53.32; H, 7.73; N, 8.48. Found: C, 53.25; H, 7.71; N, 8.27. MS(EI): 494 (31) [M$^+$], 372 (100) [M$^+$ − CrCl$_2$], 252 (30) [M$^+$ − CrCl$_2$ − C$_5$Me$_4$].

4c. Yield: 14%. No satisfactory elemental analysis could be obtained.

Synthesis of the Chromium Indenyl Complex 7. To a solution of 72 mg (0.19 mmol) of [CrCl$_3$(THF)$_3$] in 8 mL of THF was added a solution of 78 mg (0.19 mmol) of (**6**)K in 7 mL of THF. The reaction mixture was stirred for 60 min followed by evaporation of the solvent. The oily residue was extracted with 15 mL of toluene, and the solution was separated by filtration. Removal of the solvent *in vacuo* and washing with hexane afforded 55 mg (0.11 mmol, 58%) of **7** as a green solid.

Anal. Calcd for $C_{22}H_{32}Cl_2CrN_3Si$: C, 53.98; H, 6.59; N, 8.58. Found: C, 53.12; H, 6.66; N, 8.17. MS(EI): 488 (30) [M$^+$], 367 (43) [M$^+$ − CrCl$_2$], 115 (82) [Ind$^+$], 110 (100) [M$^+$ − Ind − 2 ^{i}Pr − SiMe$_2$].

Single-Crystal X-ray Structure Determinations. Numerical details are presented in Table 3. Crystals were mounted on glass fibers and measured on area detectors (Bruker SMART APEX) at low temperature (Mo Kα radiation, $\lambda = 0.71073$ Å). Absorption corrections were performed using multiscans (program SADABS, for **4c** TWINABS). The structures were refined on F^2 using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen, Germany). Hydrogen atoms were included using rigid methyl groups allowed to rotate but not tip, or a riding model. *Exceptions/special features*: For **3c**-H, the tetramethylcyclopentadienyl ring of one independent molecule is disordered over two positions. Appropriate similarity restraints were applied. Dimensions of disordered moieties should however be interpreted with caution. For **4c**, the crystal was twinned by 180° rotation about the *a* axis. The scale factor was 0.482(2). The twin refinement with the HKLF 5 option means that the number of independent reflections may not be well-defined.

Ethylene Polymerization Experiments. In a drybox, a solution of the chromium precatalyst (2−3 mg) in toluene (30 mL) was treated with 1000 equiv (Al:Cr 1000) of MAO by using a 10 wt % solution of MAO in toluene [EURECEN AL 5100-10-toluene from Crompton GmbH, Bergkamen, *d* = 0.89 g/mL, fw (MAO) = 58 g/mol]. Additional toluene was added to reach a total volume of 40 mL, and the reaction flask was connected to a Schlenk line. All tubes were evacuated several times and subsequently filled with dried ethylene gas. The polymerization was started by introducing a gas stream to the reaction mixture under vigorous stirring. The reaction mixture was quenched by addition of 10 mL of methanol and 10 mL of 0.1 M HCl. The precipitated polymer was collected by filtration, washed several times with 5 mL portions of methanol, and dried at 70 °C overnight.

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Supporting Information Available: Crystal data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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