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New Chromium(III) Complexes as Highly Active Catalysts for Olefin Polymerization

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Summary: Cyclopentadienyl ligands functionalized by quinoline or N,N-dimethylaniline have an ideal and rigid geometry for the formation of half-sandwich compounds. As a result, stable chromium(III) complexes **5−8** *with intramolecular nitrogen coordination have been obtained. Treatment with MAO leads to highly active, temperature-stable catalysts for the polymerization of ethylene.*

Chromium-based catalysts play a significant role in coordination polymerization of α-olefins. Heterogeneous, silica-supported systems such as Phillips[1] or Union Carbide[2] catalysts are among the most important catalysts for the production of polyolefins and have been put to widespread commercial use. Although homogeneous metallocene type catalysts[3] or the so-called *constrained geometry catalysts*[4] have revolutionized olefin polymerization, homogeneous chromium catalysts have been investigated by only a few groups. The most promising single-site chromium catalysts are half-sandwich Cr(III) compounds which are coordinated by an additional nitrogen donor.[5,6] These complexes exhibit high polymerization activities for ethylene, and some of them are also capable of copolymerizing ethylene with higher α-olefins. However, many of the systems described so far decompose slowly after activation or are unstable during polymerizations at high temperatures (>80 °C), which are important for industrial application.

To increase the stability of Cr(III) half-sandwich compounds, we used quinolyl- and *N*,*N*-dimethylanilinyl-functionalized cyclopentadienyl ligands. In these chelate ligands a neutral nitrogen donor group is attached via a rigid C_2 spacer to a cyclopentadienyl system in a predefined geometry. In comparison to similar ligands with flexible spacer groups, the formation of chelate complexes is favored. Due to the flexibility of many chelate ligands, intermolecular donor−metal interactions and formation of insoluble coordination polymers can occur.[6c,7] This behavior, which is undesired for homogeneous catalysis, is impossible with rigid, quinolyl-substituted ligands such as **1**, **2**, and **4** and very unlikely with **3** (Chart 1).

The synthesis of the novel chromium complexes is straightforward. The ligands **1−4** were obtained in a one-step preparation and subsequent deprotonation of the corresponding cyclopentadiene derivatives with potassium hydride (**1**, **2**, **4**) or *n*-butyllithium (**3**), respectively.[8] Reaction of **1−4** with $CrCl_3(THF)_3$ leads to the half-sandwich compounds **5−8**, which were isolated in 37−70% yield.[9] The quinolyl-substituted complexes **5**, **6**, and **8** are green, and the aniline-substituted **7** is blue. Whereas the complexes **5−7** are air-stable for several hours, the indenyl derivative **8** decomposes slowly on exposure to air. A magnetic moment of 3.6 μ_B was determined at room temperature, consistent with three unpaired electrons. The ^1H NMR spectra exhibit the expected number of signals in a range between −100 and +80 ppm. Crystals suitable for X-ray diffraction have been obtained from the compounds **5** and **7**[10] (see Figures 1 and 2). In both complexes, the chromium atom is bonded to the nitrogen donor and is η^5-coordinated by the cyclopentadienyl ring. The metal atoms are not located exactly below the centers of the five-membered rings but are shifted slightly toward the tethered donor ligands. The five-membered rings and the quinoline or the dimethylaniline, respectively, are nearly orthogonal (85.7° in **5** and 87.3° in **7**). Consequently, the nitrogen donor atoms are ideally positioned for an interaction with the metal atoms. The nitrogen−chromium distance in **5** (2.09 Å) is somewhat shorter than in **7** (2.25 Å).

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(9) Preparation of the chromium complexes **5−8**: a solution of the cyclopentadienide **1−4** in thf was added to a solution of $CrCl_3(thf)_3$ in thf at room temperature. After 15 h the solvents were evaporated, the residues washed with *n*-hexane, and the complexes extracted with hot toluene. Isolated yields: 70% (**5**), 53% (**6**), 79% (**7**), 37% (**8**).

(10) X-ray data: **5**, $C_{18}H_{18}Cl_2CrN$, orthorhombic, *Pbca*, $a = 14.1181(2)$ Å, $b = 13.6030(2)$ Å, $c = 17.5427(2)$ Å, $V = 3369.05(8)$ Å^3, $Z = 8$, $d_{calcd} = 1.464$ g/cm^3, R1 = 0.0305, wR2 = 0.0823; **7**, $C_{17}H_{22}Cl_2CrN$, monoclinic, $P2_1/a$, $a = 7.974(5)$ Å, $b = 25.353(14)$ Å, $c = 8.563(4)$ Å, $\beta = 98.43(4)°$, $V = 1712(2)$ Å^3, $Z = 4$, $d_{calcd} = 1.409$ g/cm^3, R1 = 0.0441, wR2 = 0.0908.

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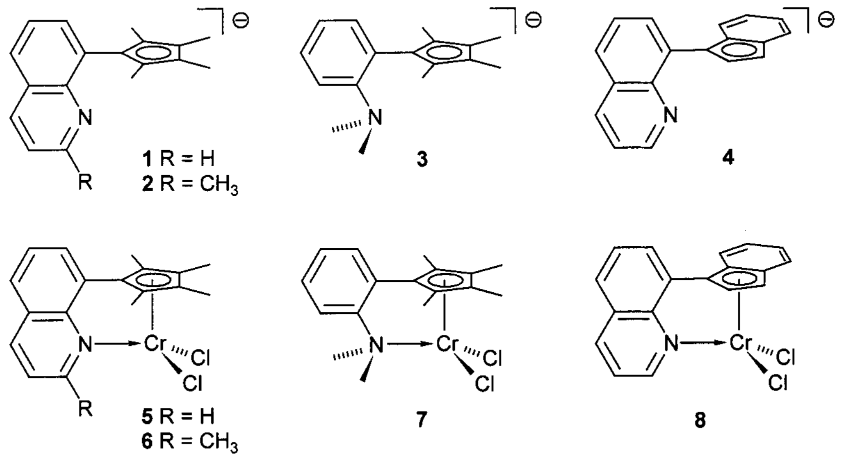
Chart 1



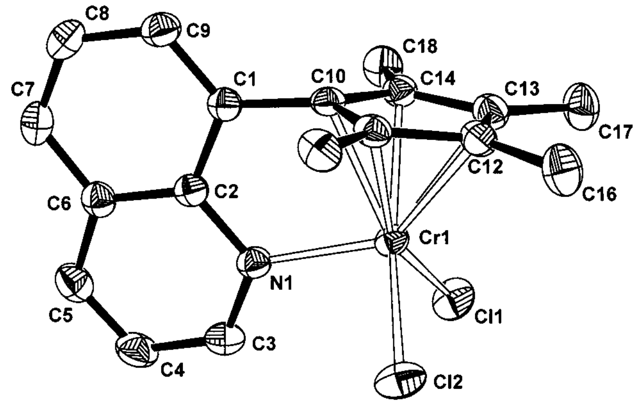


Figure 1. Solid-state structure of **5**. Selected bond lengths (Å) and angles (deg): $Cr1-C_{Cp} = 2.173(2)-2.266(2)$, $Cr1-Cl1 = 2.291(1)$, $Cr1-Cl2 = 2.292(1)$, $Cr1-N1 = 2.088(2)$; $Cl1-Cr1-Cl2 = 99.01(2)$, $C2-N1-Cr1 = 116.7(1)$, $Cr1-N1-C3 = 125.1(1)$, $C3-N1-C2 = 118.1(2)$.

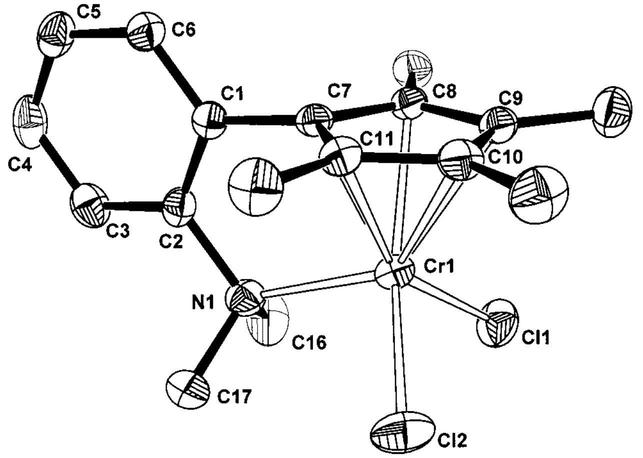


Figure 2. Solid-state structure of **7**. Selected bond lengths (Å) and angles (deg): $Cr1-C_{Cp} = 2.175(4)-2.275(4)$, $Cr1-Cl1 = 2.298(2)$, $Cr1-Cl2 = 2.312(1)$, $Cr1-N1 = 2.251(3)$; $Cl1-Cr1-Cl2 = 98.1(1)$, $C2-N1-Cr1 = 111.3(2)$, $C17-N1-C16 = 107.7(4)$.

The chromium complexes **5**, **6**, and **8**, which bear the quinoline substituent, react with methylaluminoxane (MAO) in toluene to give violet solutions. The blue complex **7** turns green upon treatment with MAO. In the absence of air, these solutions are stable at room temperature for several weeks, and we were not able to detect decomposition products. All MAO-activated toluene solutions are highly active systems for the polymerization of ethylene. Preliminary polymerization experiments were conducted simply by passing the gaseous olefin over a magnetically stirred catalyst solution at atmospheric pressure.[11] At high catalyst concentrations ($\gg 50$ μmol/L) the solution temperature raises considerably, due to the exothermic polymerization. In addition, the reaction rates are lower, probably because of a limited mass transfer of ethylene. To avoid diffusion control over the reaction rate and to keep the temperature increase below 3°, the experiments were conducted at lower catalyst concentrations (<40 μmol/L) and the flask was kept in a water bath. The polymerization results are summarized in Table 1. For comparison of catalyst activities, zirconocene dichloride (Cp_2ZrCl_2) was used as a reference under the same conditions (Table 1, entry 11). The activity for this catalyst was 938 kg mol^{-1} h^{-1} bar^{-1}. The complexes **5**, **7**, and **8** show activities for ethylene of about 3000 kg mol^{-1} h^{-1} (entries 1, 2, 7, and 9). Substitution at the quinoline leads to a decrease in activity (complex **6**, entry 5). The polyethylenes exhibit melting points between 125 and 132 °C; only the polymer obtained at 110 °C melts somewhat lower (119 °C). The molecular weights are in the range of 100 000−500 000 with a polydispersity index between 2 and 4. We have tested the time and temperature stability of the new catalysts. The polymerization was stopped after 10 min by replacing the ethylene with nitrogen gas, and the resulting turbid solution was kept at room temperature for 48 h. The polymerization restarts immediately by addition of new ethylene gas (entry 2). The overall activity does not decrease significantly. In another experiment the polymerization was run in refluxing toluene at 110 °C. The solution absorbs ethylene, and the reaction mixture remains clear until the experiment is stopped. The resulting polyethylene precipitates during cooling of the solution to room temperature. The catalyst activity is

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(11) Polymerization conditions: 2−5 μmol of chromium complex was dissolved in 150 mL of toluene, and MAO (30% solution in toluene) was added. The solution was stirred magnetically, and ethylene (propylene respectively) was passed over it. The reaction was terminated by addition of a solution of HCl in methanol, and the solid polymer was filtered off, washed with HCl/MeOH, and dried.

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Table 1. Polymerization of Ethylene and Propylene at Atmospheric Pressure

entry	compd	amt of Cr (μmol)	*t* (min)	Cr:MAO	*T* (°C)	monomer	amt of polymer (g)	acitivity (kg mol^{-1} h^{-1} bar^{-1})
1	**5**	2.8	30	1:1000	21	ethylene	4.97	3550
2	**5**	2.8	10 + 20	1:1000	21	ethylene	4.31	3080
3	**5**	2.8	30	1:1000	110	ethylene	0.83	593
4	**5**	5.6	120	1:1000	21	propylene	1.20	107
5	**6**	5.4	30	1:1000	21	ethylene	1.80	667
6	**6**	5.4	180	1:1000	21	propylene	0.18	11
7	**7**	5.2	30	1:1000	21	ethylene	8.6	3310
8	**7**	7.8	90	1:1000	21	propylene	0.53	45
9	**8**	5.6	30	1:1000	21	ethylene	10.2	3640
10	**8**	5.6	240	1:1000	21	propylene	1.06	47
11	Cp_2ZrCl_2	4.2 (Zr)	30	1:1000	21	ethylene	1.97	938

lower because of the lower solubility of ethylene (entry 3). However, when the hot reaction mixture is cooled again, the activity of the system recovers. The activities for propylene polymerizations are much lower (entries 4, 6, 8, and 10). This is not unexpected, because chromium compounds are known to have much lower activities for the polymerization of higher α-olefins compared to ethylene. The polypropylene obtained has a rubberlike consistency. NMR spectroscopy demonstrates the atactic nature of the polymer.

The preliminary polymerization results reported are promising. We are now investigating the properties of the new catalysts and the resulting polymers in more detail.

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Supporting Information Available: Text giving synthetic procedures and spectroscopic data for all complexes and tables giving X-ray crystal structure data for **5** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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