

Quinolyl-functionalised Cp–chromium polymerisation catalysts: synthesis and crystal structures of alkylation products

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Abstract

The quinolyl-functionalised Cp–chromium(III) complexes **1** and **2**, which serve as precursors for highly active olefin polymerisation catalysts, were alkylated with benzylmagnesium chloride. From these reactions, the new metal complexes **4**, **5** and **6** were obtained and structurally characterised. The expected alkylchromium compound **4** is formed together with complex **5**, where the nucleophile replaced a hydrogen atom at the quinoline substituent. The dinuclear complex **6** is formed by nucleophile addition, rearrangement and dimerisation.

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1. Introduction

Beside titanium-based Ziegler–Natta catalysts, chromium compounds play a significant role in coordination polymerisation 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. Homogeneous metallocene catalysts have revolutionised olefin polymerisation and many highly active systems with other transition metals have been developed [3].

Despite the importance of chromium in the field of olefin polymerisation, homogeneous chromium catalysts have been investigated by a few groups only. The most promising single-site systems consist of amino-functionalised cyclopentadienyl ligands coordinated to a chromium(III) centre [4].

We have developed similar systems (**1**, **2**, **3**) where the spacer group which connects the nitrogen donor with the Cp–ligand is incorporated into an aromatic system

[5]. These compounds show advantageous catalytic behaviour like very high activity and temperature stability. In addition, they are able to incorporate a lot of comonomer into high molecular weight polymers. These properties make them attractive for industrial application [6] (Fig. 1).

In order to activate compounds like **1–3**, an alkylation at the chromium atom followed by abstraction of a negatively charged ligand is necessary. These two reactions can be achieved in one step by an excess of methylaluminoxane (MAO). For a two step activation, the catalyst precursors must first be alkylated. The synthesis of dialkylated Cp–chromium compounds have been demonstrated by several groups [4,7,8]. In principle, from such dialkyl-Cp–chromium compounds an alkyl group can be abstracted by a Lewis acid (e.g. MAO, $B(C_6F_5)_3$) or by a proton source (e.g. DMAB = dimethylanilinium tetrakis(pentafluorophenyl)borate), leading to active catalysts of the type $[CpCr(L)R]^+$. In the case of compounds **1–3**, activation with MAO as well as activation with AlR_3 /DMAB leads to highly active catalyst systems. However, nucleophiles like Grignard- or organolithium reagents are known to attack pyridine derivatives in 2-position relative to the nitrogen atom, a reaction which is known as Ziegler-alkylation [9]. Recently alkylation reactions on diimi-

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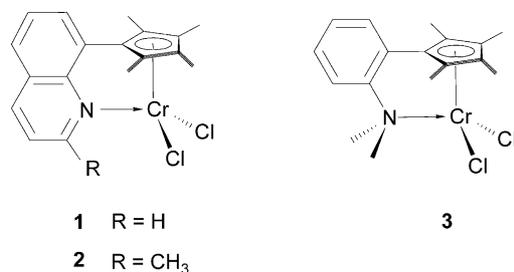


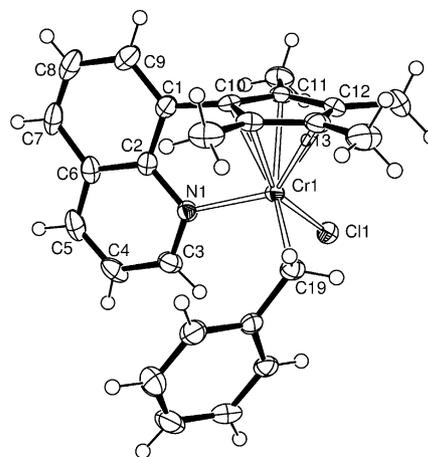
Fig. 1. Olefin polymerisation catalyst precursors 1–3.

nopyridinium based catalysts have been reported to lead also to ring alkylation [10]. In the case of quinolyl-functionalised catalysts we have also observed, that some alkylating agents react not only at the metal atom, but also at the quinolyl moiety. In order to investigate the catalyst activation, we now report about reactions of **1** and **2** with benzylmagnesium chloride.

2. Results and discussion

The chromium complex **1** was treated with one equivalent of benzylmagnesium chloride. A mixture of two products formed: the violet complex **4**, well soluble in toluene, and the green compound **5** with slightly lower solubility. Due to this similar solubility behaviour a complete separation of the two products was not possible. The complete yield of this reaction is about 80% with a ratio **4**:**5** = 1:1.3. The UV–Vis spectrum of **5** possesses two significant bands in the same range as the educt **1**, characteristic of dichloro-chromium complexes [11]. The MS-spectrum too shows the existence of two chlorine atoms and also the presence of a benzyl group incorporated into the ligand. The UV–Vis spectrum of the other product (**4**) is typical for monoalkylated-chromium(III) compounds [10]. The ratio of the two products shows, that reaction of the Grignard reagent at the ligand is faster than the chloride replacement at the chromium atom. At lower temperatures even more of complex **5** is obtained (Scheme 1).

Crystals of **4** and **5**, suitable for X-ray diffraction, were obtained from a mixture of toluene and hexane at room temperature. The results of the structure analysis reveal, that the carbon nucleophile have substituted a chlorine atom in the case of **4** (see Fig. 2) whereas reaction at the C3 atom (which is adjacent to the

Fig. 2. Molecular structure of **4**.

nitrogen atom in the quinoline substituent) occurred in the case of complex **5** (see Fig. 3) (Tables 1 and 2).

The coordination geometries around the chromium atoms are similar to the geometry in **1** [5]. Complex **4** crystallises in the monoclinic space group $P2_1/n$, **5** in the triclinic $P\bar{1}$. The Cr–N distances lie in the expected range with 2.111 Å (**4**) and 2.154 Å (**5**) [4c,5]. The distance between the metal atom and C19 in **4** (2.119 Å) is characteristic of carbon–chromium σ -bonds [4c,12,13]. In **4** as well as in **5** the almost planar quinoline ring (max. deviation from planarity 0.02 Å in **4** and 0.06 Å in **5**) and the Cp ring (max. deviation from planarity 0.01 Å in both cases) are practically

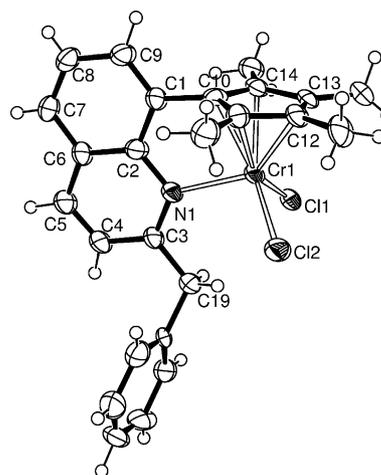
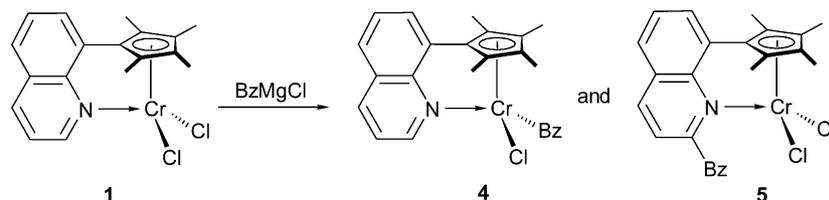
Fig. 3. Molecular structure of **5**.Scheme 1. Formation of the compounds **4** and **5** by alkylation of **1**.

Table 1
Selected bond lengths (Å) and bond angles (°) of **4**

Bond lengths			
Cr(1)–N(1)	2.111(2)	C(19)–C(20)	1.469(4)
Cr(1)–Cl(1)	2.306(1)	C(1)–C(2)	1.417(4)
Cr(1)–C(19)	2.119(3)	C(1)–C(9)	1.381(4)
Cr(1)–C(10)	2.201(3)	C(9)–C(8)	1.402(5)
Cr(1)–C(11)	2.256(3)	C(8)–C(7)	1.351(5)
Cr(1)–C(12)	2.279(3)	C(7)–C(6)	1.427(4)
Cr(1)–C(13)	2.277(3)	C(6)–C(2)	1.414(4)
Cr(1)–C(14)	2.211(3)	C(6)–C(5)	1.409(5)
C(10)–C(11)	1.418(4)	C(5)–C(4)	1.357(5)
C(11)–C(12)	1.415(4)	C(4)–C(3)	1.404(4)
C(12)–C(13)	1.419(4)	C(3)–N(1)	1.325(4)
C(13)–C(14)	1.419(4)	C(2)–N(1)	1.384(3)
C(14)–C(10)	1.439(4)		
Bond angles			
N(1)–Cr(1)–Cl(1)	98.3(1)	Cr(1)–N(1)–C(2)	116.8(2)
N(1)–Cr(1)–C(19)	103.5(1)	Cr(1)–N(1)–C(3)	125.4(2)
Cl(1)–Cr(1)–C(19)	94.9(1)	C(2)–N(1)–C(3)	117.7(2)
C(2)–C(1)–C(9)	118.9(3)	C(1)–C(10)–C(11)	124.5(2)
C(2)–C(1)–C(10)	116.8(2)	C(1)–C(10)–C(14)	125.5(2)
C(9)–C(1)–C(10)	124.3(3)	C(11)–C(10)–C(14)	108.7(2)
Cr(1)–C(19)–C(20)	113.6(2)		

Table 2
Selected bond lengths (Å) and bond angles (°) of **5**

Bond lengths			
Cr(1)–N(1)	2.154(4)	C(3)–C(19)	1.495(8)
Cr(1)–Cl(1)	2.308(2)	C(1)–C(2)	1.413(7)
Cr(1)–Cl(2)	2.309(2)	C(1)–C(9)	1.359(7)
Cr(1)–C(10)	2.165(5)	C(9)–C(8)	1.410(8)
Cr(1)–C(11)	2.203(5)	C(8)–C(7)	1.368(8)
Cr(1)–C(12)	2.272(5)	C(7)–C(6)	1.402(7)
Cr(1)–C(13)	2.273(5)	C(6)–C(2)	1.417(7)
Cr(1)–C(14)	2.214(5)	C(6)–C(5)	1.410(7)
C(10)–C(11)	1.429(7)	C(5)–C(4)	1.356(8)
C(11)–C(12)	1.426(7)	C(4)–C(3)	1.424(7)
C(12)–C(13)	1.401(7)	C(3)–N(1)	1.343(6)
C(13)–C(14)	1.440(7)	C(2)–N(1)	1.394(6)
C(14)–C(10)	1.404(7)		
Bond angles			
N(1)–Cr(1)–Cl(1)	97.7(1)	Cr(1)–N(1)–C(2)	114.5(3)
N(1)–Cr(1)–Cl(2)	101.0(1)	Cr(1)–N(1)–C(3)	127.2(3)
Cl(1)–Cr(1)–Cl(2)	100.2(1)	C(2)–N(1)–C(3)	118.2(4)
C(2)–C(1)–C(9)	120.8(5)	C(1)–C(10)–C(11)	123.6(5)
C(2)–C(1)–C(10)	116.2(4)	C(1)–C(10)–C(14)	125.5(4)
C(9)–C(1)–C(10)	122.9(4)	C(11)–C(10)–C(14)	109.8(4)

orthogonal. Consequently, the nitrogen donor atoms are ideally positioned for an interaction with the metal atoms. The angles around N1 sum up to 359.9° in both cases, so that the lone pair at nitrogen points directly to the metal centre.

In order to avoid substitution at the ligand, complex **2** was used where the reactive C3 position at the quinoline substituent is blocked by a CH₃ group. Addition of one equivalent of benzylmagnesium chloride to a solution of

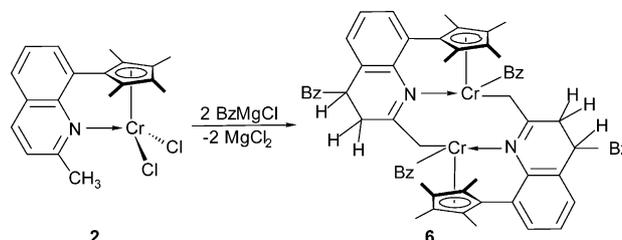
2 in THF did not lead to isolable products. Therefore the reaction was performed with two equivalents of the alkylating agent. By this procedure compound **6** was isolated by extraction of the reaction mixture with hexane (Scheme 2). The EI-mass spectrum shows the presence of a dimeric compound with four benzyl groups. The isotopic pattern proves that no chlorine atoms are present.

Crystals of **6** precipitated from the solution at room temperature. The result of the X-ray analysis is shown in Fig. 4 (Table 3).

One benzyl group replaced a chlorine atom, and the second one added to the heterocycle at the *para* position (C5) relative to the nitrogen atom. This leads to an activation of the CH₃ group from which a hydrogen atom is transferred to the neighbouring carbon atom. The resulting complex fragment dimerises to give the complex **6**. During this sequence, one double bond of the quinoline is reduced leading to a C–C single bond (C4–C5 1.513 Å). The molecular ion of **6** (*m/z* = 992) is not visible in the mass spectrum, but an ion at *m/z* = 988 (6%). Consequently four hydrogen atoms are eliminated during ionisation and the aromaticity of the two quinoline systems is recovered.

3. Conclusion

At the beginning of the activation of catalyst precursors for olefin polymerisation an alkylation at the metal centre is required. In a second step, a chloride or R[−] is abstracted leading to cationic complexes which are active catalysts. In the case of quinolyl-substituted compounds, a side reaction may occur depending on the alkylating agent. When MAO is used, no alkylation reaction at the quinolyl moiety was observed. However, organolithium reagents as well as Grignard reagents are highly reactive for the substitution at the quinoline and at the metal. Therefore, the quinolyl substituted product **5** as well as the benzyl chromium complex **4** were isolated and the solid state structures were determined. Surprisingly, when the quinoline ring is already substituted, another side reaction was found. By this route, the unprecedented dinuclear compound **6** was isolated and structurally identified. These investigations are



Scheme 2. Synthesis of the dinuclear compound **6** from addition of BzMgCl to **2**.

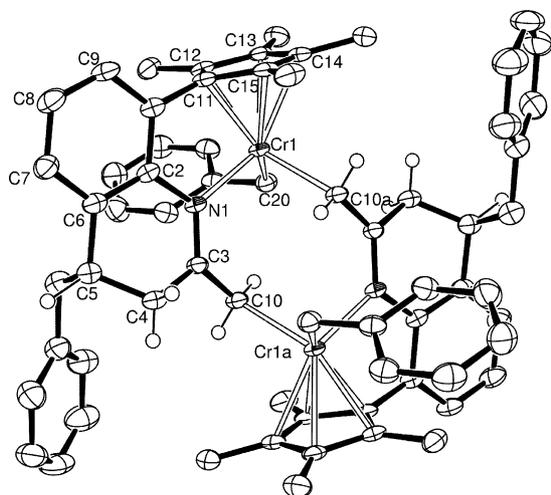


Fig. 4. Molecular structure of **6**. Only H atoms at C4, C5 and C10 are shown for clarity.

Table 3
Selected bond lengths (Å) and bond angles (°) of **6**

Bond lengths			
Cr(1)–N(1)	2.112(2)	C(3)–C(10)	1.418(3)
Cr(1)–C(20)	2.130(2)	C(1)–C(2)	1.397(3)
Cr(1)–C(10A)	2.186(2)	C(1)–C(9)	1.392(3)
Cr(1)–C(11)	2.213(2)	C(9)–C(8)	1.384(4)
Cr(1)–C(12)	2.251(2)	C(8)–C(7)	1.384(4)
Cr(1)–C(13)	2.304(2)	C(7)–C(6)	1.396(3)
Cr(1)–C(14)	2.319(2)	C(6)–C(2)	1.406(3)
Cr(1)–C(15)	2.290(2)	C(6)–C(5)	1.505(3)
C(11)–C(12)	1.428(3)	C(5)–C(4)	1.513(3)
C(12)–C(13)	1.425(3)	C(4)–C(3)	1.515(3)
C(13)–C(14)	1.417(3)	C(3)–N(1)	1.329(3)
C(14)–C(15)	1.428(3)	C(2)–N(1)	1.435(3)
C(15)–C(11)	1.418(3)		
Bond angles			
N(1)–Cr(1)–C(20)	106.8(1)	Cr(1)–N(1)–C(2)	115.4(1)
N(1)–Cr(1)–C(10A)	93.3(1)	Cr(1)–N(1)–C(3)	126.4(1)
C(20)–Cr(1)–C(10A)	99.8(1)	C(2)–N(1)–C(3)	117.8(2)
C(2)–C(1)–C(9)	120.1(2)	C(1)–C(11)–C(12)	123.2(2)
C(2)–C(1)–C(11)	117.5(2)	C(1)–C(11)–C(15)	126.6(2)
C(9)–C(1)–C(11)	122.3(2)	C(12)–C(11)–C(15)	109.4(2)
N(1)–C(3)–C(10)	123.6(2)	C(3)–C(10)–Cr(1A)	120.8(2)

important for the understanding of different catalyst behaviours depending on the activating agents used.

4. Experimental

All manipulations were carried out under a nitrogen atmosphere with anhydrous solvents saturated with nitrogen. Glassware was heated under vacuum prior to use. Benzylmagnesium chloride [14], dichloro- η^5 -[2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl]chromium(III) (**1**) [5] and dichloro- η^5 -[2,3,4,5-tetramethyl-1-(2-methyl-8-quinolyl)cyclopentadienyl]chro-

mium(III) (**2**) [15] were synthesized by literature procedures.

4.1. Synthesis of benzylchloro- η^5 -[2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl]chromium(III) (**4**) and dichloro- η^5 -[2,3,4,5-tetramethyl-1-[8-(2-benzyl)quinolyl]cyclopentadienyl]chromium(III) (**5**)

A 2.51 M solution of benzylmagnesium chloride in diethylether (2.1 ml, 5.2 mmol) was added dropwise to a green solution of 1.92 g (5.2 mmol) of dichloro- η^5 -[2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl]chromium(III) in 60 ml of THF. The colour changed to purple and, after 2 h, four drops of 1,4-dioxane were added to aid the precipitation of magnesium chloride. The solvent was removed in vacuum and the solid was extracted with 50 ml of toluene to obtain a violet solution. Addition of another 100 ml of toluene afforded a green coloured second fraction. The solvents were removed in vacuum to obtain 0.82 g (1.9 mmol, 36%) of a violet solid and 1.10 g (2.4 mmol, 46%) of a green powder, respectively. After 24 h in toluene–hexane at room temperature (r.t.) small crystals of the complexes **4** and **5**, respectively were obtained from each fraction.

Complex 4: UV–Vis (THF), λ_{\max} (ϵ): 520 (710) nm. MS(EI): m/z (%) = 426 (1) [M^+], 334 (100) [$M^+ - C_7H_8$], 298 (16) [$M^+ - C_7H_8 - HCl$], 91 (72) [$C_7H_7^+$].

Complex 5: UV–Vis (THF), λ_{\max} (ϵ): 474 (531); 682 (542) nm. MS(EI): m/z (%) = 460 (1) [M^+], 424 (4) [$M^+ - HCl$], 388 (2) [$M^+ - 2HCl$], 339 (100) [ligand + H^+], 91 (82) [$C_7H_7^+$].

4.2. Synthesis of the dinuclear compound **6**

A 2.51 M solution of benzylmagnesium chloride in diethylether (1.42 ml, 3.6 mmol) was added dropwise to a green solution of 1.39 g (3.6 mmol) of dichloro- η^5 -[2,3,4,5-tetramethyl-1-[8-(2-methyl)quinolyl]cyclopentadienyl]chromium(III) in 50 ml of THF. No change of colour was observed. After 2 h at r.t., four drops of 1,4-dioxane were added and the solvents were removed in vacuum. The product was extracted with hexane (3 \times 50 ml) and crystallised in toluene/hexane at room temperature to obtain crystals of complex **6**.

MS(EI): m/z (%) = 988 (6) [$M^+ - 4H$], 900 (38) [$M^+ - C_7H_8$], 806 (12) [$M^+ - 4H - 2Bz$], 403 (32) [$C_{26}H_{25}NCr^+$], 349 (100) [$C_{26}H_{23}N^+$].

4.3. X-ray crystal structure determinations of **4**, **5** and **6**

Crystal data were collected for **4**, **5** and **6** with a Bruker AXS area detector SMART 1000 (Mo– K_{α} radiation, ω -scan, $T = -100$ °C). The structures were solved by direct methods and refined by full-matrix least-squares against F^2 with all reflections using the SHELXTL-program system [16]. All non-hydrogen atoms

Table 4
Crystal data and structure refinement details for **4**, **5** and **6**

	4	5	6
Empirical formula	C ₂₅ H ₂₅ ClCrN	C ₂₅ H ₂₄ Cl ₂ CrN	C ₆₆ H ₆₈ Cr ₂ N ₂
Formula weight	426.91	507.42	993.22
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
Unit cell dimensions			
<i>a</i> (Å)	10.1365(9)	9.8385(6)	10.9101(3)
<i>b</i> (Å)	20.695(2)	10.0094(7)	11.3734(3)
<i>c</i> (Å)	11.095(1)	13.8402(9)	12.4951(3)
α (°)	90	77.256(5)	67.848(2)
β (°)	114.959(2)	71.560(5)	65.251(2)
γ (°)	90	77.240(5)	87.142(2)
<i>V</i> (Å ³)	2110.0(3)	1244.2(1)	1293.3(1)
<i>Z</i>	4	2	1
<i>D</i> _{calc} (g cm ⁻³)	1.344	1.354	1.275
Absorption coefficient (mm ⁻¹)	0.679	0.691	0.464
<i>F</i> (000)	892	528	526
Crystal size (mm ³)	0.52 × 0.07 × 0.07	0.30 × 0.20 × 0.04	0.30 × 0.20 × 0.14
Theta range for data collection (°)	1.97–26.38	1.57–23.25	1.95–28.38
Index ranges	−12 ≤ <i>h</i> ≤ 11, 0 ≤ <i>k</i> ≤ 25, 0 ≤ <i>l</i> ≤ 13	−10 ≤ <i>h</i> ≤ 10, −10 ≤ <i>k</i> ≤ 11, 0 ≤ <i>l</i> ≤ 15	−13 ≤ <i>h</i> ≤ 14, −13 ≤ <i>k</i> ≤ 15, 0 ≤ <i>l</i> ≤ 16
Reflections collected	14419	11652	17532
Independent reflections	4320	3574	6335
Goodness-of-fit on <i>F</i> ²	0.959	0.985	1.056
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0431, <i>wR</i> ₂ = 0.1045	<i>R</i> ₁ = 0.0601, <i>wR</i> ₂ = 0.1462	<i>R</i> ₁ = 0.0548, <i>wR</i> ₂ = 0.1428
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0667, <i>wR</i> ₂ = 0.1150	<i>R</i> ₁ = 0.0872, <i>wR</i> ₂ = 0.1595	<i>R</i> ₁ = 0.0762, <i>wR</i> ₂ = 0.1601
Largest difference peak and hole (e Å ⁻³)	0.554 and −0.672	1.561 and −0.668	0.846 and −0.884

were refined anisotropically. Crystal data and experimental details are listed in Table 4.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 187968–187970. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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