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Synthesis of Main Group and Transition Metal Complexes with the (8-Quinolyl)cyclopentadienyl Ligand and Their Application in the Polymerization of Ethylene

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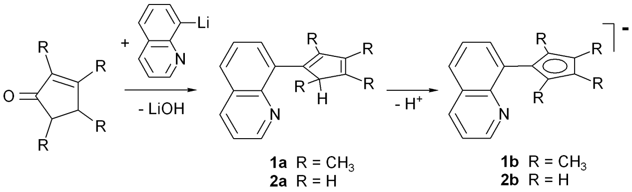
Nucleophilic addition of 8-lithioquinoline to the Cp_2Co^+ cation leads to the formation of η^4-(8-quinolylcyclopentadiene)(η^5-cyclopentadienyl)cobalt(I) (**7**). Oxidative decomplexation with $FeCl_3$ liberates the quinolyl-substituted cyclopentadiene derivative **2a**, which is stable at low temperature only. Deprotonation by strong bases such as NaH or KH leads to the alkali metal quinolyl cyclopentadienide salts, which are used as precursors for the synthesis of the corresponding Ti, Cr, and Al complexes. Whereas after its activation the aluminum compound **13** does not yield an olefin polymerization catalyst, the chromium(III) complex **12** reacts with methylaluminoxane (MAO) to give a highly active catalyst for the polymerization of ethylene.

Introduction

The cyclopentadienyl ligand, C_5H_5 (Cp), is a highly versatile ligand, and complexes are known with most metals of the periodic table. Functionalized Cp ligands bearing a donor group connected to the Cp ring by a suitable spacer have been intensely investigated in the past decade.[1] In most cases the five-membered cycle binds strongly, whereas an interaction of the donor atom (e.g., N, O, P) to the metal occurs only if needed. This concept of so-called hemilabile ligands[2] has been used for the stabilization of reactive intermediates or for catalytic applications. We have synthesized *N*-functionalized cyclopentadienes such as **1a** in which the C_2 spacer and the nitrogen atom are embedded in an aromatic system.[3] This ligand has a predefined geometry and prefers to form half-sandwich chelate complexes. Whereas the synthetic route shown in Scheme 1 yields the tetramethylcyclopentadiene derivative **1a** ($R = CH_3$) as a pure compound in large quantity, it was not possible to obtain the cyclopentadiene derivative **2a** ($R = H$) in good yield and sufficient purity by this pathway.

Scheme 1. Synthesis of Quinolyl-Substituted Cyclopentadienes and -dienides



Recently we reported the synthesis of metal complexes of the η^5-(8-quinolyl)cyclopentadienyl ligand (**2b**) through palladium-catalyzed cross-coupling.[4] However, this synthetic pathway is only possible when the original η^5-C_5H_5 metal complex can be metalated at the five-membered ring. In many cases this is impossible; therefore we tried to develop a synthesis for the cyclopentadiene **2a** or the cyclopentadienide **2b**, respectively.

Results and Discussion

The synthesis of the ligand **2b** in a metal complex environment was shown to be successful.[4] Therefore, we tried to liberate **2b** from the ferrocene derivative **4**. It is known that treatment of ferrocene itself with an excess of elemental lithium leads to the reductive cleavage of the metallocene framework under formation of C_5H_5Li and elemental iron.[5] Brintzinger and coworkers found that the aromatic-substituted ferrocene derivative 2,2-diferrocenylbiphenyl is not reduced under these experimental conditions. However, its reductive decomplexation is possible by treatment with lithium 4,4′-di-*tert*-butylbiphenylide (LiDBB).[6] Thus, we treated 1,1′-bis(8-quinolyl)ferrocene (**4**) with LiDBB under varying conditions. Subsequent hydrolysis of the reaction mixture should lead to the cyclopentadiene **2a**. However, GC/MS analysis showed no evidence for the formation of **2a**.

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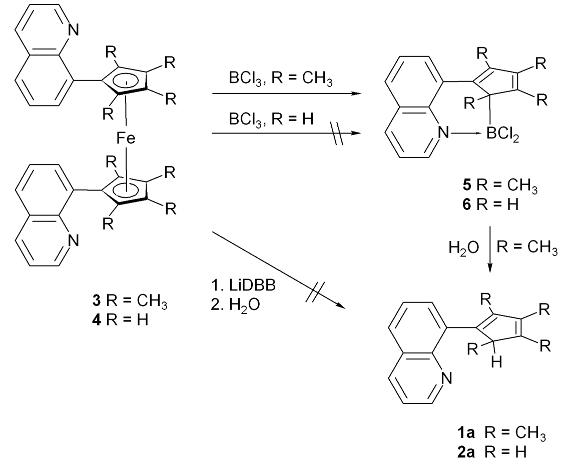
Scheme 2. Reactions of Quinolyl-Substituted Ferrocene Derivatives



Recently, we found that the ferrocene derivative **3**, which bears methyl substituents at the Cp rings, can be decomplexed by reaction with boron trichloride. Hydrolysis of the boron compound **5** leads to the cyclopentadienyl derivative **1a** (see Scheme 2).[7] However, a similar reaction with **4** leads to a mixture of products, and the boron compound **6** or its hydrolysis product **2a** could not be detected. Therefore, another pathway to the desired ligand was investigated.

Synthesis and Oxidative Decomplexation of η^4-(8-Quinolylcyclopentadiene)(η^5-cyclopentadienyl)cobalt(I) (7). The cobalticinium cation $[(\eta^5\text{-}C_5H_5)_2Co)]^+$ is isoelectronic to ferrocene, but it shows a different reactivity toward nucleophilic agents due to its positive charge. Whereas ferrocene is ring-metalated by lithium organyls, these reagents react with Cp_2Co^+ ions under exo-addition of the anionic organyl to the Cp ring. The attacked η^5-bonded cyclopentadienyl ring is transformed into a η^4-bonded cyclopentadiene ligand, and the metal center is reduced from Co(III) to Co(I).[8] The reaction can also be described in the following way. Formally, $[Cp_2Co]^+$ consists of a $C_5H_5^+$ cation that is stabilized by the neutral CpCo fragment. Therefore, the nucleophilic 8-lithioquinoline adds to the electrophilic $C_5H_5^+$ fragment to form the neutral product η^4-(8-quinolylcyclopentadiene)(η^5-cyclopentadienyl)cobalt(I) (**7**) and Li^+, which comes out from the reaction as LiI.[9] After column chromatography, **7** can be obtained in good yields as a dark red solid (Scheme 3).

Crystals of **7** could be obtained from a toluene solution at −28 °C. The X-ray analysis shows that the complex crystallizes in two different conformations, in a 4:1 ratio, which differ only in the arrangement of the cyclopentadiene ring. Due to this disorder, some distances and angles of the molecule could not be determined precisely. The distance of the cobalt atom to the plane defined by the C_5H_5 ring is 1.67 Å, and to the plane of the four sp^2-C atoms of the cyclopentadiene ring it is 1.62 Å. The sp^3-hybridized C atom C10 lies 0.55 Å above the butadiene plane, which corresponds to a folding of the cyclopentadiene ring of 32.5° (Figure 1).

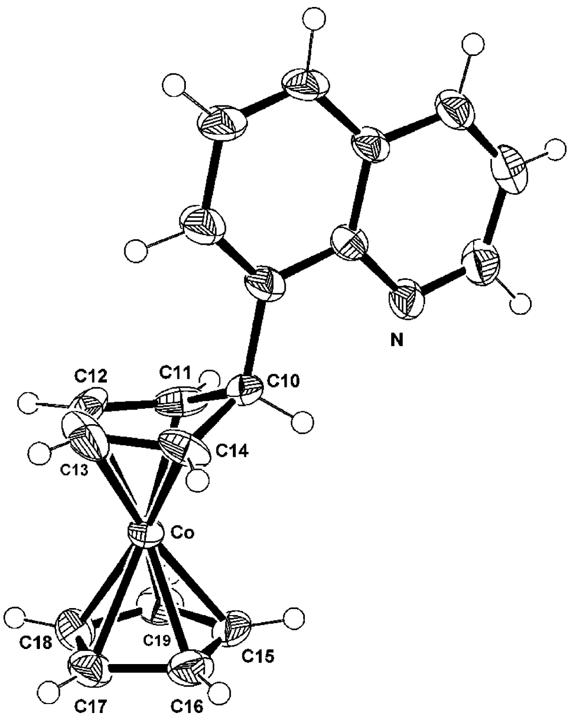
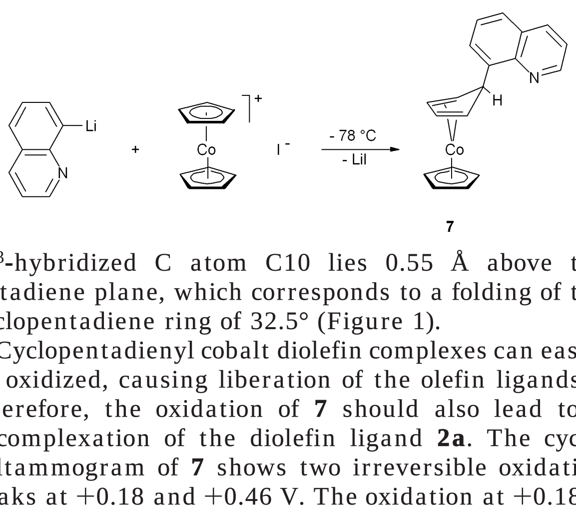


Figure 1. Solid state structure of **7**. Selected bond lengths (Å): Co−C11 2.029(4); Co−C12 1.970(4); Co−C13 1.973(8); Co−C14 1.996(4); Co−C15 2.041(3); Co−C16 2.047(3); Co−C17 2.086(3); Co−C18 2.086(3); Co−C19 2.044(3).

Scheme 3. Nucleophilic Addition of 8-Lithioquinoline to Cp_2Co^+



Cyclopentadienyl cobalt diolefin complexes can easily be oxidized, causing liberation of the olefin ligands.[10] Therefore, the oxidation of **7** should also lead to a decomplexation of the diolefin ligand **2a**. The cyclic voltammogram of **7** shows two irreversible oxidation peaks at +0.18 and +0.46 V. The oxidation at +0.18 V leads to a compound that is irreversibly reduced at −0.90 V. These results indicate that the cobalt compound **7** can be cleaved by mild oxidation agents.

The reaction of **7** with 2 equiv of anhydrous ferric chloride in a toluene/thf mixture at −78 °C leads to its oxidative decomposition, which results in the liberation of the cyclopentadiene derivative **2a**. The two byproducts, cyclopentadienylcobalt(III) dichloride and the reduced iron salt $FeCl_2$, can be removed by filtration over Al_2O_3/5% H_2O at −30 °C with toluene as the eluent (Scheme 4).

The cyclopentadiene derivative **2a** is stable at low temperatures only. Any attempts to isolate it without

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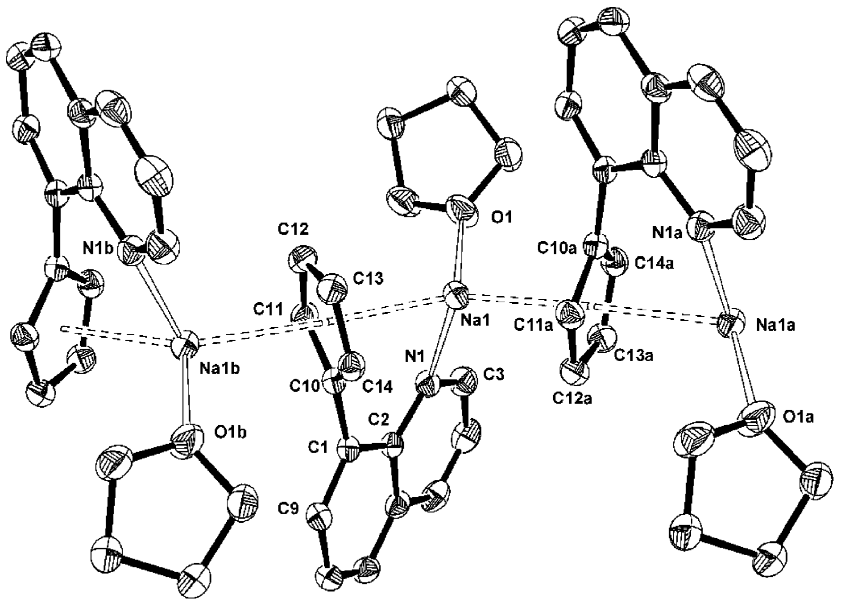
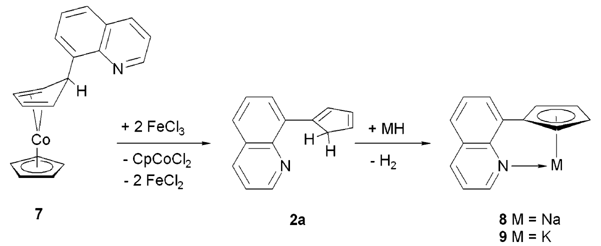


Figure 2. Solid state structure of **8** showing the arrangement as an infinite zigzag chain polymer. Hydrogen atoms are omitted for clarity. For selected bond lengths and angles see Table 1.

Scheme 4. Oxidative Decomplexation of the CpCo Diolefin Complex 7



solvent resulted in decomposition. Therefore, it is favorable to transform **2a** into its alkali metal salts by reaction with strong alkali metal bases. With sodium or potassium hydride the corresponding cyclopentadienide compounds **8** and **9**, respectively, are obtained in good yields.

Solutions of (8-quinolyl)cyclopentadienylsodium(I) (**8**) and (8-quinolyl)cyclopentadienylpotassium(I) (**9**) in thf are intensely red. In the visible region of the UV/vis spectra an absorption band is found at $\lambda = 472$ nm (**8**) and 482 nm (**9**), respectively. The extinction coefficients are $\epsilon = 3200$ (**8**) and $\epsilon = 3050$ (**9**), respectively. These intense absorptions are due to a charge transfer transition from the cyclopentadienide to low lying π^*-orbitals of the quinolyl moiety. Removal of the thf in a vacuum results in the formation of a yellow-brown (**8**) or a yellow-green (**9**) powder. In the dry compounds, no thf is coordinated to the central metals, as proven by NMR spectroscopy after dissolution in d_8-thf.

The ^{1}H NMR spectra show two pseudotriplets for the protons of the cyclopentadienyl rings at $\delta = 5.85$ and 6.18 (**8**) and $\delta = 5.70$ and 6.03 (**9**), respectively, which are typical for the AA′BB′ spin system in monosubstituted cyclopentadienyl derivatives and show the presence of a mirror plane orthogonal to the Cp ring.

Cyclopentadienylsodium compounds are described in the literature in which the coordination sphere of the metal center is saturated through the coordination of three additional ligands. Therefore, it can be assumed that in solutions of **8** besides the nitrogen atom of the quinoline moiety two further molecules of thf are coordinated to the Na atom. This assumption is supported by the ^{23}Na NMR spectrum, which shows a signal at $\delta = -22$. This is close to the value found for (C_5Me_5)-Na(pyridine)$_3$, in which the coordination of three molecules of pyridine was proven by X-ray analysis.[11] As the values of the resonances in the ^{1}H and ^{13}C NMR spectra of both alkali metal complexes are quite similar, the coordination of two molecules of thf to the metal atom is also probable in the potassium compound **9**.

Red crystals of **8** suitable for X-ray analysis (Figure 2) could be obtained from a thf solution at −28 °C. The compound crystallizes in a polymer chain arrangement. Each sodium atom is coordinated by two Cp rings, one nitrogen atom of a quinolyl moiety, and one thf molecule. For quinolyl-substituted Cp complexes such a chain structure was first found in the case of the thallium compound [Tl **1b**]$_n$.[12] Chain structures are also known from various alkali metal cyclopentadienide salts.[11,13] A potassium compound of a donor-functionalized Cp ligand crystallizes also as a polymer chain with the five-membered ring, the donor group, and an additional molecule thf coordinated to the metal center.[14]

The Na−Na−Na angle of 131.5° in **8** is slightly larger than in (C_5H_5)Na·tmeda (128° and 119°, respectively).[13b] The distances of the metal atom to the two five-membered rings are 2.58 Å (intramolecular) and 2.63 Å (intermolecular). The bond lengths of the alkali metal atom to the different C atoms of the five-membered rings differ significantly. There are three relatively short contacts to the atoms C10 (2.722(1) Å), C11 (2.795(1) Å), and C14 (2.831(1) Å), whereas the distances to C12 (2.939(1) Å) and C13 (2.953(1) Å) are much longer. The

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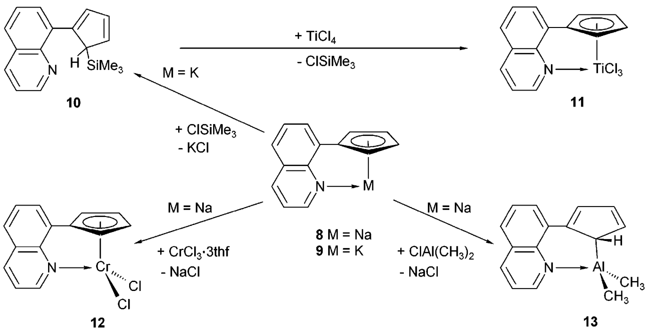
Scheme 5. Synthesis of the Metal Complexes 11, 12, and 13



distances to the carbon atoms C12a and C13a of the neighboring π-ligand are quite short (2.757(1) Å). A comparable range of bond lengths was also found in $(C_5H_5)Na{\cdot}tmeda$ (2.829(14)−3.033(12) Å),[13b] although all values are about 0.1 Å longer than in **8**. The Na−O bond length in **8** is somewhat longer (2.380(1) Å) than in acetylcyclopentadienylsodium·thf (2.354(8) Å)[15] or in tetraphenylcyclopentadienylsodium·3thf (2.319(3)−2.335 Å).[16] The Na−N distance (2.545(1) Å) lies between the distances found in $(C_5Me_5)Na{\cdot}(pyridine)_3$ (2.45−2.49 Å)[11] and CpNa·tmeda (2.62−2.63 Å).[13b] The angles around the nitrogen atom sum up to only 356.8° instead of the ideal 360°. The angle of the cyclopentadienyl and the quinolyl best planes is 58.2°. This small angle causes an unfavorable arrangement of the lone pair of the nitrogen atom so that it cannot point directly to the sodium atom.

Quinolyl-Substituted Titanium, Chromium, and Aluminum Complexes. Titanium, chromium, and aluminum compounds play an important role in the homogeneous polymerization of olefins. Therefore, we used the new alkali metal compounds **8** and **9** for the synthesis of metal complexes, which were tested after their activation as catalysts in the polymerization of ethylene.

The use of alkali metal cyclopentadienides in the synthesis of Ti(IV) half-sandwich compounds can lead to a reduction of the metal. Therefore, it is preferable to use the corresponding trimethylsilyl-substituted cyclopentadiene derivative.[17] (8-Quinolyl)trimethylsilylcyclopentadiene (**10**) can be obtained by reaction of trimethylsilyl chloride with [η^5-(8-quinolyl)cyclopentadienyl]potassium (**9**). The titanium compound trichloro-[η^5-(8-quinolyl)cyclopentadienyl]titanium(IV) (**11**) results from the reaction of equimolar amounts of $TiCl_4$ and **10** as an orange solid (Scheme 5).

Chromium(III) is less affected by redox reactions, and therefore the complex dichloro[η^5-(8-quinolyl)cyclopentadienyl]chromium(III) (**12**) can be obtained directly by adding a solution of the sodium compound **8** to $CrCl_3{\cdot}3thf$. In a similar manner the aluminum compound **13** was synthesized from **8** and $AlCl(CH_3)_2$ (Scheme 5).

All compounds (**11**−**13**) were obtained as solids in good yields (65−84%). The diamagnetic complex **11** shows the expected spectroscopic data. On the ^1H NMR time scale the compound has C_s-symmetry. The coordination of the nitrogen atom to the titanium atom is obvious from a comparison of the chemical shift of the proton neighboring the N atom. By coordination to the acidic metal center Ti(IV) the resonance is shifted to 9.3 ppm in the case of **11**, whereas in the free cyclopentadiene derivative **2a**[3a] or in [2,3-dimethyl-1-(8-quinolyl)-cyclopentadiene[3b] it is located at 8.9 ppm.

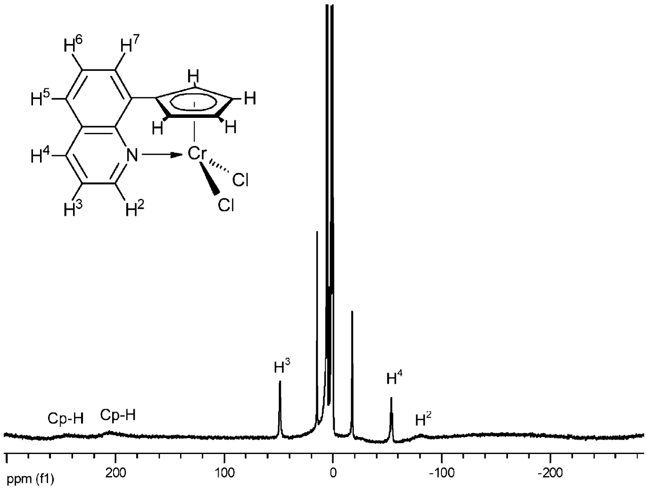


Figure 3. ^1H NMR spectrum of **12** in $CDCl_3$.

The ^1H NMR spectrum of paramagnetic **12** exhibits four well-resolved signals. A fifth signal cannot be detected clearly, as it lies in the diamagnetic region. The resonance of the H^2 atom which is in the direct neighborhood of the nitrogen atom and therefore also to the paramagnetic complex center, appears strongly broadened at −80 ppm ($\nu_{1/2} = 2000$ Hz). The signal of the ortho H atom of pyridine in $CpCrCl_2(C_5H_5N)$ is also found at high frequencies ($\delta = -36$).[18] The protons of the five-membered ring produce two very broad resonances at $\delta = 208$ ($\nu_{1/2} = 3000$ Hz) and 248 ($\nu_{1/2} = 3800$ Hz). A similar value was described for $CpCrCl_2(C_5H_5N)$ ($\delta = 247$).[18] The assignment of the resonances of the quinolyl protons H^2−H^4 is possible by estimating the sign and the size of the Fermi-contact contribution.

Crystals of **12** suitable for X-ray diffraction have been obtained from a dichloromethane solution at room temperature. The chromium atom is bonded to the nitrogen donor and is η^5-coordinated by the cyclopentadienyl ring and two additional chloride ligands. The metal atom is not located exactly below the center of the five-membered ring but is shifted slightly toward the attached donor ligand. The five-membered ring and the quinolyl moiety form an angle of 79.8°. The nitrogen−chromium distance in **12** (2.073(1) Å) is somewhat shorter than in related compounds.[19,20] The angles around the nitrogen atom sum up to 359.8° (Figure 4).

The aluminum compound dimethyl[η^1-(8-quinolyl)-cyclopentadienyl]aluminum(III) (**13**) is obtained by reaction of the sodium complex **8** with chlorodimethylaluminum.

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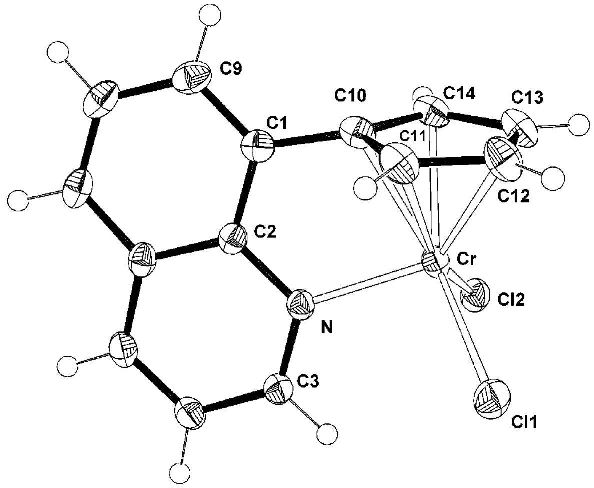

Figure 4. Solid state structure of **12**. Selected bond lengths (Å) and angles (deg): Cr−N 2.073(1); Cr−Cl1 2.287(1); Cr−Cl2 2.304(1); Cr−C10 2.196(1); Cr−C11 2.213(1); Cr−C12 2.261(1); Cr−C13 2.252(1); Cr−C14 2.223(1); N−Cr−Cl1; 97.0(1); N−Cr−Cl2 94.0(1); Cl1−Cr−Cl2 98.82(2); C2−N−Cr 117.0(1); C3−N−Cr 124.0(1); C2−N−C3 118.8(1); C2−C1−C10 115.5(1); C9−C1−C10 125.6(1).

Crystals of **13** were obtained from a solution in dichloromethane at −28 °C. The aluminum atom is coordinated by two methyl groups, by the N atom of the quinolyl moiety, and by one carbon atom of the Cp ring. Such a η^1-coordination mode was also found in the case of other Cp-Al compounds.[21] The Al−N distance of 2.010(1) Å is slightly shorter than in other trialkylaluminum-amine aducts.[21,22] The angles around the quinolyl nitrogen atom sum up to 360°, which shows the presence of a good N−Al interaction. The angle between the five-membered ring and the heterocycle is 46.6° (Figure 5).

The low symmetry that is found in the solid state of **13** is not observed in solution. The ^{1}H NMR spectrum shows a singlet for the methyl groups at the Al atom at $\delta = -0.99$. Two resonances at $\delta = 5.81$ and 6.75 are found for the protons of the Cp ring. Consequently, a mirror plane is present in **13** on the NMR time scale, which stems from a fast shift of the dimethylaluminum group. A similar rearrangement was described in the case of [η^1-1-(2-(dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl]dimethylaluminum(III).[21] Differing from this compound, the dynamic rearrangement of **13** can be frozen at low temperatures. Below the coalescent temperature of −83 °C (200 MHz ^{1}H NMR) two signals appear at $\delta = -0.55$ and −1.72 for the CH_3 groups bound to the Al atom. Three cyclopentadienyl protons give a resonance at $\delta = 7.01$, whereas the signal of the fourth hydrogen atom appears at $\delta = 5.00$. The signals of the quinolyl H atoms ($\delta = 7.61$ to 8.81) show only a slight broadening upon cooling.

The number of ligands bound to an aluminum atom is directly correlated to the chemical shift in the ^{27}Al NMR spectrum. The lower the coordination number, the larger the shift.[23] The ^{27}Al NMR spectrum of **13** shows a broad signal at $\delta = 150$, which indicates a coordination number of four.[21]

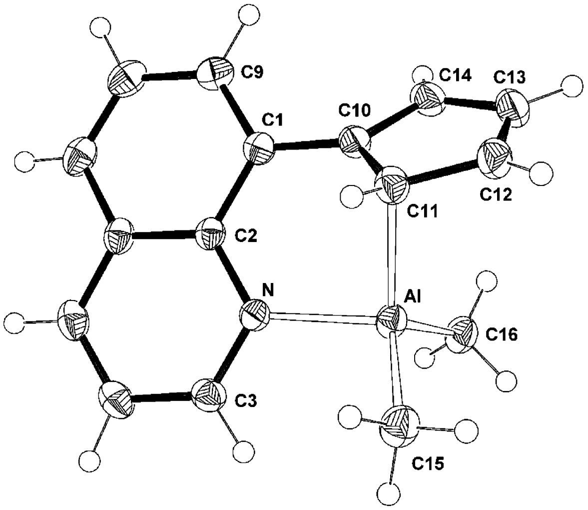

Figure 5. Solid state structure of **13**. Selected bond lengths (Å) and angles (deg): Al−N 2.010(1); Al−C11 2.080(1); Al−C15 1.966(1); Al−C16 1.959(1); C10−C11 1.452(1); C11−C12 1.441(1); C12−C13 1.378(2); C13−C14 1.420(2); C14−C10 1.391(1); N−Al−C11 93.7(1); N−Al−C15 103.6(1); N−Al−C16 109.6(1); C11−Al−C15 108.9(1); C11−Al−C16 118.1(1); C15−Al−C16 118.9(1); C2−N−Al 123.3(1); C3−N−Al 117.4(1); C2−N−C3 119.3(1).

Ethylene Polymerization with the Titanium, Chromium, and Aluminum Complexes 11−13 as Precatalysts. Titanium,[24−28] chromium,[20,29,30] and also aluminum compounds of the type $AlLX_2^+$ (L = neutral, X = anionic two electron donor)[31] are able to act as catalysts in the polymerization reaction of olefins. The activation of the metal complexes **11**−**13** was performed with methylaluminoxane (MAO) and in the case of the aluminum compound **13** also with trityl tetrakis(pentafluorphenyl)boranate $[(C_6H_5)_3C]^+[(C_6F_5)_4B]^-$.

The activities of the tested complexes vary significantly. Whereas the titanium compound **11** shows only a modest activity, the activity of the chromium complex **12** of 952 kg mol^{-1} h^{-1} bar^{-1} is in the range that was determined for Cp_2ZrCl_2 under comparable conditions.[20] Its activity was found to be 3 times less than that of the analogous dichloro[η^5-2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl]chromium(III) complex.[20] The aluminum compound **13** is completely inactive after its

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activation with MAO as well as with trityl tetrakis(pentafluorphenyl)boranate (Table 2).

Conclusion

As the synthesis of the quinolyl-functionalized cyclopentadiene **2a** was not successful neither by reaction of cyclopentenone with 8-lithioquinoline nor by reduction of bis(8-quinolyl)ferrocene (**4**), we developed a new strategy involving the nucleophilic addition of 8-lithioquinoline to the cobalticinium cation and oxidative decomplexation of the resulting CpCo diolefin complex **7**. Deprotonation of **2a** with sodium or potassium hydride leads to the corresponding alkali metal cyclopentadienides **8** and **9**, which were used to synthesize complexes of the ligand **2b** with metals such as titanium, chromium, or aluminum. After its activation with methylaluminoxane (MAO) the dichloro chromium(III) complex **12** showed a high activity in the polymerization of ethylene.

Experimental Section

All experiments were carried out under an atmosphere of dry argon. Solvents were dried by using standard procedures and distilled prior to use. 8-Bromoquinoline,[32] cobalticinium iodide,[33] $CrCl_3 \cdot 3thf$,[34] and trityl tetrakis(pentafluorphenyl)boranate[35] were prepared according to literature procedures. All other reagents were used as purchased. NMR: Bruker DRX 200 (200.13 MHz for ^1H, 50.32 MHz for ^{13}C), JEOL FX-90 Q (24 MHz for ^{23}Na, 23 MHz for ^{27}Al). The ^1H NMR spectra were calibrated using signals of residual protons from the solvent referenced to $SiMe_4$. The ^{13}C spectral chemical shifts are reported relative to the ^{13}C solvent signals. MS: JEOL JMS-700 and VG ZAB-2F. Microanalyses: Mikroanalytisches Laboratorium des Organisch-Chemischen Instituts der Universität Heidelberg. Magnetic measurements: ALFA magnetic balance (at room temperature).

[η^4-(8-Quinolyl)cyclopentadiene](η^5-cyclopentadienyl)cobalt(I) (7). A total of 12.8 mL (32 mmol) of a 2.5 M solution of *n*-BuLi in hexane was added to a solution of 6.63 g (31.8 mmol) of 8-bromoquinoline in 100 mL of thf at −90 °C. After stirring for 15 min at this temperature the dark mixture was added to a −78 °C cold suspension of 10.00 g (31.6 mmol) of cobalticinium iodide in 200 mL of thf via cannula. The resulting red solution was warmed to room temperature overnight. After the addition of a few grams of Al_2O_3/5% H_2O the solvent was evaporated in a vacuum. Column chromatography on Al_2O_3/5% H_2O using toluene as eluent yielded 8.15 g (25.7 mmol, 81%) of **7** as a red solid. ^1H NMR ($CDCl_3$): δ 3.13 (m, 2H, Cp-C*H*); 4.87 (s, 6H, C_5H_5 and quinolyl-Cp-C*H*); 5.26 (pt, 2H, Cp-C*H*); 7.03−7.09 (m, 1H, H^7); 7.27−7.37 (m, 2H, H^3 and H^6); 7.51 (dd, $^3J(H^5,H^6) = 8.1$ Hz, $^4J(H^5,H^7) = 1.5$ Hz, 1H, H^5); 8.01 (dd, $^3J(H^4,H^3)$ 8.3 = Hz, $^4J(H^4,H^2) = 1.9$ Hz, 1H, H^4); 8.91 (dd, $^3J(H^2,H^3) = 4.2$ Hz, $^4J(H^2,H^4) = 1.8$ Hz, 1H, H^2). ^{13}C NMR ($CDCl_3$): δ 44.3, 50.8, 74.8 (quinoline-Cp-*C*H); 79.3 (C_5H_5); 120.6, 125.5, 125.9, 126.3, 135.9, 149.1 (quinoline-*C*H); 128.0, 143.5, 144.6 (quart. $C_{\mathrm{quinoline}}$). MS (EI): *m*/*z* (%) 317 (10) [M^+], 251 (100) [$M^+ - CpH$]. Anal. Calcd for $C_{19}H_{16}NCo$ (317.28): C 71.93, H 5.08, N 4.41. Found: C 70.93, H 5.60, N 4.54.

[η^5-(8-Quinolyl)cyclopentadienyl]sodium(I) (8). A solution of 5.37 g (33.1 mmol) of anhydrous $FeCl_3$ in 80 mL of thf was cooled to −78 °C and added to a −78 °C cold solution of 4.36 g (13.7 mmol) of **7** in a mixture of 50 mL of toluene and 50 mL of thf. The resulting reaction mixture was stirred for 1 h at the same temperature and then filtered over 30 cm of Al_2O_3/5% H_2O (⌀ 2 cm) at −30 °C using toluene as eluent. The first yellow fraction was collected in a 500 mL Schlenk tube containing 900 mg (37.5 mmol) of NaH. After stirring overnight the color of the solution had changed to red. The solvents were evaporated in a vacuum, and the residue was washed with toluene until the washing solution remained colorless. The remaining solid was treated with thf, and the resulting red solution was separated from excess NaH by filtration. Evaporation of the solvent yielded 2.58 g (12.0 mmol, 87%) of **8** as a yellowish-brown solid. ^1H NMR (d_8-thf): δ 5.85 (pt, 2H, Cp-C*H*); 6.18 (pt, 2H, Cp-C*H*); 7.17 (dd, $^3J(H^3,H^2) = 4.1$ Hz, $^3J(H^3,H^4) = 8.2$ Hz, 1H, H^3); 7.22−7.32 (m, 2H, H^6 and H^5 or H^7); 7.63 (dd, $^3J(H^5,H^6) = 6.3$ Hz, $^4J(H^5,H^7) = 2.6$ Hz, 1H, H^5 or H^7); 8.01 (dd, $^3J(H^4,H^3) = 8.2$ Hz, $^4J(H^4,H^2) = 1.8$ Hz, 1H, H^4); 8.57 (dd, $^3J(H^2,H^3) = 4.1$ Hz, $^4J(H^2,H^4)$ 1.8 = Hz, 1H, H^2). ^{13}C NMR (d_8-thf): δ 107.0, 107.9 (Cp-*C*H); 117.3 (quart. C_{Cp}); 120.8, 121.1, 127.6, 127.9, 137.0, 148.6 (quinoline-*C*H); 130.6, 145.3, 148.7 (quart. $C_{\mathrm{quinoline}}$). ^{23}Na NMR (d_8-thf): δ −22. $C_{14}H_{10}NNa$ (215.23).[36]

[η^5-(8-Quinolyl)cyclopentadienyl]potassium(I) (9). The procedure is analogous to that for the synthesis of **8**. Scale: 3.3 g (10.5 mmol) of **7**, 3.98 g (24.5 mmol) of anhydrous $FeCl_3$, 1.47 g (36.6 mmol) of KH. **9** was obtained in a yield of 1.76 g (7.61 mmol, 73%) as a yellowish-green solid. ^1H NMR (d_8-thf): δ 5.70 (pt, 2H, Cp-C*H*); 6.03 (pt, 2H, Cp-C*H*); 7.12 (dd, $^3J(H^3,H^2) = 4.1$ Hz, $^3J(H^3,H^4) = 8.2$ Hz, 1H, H^3); 7.19−7.26 (m, 2H quinoline-C*H*); 7.45−7.55 (m, 1H, quinoline-C*H*); 7.97 (dd, $^3J(H^4,H^3) = 8.2$ Hz, $^4J(H^4,H^2) = 1.8$ Hz, 1H, H^4); 8.54 (dd, $^3J(H^2,H^3) = 4.1$ Hz, $^4J(H^2,H^4) = 1.8$ Hz, 1H, H^2). ^{13}C NMR (d_8-thf): δ 107.6, 109.4 (Cp-*C*H); 119.3 (quart. C_{Cp}); 120.7, 121.2, 127.5, 127.6, 136.6, 149.0 (quinoline-*C*H); 130.6, 144.6, 148.5 (quart. $C_{\mathrm{quinoline}}$). $C_{14}H_{10}NK$ (231.34).[36]

Trimethylsilyl(8-quinolyl)cyclopentadiene (10). A total of 1.35 g (12.4 mmol) of chlorotrimethylsilane was added dropwise to a solution of **9** (2.40 g, 10.4 mmol) in 100 mL of thf. The resulting mixture was refluxed for 1 h and then rapidly cooled to room temperature. After the evaporation of the solvent, the residue was redissolved in hexane and filtered. After the removal of the solvent the trimethylsilylcyclopentadiene derivative **9** was obtained in a yield of 2.14 g (8.06 mmol, 78%) as a brown viscous oil, which was shown to be pure enough for further reactions. GC/MS analysis showed no byproducts, whereas distillation led to a redistribution of the $Si(CH_3)_3$ group. MS (EI): *m*/*z* (%) 265 (52) [M^+], 250 (65) [$M^+ - CH_3$], 192 (100) [$M^+ - Si(CH_3)_3$], 73 (26) [$Si(CH_3)_3{}^+$]. $C_{17}H_{19}NSi$ (265.43).

Trichloro[η^5-(8-quinolyl)cyclopentadienyl]titanium(IV) (11). A solution of 540 mg (2.03 mmol) of **10** in 30 mL of toluene was added to a solution of 368 mg (2.03 mmol) of $TiCl_4$ in 40 mL of toluene at −5 °C. The resulting mixture was stirred overnight at room temperature and then filtered. The residue was extracted with CH_2Cl_2. After the evaporation of the solvent the titanium complex **11** was obtained in a yield of 457 mg (1.32 mmol, 65%) as an orange solid. ^1H NMR ($CDCl_3$): δ 7.10−7.21 (m, 4H, Cp-C*H*); 7.63 (dd, $^3J(H^3,H^2) = 5.1$ Hz, $^3J(H^3,H^4) = 8.4$ Hz, 1H, H^3); 7.68−7.77 (m, 1H, H^6); 7.80 (dd, $^3J(H,H) = 7.1$ Hz, $^4J(H,H) = 1.8$ Hz, 1H, H^5 or H^7); 7.99 (dd, $^3J(H,H) = 7.8$ Hz, $^4J(H,H) = 1.7$ Hz, 1H, H^5 or H^7); 8.39 (dd, $^3J(H^4,H^3) = 8.4$ Hz, $^4J(H^4,H^2) = 1.2$ Hz, 1H, H^4); 9.31 (dd, $^3J(H^2,H^3) = 5.1$ Hz, $^4J(H^2,H^4) = 1.2$ Hz, 1H, H^2). ^{13}C NMR ($CDCl_3$): δ 124.1, 124.5 (Cp-*C*H); 122.1, 127.7, 128.4, 130.3, 138.9, 151.9 (quinoline-*C*H); 129.2, 132.0, 141.2, 151.1 (quart.

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for 8 (C10−C14 = Cp1, C10a−C14a = Cp2)

bond lengths		bond angles	
Na1−N1	2.545(1)	C2−N1−Na1	117.6(1)
Na1−O1	2.380(1)	C3−N1−Na1	121.0(1)
Na1−C10	2.722(1)	C2−N1−C3	118.2(1)
Na1−C11	2.795(1)	N1−Na1−O1	84.9(1)
Na1−C12	2.939(1)	C2−C1−C10	112.0(1)
Na1−C13	2.953(1)	C2−C1−C9	117.7(1)
Na1−C14	2.831(1)	C9−C1−C10	122.4(1)
Na1−C10a	3.052(1)	Na1a-Na1−Na1b	131.5
Na1−C11a	2.941(1)	Cp1-Na1−N1	88.1
Na1−C12a	2.757(1)	Cp1-Na1−O1	116.8
Na1−C13a	2.757(1)	Cp2-Na1−N1	115.6
Na1−C14a	2.935(1)	Cp2-Na1−O1	107.5
Na1−Cp1	2.584	Cp-quinoline	58.2
Na1−Cp2	2.629		

C). MS (EI): *m*/*z* (%) 310 (100) $[M^+ - Cl]$, 275 (34) $[M^+ - 2\,Cl]$, 192 (62) [**1**$^+$]. Anal. Calcd for $C_{14}H_{10}NTiCl_3$ (346.48): C 48.53, H 2.91, N 4.04. Found: C 48.84, H 3.43, N 4.03.

Dichloro[η^5-(8-quinolyl)cyclopentadienyl]chromium(III) (12). A solution of 370 mg (1.72 mmol) of **8** in 50 mL of thf was added dropwise to a suspension of 644 mg (1.72 mmol) of $CrCl_3 \cdot 3thf$ in 50 mL of thf. The resulting green suspension was stirred overnight. After the evaporation of the solvent CH_2Cl_2 was added to the residue and undissolved NaCl was separated from the solution by filtration. The solvent was removed by vacuum distillation, and the remaining solid was washed with toluene followed by hexane. Crystallization from CH_2Cl_2 and drying in a vacuum yielded 414 mg (1.31 mmol, 76%) of **12** as a blue solid. ^1H NMR ($CDCl_3$): δ −80 ($\nu_{1/2}$ = 2000 Hz, *H*^{2}); −53.8 (*H*^{4}); −17.5 (quinoline-C*H*); 14.6 (quinoline-C*H*); 49.0 (*H*^{3}); 208 ($\nu_{1/2}$ = 3000 Hz, Cp-C*H*); 248 ($\nu_{1/2}$ = 3800 Hz, Cp-C*H*); one C*H* signal in diamagnetic region could not be assigned precisely. MS (EI): *m*/*z* (%) 314 (39) $[M^+]$, 279 (100) $[M^{+} - Cl]$, 192 (51) [**1**$^+$]. HR-MS (EI): calcd 313.9595 ($C_{14}H_{10}N^{52}Cr^{35}Cl_2$); found 313.9616. Magnetic moment μ_{eff} (RT): 3.2 μ_B. Anal. Calcd for $C_{14}H_{10}NCrCl_2$ (315.14): C 51.36, H 3.20, N 4.44. Found: C 51.64, H 3.41, N 4.35.

Dimethyl[η^1-(8-quinolyl)cyclopentadienyl]aluminum(III) (13). A total of 3.1 mL of a 1 M solution of chlorodimethylaluminum in hexane was added dropwise to 667 mg (3.1 mmol) of **8** dissolved in 40 mL of thf. The resulting mixture was stirred 2 h at room temperature. The solvents were evaporated, and the residue was treated with CH_2Cl_2 and filtered. The dark yellow solution was concentrated in a vacuum and stored at −28 °C. After 3 days the solution was removed from the precipitated orange crystals with the aid of a syringe. After washing with pentane and drying in a vacuum, **13** was obtained as an orange solid in a yield of 647 mg (2.6 mmol, 84%). ^1H NMR (CD_2Cl_2): δ −0.99 (s, 6H, C*H*$_3$); 5.81 (m, 2H, Cp-C*H*); 6.75 (m, 2H, Cp-C*H*); 7.61−7.79 (m, 3H, quinoline-C*H*); 7.96 (dd, ^3J(H,H) = 6.6 Hz, ^4J(H,H) = 1.7 Hz, 1H, quinoline-C*H*); 8.56 (dd, $^3J(H^4,H^3)$ = 8.2 Hz, $^4J(H^4,H^2)$ = 1.3 Hz, 1H, *H*^{4}); 8.81 (dd, $^3J(H^2,H^3)$ = 5.0 Hz, $^4J(H^2,H^4)$ = 1.3 Hz, 1H, *H*^{2}). ^1H NMR ($CDCl_3$): δ −0.94 (s, 6H, C*H*$_3$); 5.83 (pt, 2H, Cp-C*H*); 6.80 (pt, 2H, Cp-C*H*); 7.63 (dd, ^3J(H,H) = 5.0 Hz, ^3J(H,H) = 8.2 Hz, 1H, *H*^{3}); 7.68−7.74 (m, 2H, quinoline-C*H*); 7.97 (dd, ^3J(H,H) = 5.8 Hz, ^4J(H,H) = 2.9 Hz, 1H, quinoline-C*H*); 8.51 (dd, $^3J(H^4,H^3)$ = 8.3 Hz, $^4J(H^4,H^2)$ = 1.5 Hz, 1H,

Table 2. Polymerization of Ethylene at Atmospheric Pressure[a]

complex	amount of complex (μmol)	*t* (min)	metal:MAO	amount of polymer (g)	activity (kg mol^{-1} h^{-1} bar^{-1})
11	54	30	1:1000	0.07	2.7
12	10	30	1:1000	4.76	952
13	11	30	1:1000[b]	0.00	0
Cp_2ZrCl_2[20]	4.2	30	1:1000	1.97	938

[a] Polymerization conditions: see Experimental Section. [b] $[(C_6H_5)_3C]^+[(C_6F_5)_4B]^-$ was also used as activator.

Table 3. Crystal Data and Experimental Details

	7	8	12	13
empirical formula	$C_{19}H_{16}CoN$	$C_{18}H_{18}NNaO$	$C_{14}H_{10}Cl_2CrN$	$C_{16}H_{16}AlN$
fw	317.26	287.32	315.13	249.28
cryst syst	orthorhombic	orthorhombic	triclinic	triclinic
space group	$P2_12_12_1$	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$
unit cell dimens: *a*, Å	7.362(2)	9.503(1)	8.352(1)	7.5625(3)
b, Å	8.434(2)	9.806(2)	9.036(1)	9.6919(4)
c, Å	22.984(6)	15.880(2)	10.156(1)	9.7119(4)
α, deg	90	90	100.079(2)	656.22(5)
β, deg	90	90	114.016(2)	80.482(1)
γ, deg	90	90	107.594(2)	80.429(1)
volume, Å^3	1427.1(6)	1479.8(4)	627.0(1)	70.293(1)
Z	4	4	2	2
density (calc), g/cm^3	1.477	1.290	1.669	1.262
absorp coeff, mm^{-1}	1.194	0.104	1.315	0.135
F(000)	656	608	318	264
cryst size, mm^3	0.35 × 0.25 × 0.21	0.46 × 0.42 × 0.30	0.20 × 0.20 × 0.40	0.53 × 0.42 × 0.28
θ range for data collection, deg	1.77 to 28.27	2.44 to 32.03	2.34 to 32.13	2.14 to 32.00
index ranges	$-9 \le h \le 9$, $0 \le k \le 11$, $0 \le l \le 30$	$-13 \le h \le 14$, $0 \le k \le 14$, $0 \le l \le 23$	$-12 \le h \le 10$, $-13 \le k \le 13$, $0 \le l \le 15$	$-10 \le h \le 11$, $-14 \le k \le 14$, $0 \le l \le 14$
no. of reflns collected	11 071	19 547	10 487	11 313
no. of indep reflns	3506 [*R*(int) = 0.0375]	4969 [*R*(int) = 0.0278]	4130 [*R*(int) = 0.0246]	4304 [*R*(int) = 0.0207]
max. and min. transmn	1.000 and 0.7239	1.0000 and 0.9143	1.0000 and 0.8576	1.0000 and 0.8781
no. of params	276	262	203	227
goodness-of-fit on *F*^{2}	1.141	1.039	1.068	1.072
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0419, wR2 = 0.1039	R1 = 0.0403, wR2 = 0.1071	R1 = 0.0255, wR2 = 0.0719	R1 = 0.0354, wR2 = 0.1046
R indices (all data)	R1 = 0.0449, wR2 = 0.1058	R1 = 0.0449, wR2 = 0.1127	R1 = 0.0285, wR2 = 0.0742	R1 = 0.0395, wR2 = 0.1091
largest diff peak and hole, e Å^{-3}	1.140 and −0.576	0.543 and −0.191	0.513 and −0.279	0.410 and −0.197

H^4); 8.78 (dd, ^3J(H^2,H^3) = 5.0 Hz, ^4J(H^2,H^4) = 1.6 Hz, 1H, *H*^{2}). ^{13}C NMR (CDCl$_3$): δ −11.2 (*C*H$_3$); 97.4, 120.8, 124.2, 124.5, 129.0, 130.1, 142.0, 147.9 (*C*H), 129.3, 129.7, 137.0 (quart. *C*). ^{27}Al NMR (CDCl$_3$): δ 150 ($\nu_{1/2} \approx$ 1800 Hz). MS (EI): *m*/*z* (%) 234 (100) [M$^+$ − CH$_3$], 218 (13) [M$^+$ − 2 CH$_3$], 192 (65) [**1**$^+$]. HR-MS (EI): calcd 234.0863 (C$_{15}$H$_{13}$NAl); found 234.0867. C$_{16}$H$_{16}$NAl (249.29).

Ethylene Polymerization Procedure. The precatalyst (10−54 μmol) was dissolved in 50 mL of toluene, and MAO (10 wt % solution in toluene, Al/Cr = 1000) was added. A stream of ethylene (at atmospheric pressure) was passed over the vigorously stirred solution. After 30 min the reaction was stopped by adding 50 mL of a mixture of methanol and concentrated aqueous HCl (2:1). The resulting polymer was filtered and washed with a methanol/HCl (2:1) mixture. The polymer was dried overnight at 90 °C.

Crystal Structure Determination of 7, 8, 12, and 13. Crystal data for **7**, **8**, **12**, and **13** were collected on a Bruker AXS SMART 1000 diffractometer with a CCD area detector (Mo Kα radiation, graphite monochromator, λ = 0.71073 Å) at −83° (**8**, **12**, **13**) and −100 °C (**7**), respectively. An absorption correction was applied (SADABS).[37] The structures were solved by direct methods and refined by full-matrix least squares based on F^2 with all reflections using the SHELXTL programs.[38] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in difference Fourier maps and refined isotropically. Crystal data and experimental details are listed in Table 3.

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Supporting Information Available: The NMR spectra of **7**, **8**, **9**, **11**, and **13** and tables giving X-ray crystal structure data for **7**, **8**, **12**, and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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