



Catalytic activity of phenyl substituted cyclopentadienyl neodymium complexes in the ethylene oligomerization process



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ABSTRACT

New mono- and bis-cyclopentadienyl neodymium *ate*-complexes, bearing phenyl-substituents in the cyclopentadienyl ring, have been synthesized: $\text{KNdCp}'\text{Cl}_3(\text{thf})_x$ ($\text{Cp}' = 1,3\text{-Ph}_2\text{C}_5\text{H}_3$ (**1**), $1,2,4\text{-Ph}_3\text{C}_5\text{H}_2$ (**2**)) and $\text{KNdCp}'_2\text{Cl}_2(\text{thf})_x$ ($\text{Cp}' = 1,3\text{-Ph}_2\text{C}_5\text{H}_3$ (**3**), $1,2,4\text{-Ph}_3\text{C}_5\text{H}_2$ (**4**), $1,2\text{-Me}_2\text{-4-PhC}_5\text{H}_2$ (**5**), $1,2\text{-Ph}_2\text{-4-(4-MeO-C}_6\text{H}_4)\text{C}_5\text{H}_2$ (**6**)). Their catalytic activity has been studied in ethylene oligomerization process in the presence of Bu_2Mg as a chain transfer reagent with the Nd:Mg molar ratios being of 1:20, 1:40 or 1:80. Complex **4** exhibits catalytic activity close to the activity of the known complex $[(\text{C}_5\text{Me}_5)_2\text{NdCl}_2\text{Li}(\text{OEt}_2)_2]$ (**7**). The complex **6** has demonstrated the best catalytic activity among all studied complexes. Using selected complexes **2**, **4** and **6** as pre-catalysts, terminal iodo-functionalized oligoethylenes have been prepared. Obtained iodo-oligoethylenes have been studied by ^1H NMR technique and MALDI mass-spectrometry with preliminary derivatization, demonstrating 70–90% of functionalization. Crystal structures of *ate*-complexes $[\{(1,2,4\text{-Ph}_3\text{C}_5\text{H}_2)\text{Nd}(\text{thf})_2\text{Cl}_5\text{K}\}_2(\text{toluene})_4]$ (**2a**), $[\{(1,2,4\text{-Ph}_3\text{C}_5\text{H}_2)_2\text{NdCl}_2\text{K}(\text{thf})_{0.53}(1,4\text{-dioxane})_{1.47}\}_2(\text{dioxane})]$ (**4a**) and $[\{(1,2\text{-Ph}_2\text{-4-(4-MeO-C}_6\text{H}_4)\text{C}_5\text{H}_2)_2\text{NdCl}_2\text{K}\}_2(1,4\text{-dioxane})](\text{toluene})_4]$ have been studied by the single crystal X-ray diffraction.

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1. Introduction

Polyethylene is one of the most studied and most demanded polymers, possessing a combination of attractive chemical and physical properties as well as a low production cost. Therefore, the synthesis, exploration and manufacture of new polymeric materials, based on polyethylene, are of a special interest, although polyethylene itself has a poor compatibility with other materials, leading to limitation of its applications [1]. Functionalized oligo- and polyethylenes can serve starting materials or building units in the preparation of new various co-polymers and composite materials. Introduction of functional groups into a polyethylene chain has been an especially challenging chemical and technological

problem since functional groups can hardly be incorporated into being formed polyethylene during industrial catalytic olefin polymerization process [1–3]. However, this problem has been successfully solved for oligo- and polyethylene with a terminal functional group being a good reactive site for versatile applications. One of possible solutions to the mentioned problem can be achieved by applying neodymium cyclopentadienyl complexes as pre-catalysts along with Alkyl_2Mg on a stage of catalytic ethylene polymerization followed by replacing the Mg atom at the end of polyethylene chain with a functional group [4–6]. The primary goal of the current work is to explore some of such catalytic systems in the synthesis of iodo-functionalized oligoethylenes, using a variety of new mono- and biscyclopentadienyl neodymium derivatives containing phenyl-substituents in the cyclopentadienyl ring.

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2. Results and discussion

2.1. Synthesis of the complexes 1–6

Mono- and biscyclopentadienyl neodymium complexes **1–6** (Scheme 1) were obtained by reacting $\text{NdCl}_3(\text{thf})_x$ in THF with solutions of potassium cyclopentadienides which were synthesized from benzyl potassium and corresponding substituted cyclopentadienes in THF media.

In order to confirm the formation of corresponding mono- and bis-cyclopentadienyl compounds, the X-ray structure determination was performed for compounds obtained by recrystallization of the *ate*-complexes **2**, **4** and **6** from suitable solvent mixtures (Scheme 2), using toluene as a main component, since ethylene oligomerization experiments were carried out in toluene solutions. Recrystallization of **2** from a toluene/THF/hexane mixture resulted in formation of $[(\eta^5-1,2,4-\text{Ph}_3\text{C}_5\text{H}_2)\text{Nd}(\text{thf})_2(\mu_2-\text{Cl})_2(\mu_3-\text{Cl})_3\text{K}]_2(\text{C}_6\text{H}_5\text{CH}_3)_4$ (**2a**). Crystallization of **4** and **6** from a toluene/1,4-dioxane mixture by slow solvent evaporation under reduced pressure led to $[(\eta^5-1,2,4-\text{Ph}_3\text{C}_5\text{H}_2)_2\text{Nd}(\mu_2-\text{Cl})(\mu_3-\text{Cl})\text{K}(\text{thf})_{0.53}(1,4\text{-dioxane})_{1.47}]_2(1,4\text{-dioxane})$ (**4a**) and $[(\eta^5-1,2-\text{Ph}_2-4-(4\text{-MeO-C}_6\text{H}_4)\text{C}_5\text{H}_2)_2\text{Nd}(\mu_2-\text{Cl})(\mu_3-\text{Cl})\text{K}]_2(\mu_2-1,4\text{-dioxane-}1\kappa^1,2\kappa^{\text{O}^4})(\text{toluene})_4$ (**6a**), correspondingly.

For ethylene oligomerization experiments, freshly prepared toluene solutions of the complexes **1–6** were used. Neodymium concentration in the toluene solutions was determined by direct complexometric titration.

2.2. X-ray crystal structures

Polyphenyl substituted cyclopentadienyl complexes of rare-earth metals have been poorly explored until recently. Presently, crystal structures of 20 rare-earth complexes, bearing $\text{C}_5\text{Ar}_n\text{H}_{5-n}$ ($n = 2-5$) ligands, are known: $[\text{Ln}(1,3\text{-Ph}_2\text{C}_5\text{H}_3)\text{Cl}_2(\text{thf})_3]$ ($\text{Ln}=\text{Yb}$, CCDC: 863836 [7]; Lu, CCDC: 707661 [8]); $[\text{Lu}(1,3\text{-Ph}_2\text{C}_5\text{H}_3)(\text{Ph}_4\text{C}_2)(\text{thf})]$, CCDC: 707662 [8]; $[\text{Mg}(\text{thf})_6][\text{Nd}(1,2,4\text{-Ph}_3\text{C}_5\text{H}_2)(\text{BH}_4)_3]$, CCDC: 618596 [9]; $[(1,2,4\text{-Ph}_3\text{C}_5\text{H}_2)_3\text{Lu}_4\text{Cl}_7\text{O}(\text{thf})_3](\text{thf})_2$, CCDC: 863838 [7]; $[(1,2,4\text{-Ph}_3\text{C}_5\text{H}_2)\text{YCl}_2(\text{thf})_3](\text{thf})_{0.5}$, CCDC: 863837 [7]; $[\text{Yb}(\text{C}_5\text{Ph}_4\text{H})(\mu\text{-F})(\text{thf})_2]_2$, CCDC: 1007139 [10]; $[\text{Yb}(\text{C}_5\text{Ph}_4\text{H})(\mu\text{-Br})(\text{thf})_2](\text{solv})_x$ ($\text{solv} = \text{thf}$, $x = 3$, CCDC: 1032414; $\text{solv} = \text{toluene}$, $x = 4$, CCDC: 1032415 [11]; $[\text{Ln}(\text{C}_5\text{Ph}_4\text{H})_2(\text{thf})]$ ($\text{Ln}=\text{Yb}$, CCDC: 1007140 [10]; Sm, CCDC: 1428959 [12]); $[\text{Eu}(\text{C}_5\text{Ph}_4\text{H})_2(\text{dme})(\text{dme})_{1.5}]$, CCDC: 1428960 [12]; $[\text{Sm}(\text{C}_5\text{Ph}_4\text{H})(\text{thf})_3](\text{thf})$, CCDC: 1428962 [12]; $[\text{La}(\text{C}_5\text{Ph}_4\text{H})_2[\text{N}(\text{-SiHMe}_2)_2]]$, CCDC: 172415 [13]; $[\text{Ln}(\text{C}_5\text{Ph}_5)_2]$, ($\text{Ln}=\text{Yb}$, CCDC: 689374 [14]; Eu, CCDC: 1428957 [12]); $[\text{Sm}(\text{C}_5\text{Ph}_5)(\mu\text{-Br})(\text{thf})_2](\text{thf})_6$, CCDC: 1428958 [12]; $[\text{Yb}(\text{C}_5\text{Ph}_5)(\text{thf})_2](\mu\text{-C}_2\text{Ph}_2)$, CCDC: 286666 [15]; $[\text{Ln}(\text{C}_5(4\text{-Bu-C}_6\text{H}_4)_5)_2]$ ($\text{Ln}=\text{Yb}$, CCDC: 665304 [16]; Sm, CCDC: 665305 [16]; Eu, CCDC: 837949 [17]). Only three of them have the triphenyl-substituted cyclopentadienyl ligand. Within the current work, we have extended the family of

crystallographically characterized triphenylcyclopentadienyl complexes by establishing X-ray structures of **6a** (Fig. 1), **4a** (Fig. 2) and **2a** (Fig. 3). X-ray crystallographic data are summarized in Table 1. Selected bond distances and angles are given in the supplementary material for this paper.

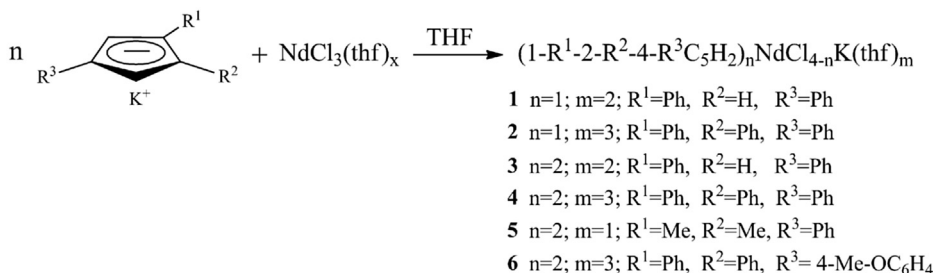
The *ate*-complex $[(\eta^5-1,2-\text{Ph}_2-4-(4\text{-MeO-C}_6\text{H}_4)\text{C}_5\text{H}_2)_2\text{Nd}(\mu_2-\text{Cl})(\mu_3-\text{Cl})\text{K}]_2(\mu_2-1,4\text{-dioxane-}1\kappa^1\text{O}^1,2\kappa^1\text{O}^4)(\text{toluene})_4$ (**6a**, Fig. 1) represents a 1D coordination polymer. Two neighboring dimeric units $[(1,2-\text{Ph}_2-4-(4\text{-MeO-C}_6\text{H}_4)\text{C}_5\text{H}_2)_2\text{NdCl}_2\text{K}]_2$, located at inversion centers, are bridged by a 1,4-dioxane molecule via oxygen atoms. An unusual structural motif $[\text{Nd}(\mu_2-\text{Cl})(\mu_3-\text{Cl})\text{K}]_2$ (Fig. 4, top left) connects the Nd, K and Cl core atoms together. The Nd(1)-Cl(1)-K(1)-Cl(2) and K(1)-Cl(2)-K(1A)-Cl(2A) fragments are planar with the folding angle of $38.12(6)^\circ$.

According to the Cambridge Structural Database (CSD, v.5.36) [18], the same structural motif $[\text{Ln}(\mu_2\text{-Hal})(\mu_3\text{-Hal})\text{M}]_2$ ($\text{M} = \text{alkali metal}$) is quite rare among organometallic complexes. Five following crystal structures have been revealed up to date: $[(^1\text{Pr}_4\text{C}_5\text{H})_2\text{NdCl}_2\text{Na}(\text{Et}_2\text{O})_2]_2$, CCDC: 212171 [19]; $[(1,5\text{-}^t\text{Bu}_2\text{NC}_4\text{H}_2)_2\text{NdCl}_2\text{Na}(\text{thf})_2]_2$, CSD: 57704 (FIZ Karlsruhe) [20]; $[(\text{C}_9\text{H}_6\text{-C}_2\text{B}_{10}\text{H}_{10})\text{Ln}(\text{thf})_2\text{Cl}_2\text{K}(\text{thf})_2]_2$ ($\text{Ln}=\text{Y}$, CCDC: 709813; Gd, CCDC: 709814) [21]; and $[(1\text{-NMe}_2\text{-}3,5\text{-Me}_2\text{-C}_5\text{BH}_3)_2\text{YCl}_2\text{Li}]_2$, CCDC: 166215 [22].

The crystal structure of $[(\eta^5-1,2,4\text{-Ph}_3\text{C}_5\text{H}_2)_2\text{Nd}(\mu_2-\text{Cl})(\mu_3-\text{Cl})\text{K}(\text{solv})(1,4\text{-dioxane})_2](\text{dioxane})$ (**4a**, Fig. 2) ($\text{solv} = \text{thf}$ or 1,4-dioxane with the 0.53(1):0.47(1) occupancy ratio, correspondingly) contains the *ate*-complex, lying on an inversion center, and disordered molecules of non-coordinating solvents. Some of solvent molecules in the crystal channels were not resolved, therefore they were removed by the SQUEEZE method [23]. The main moiety has the same core (Fig. 4, top right) as **6a**, however the Nd(1)-Cl(1)-K(1)-Cl(2) fragment is not flat presumably because of the presence of two σ -donor ligands coordinated to the K^+ cation in contrast with **4a** having only one dioxane ligand bound to K^+ . The crystal structures of $[(^1\text{Pr}_4\text{C}_5\text{H})_2\text{NdCl}_2\text{Na}(\text{Et}_2\text{O})_2]_2$ [19] and $[(\text{C}_9\text{H}_6\text{-C}_2\text{B}_{10}\text{H}_{10})\text{Ln}(\text{thf})_2\text{Cl}_2\text{K}(\text{thf})_2]_2$ ($\text{Ln}=\text{Y}$, Gd) [21] supports this idea.

The dimeric unit $[(\eta^5-1,2,4\text{-Ph}_3\text{C}_5\text{H}_2)\text{Nd}(\text{thf})_2(\mu_2-\text{Cl})_2(\mu_3-\text{Cl})_3\text{K}]_2$ (Fig. 3) of the *ate*-complex $[(\text{Ph}_3\text{C}_5\text{H}_2)\text{Nd}(\text{thf})_2\text{Cl}_5\text{K}]_2(\text{toluene})_4$ (**2a**) is also located at an inversion center. The arrangement of chloride anions in the unit $[\text{Nd}_2(\mu_2-\text{Cl})_2(\mu_3-\text{Cl})_3\text{K}]_2$ (Fig. 4, bottom) resembles a trigonal bipyramid with Cl(4), Cl(5) atoms being in axial positions, and Cl(1), Cl(2), Cl(3) being in equatorial positions. Two units are connected together via K(1)-Cl(1A) and K(1A)-Cl(1) bonds, forming a $[\text{Nd}_4\text{Cl}_{10}\text{K}_2]$ core. The folding angle between a nearly flat fragment K(1)-Cl(1)-Nd(1)-Cl(3)-Nd(2)-Cl(2) and the K(1)-Cl(1)-K(1A)-Cl(1A) plane is $40.49(3)^\circ$. The $[\text{Nd}_2(\mu_2-\text{Cl})_2(\mu_3-\text{Cl})_3\text{K}]_2$ core is unprecedented for rare-earth and alkali metals (CSD, v.5.36 [18]).

$\text{C}_{\text{ipso}(\text{Ph})}\text{-C}_{\text{ipso}(\text{Cp})}$ bond lengths (1.463(10)–1.494(9) Å) are slightly shorter than a single C–C bond length. All $\text{C}_{\text{ipso}(\text{Ph})}$ atoms are slightly out of the plane of the cyclopentadienyl rings by



Scheme 1.

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