Efficient Recycling of a Versatile Titanocene Precatalyst: Significance of Side-Chain Functionalization

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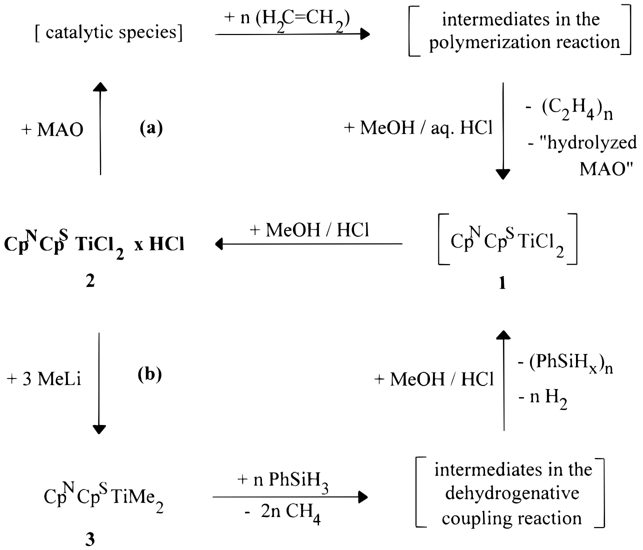
Summary: The dramatic influence of the (diisopropylamino)ethyl side chain provides sufficient stability to allow for efficient recycling of $Cp^NCp^STiCl_2\cdot HCl$ **(2)** *(*$Cp^N = C_5H_4CH_2CH_2N^iPr_2$, $Cp^S = C_5H_4SiMe_3$*), a precatalyst for the polymerization of ethylene and for the dehydrogenative coupling of phenylsilane, by a simple extraction procedure with methanol and aqueous HCl.*

We recently introduced the [2-(diisopropylamino)-ethyl]cyclopentadienyl ligand ($Cp^N \equiv C_5H_4CH_2CH_2N^iPr_2$) into the chemistry of titanium by synthesizing bent sandwich complexes[1] of the type $Cp^N{}_2TiR_2$ and $Cp^N{}_2TiCl_2\cdot 2HCl$ as well as mixed bent sandwich complexes[2] of the type $Cp^NCp^STiR_2$ and $Cp^NCp^STiCl_2\cdot HCl$ ($Cp^S = C_5H_4SiMe_3$). Some of the chemical and physical properties of these complexes are surprising, especially in comparison with those of the nonfunctionalized compounds:

(I) The titanocene dichloride $Cp^NCp^STiCl_2$ **(1)** reacts with 1 equiv of methanolic hydrogen chloride resulting in protonation of the amino group to give the hydrochloride $Cp^NCp^STiCl_2\cdot HCl$ **(2)** in high yields.[2] In contrast to **1**, which is extremely moisture-sensitive, **2** shows an excellent solubility and stability in polar protic solvents such as methanol or water and hydrolysis of the M−Cl bonds was not observed, even after exposure for several hours. Both compounds, in combination with the cocatalyst MAO, catalyze the polymerization of ethylene, and therefore the easy handling of the hydrochloride **2** is particulary interesting. (II) The dimethyl derivative $Cp^NCp^STiMe_2$ **(3)**, which catalyzes the dehydrogenative coupling of phenylsilane furnishing oligosilanes in excellent yields, is obtained in nearly quantitative yield by the reaction of **2** with 3 equiv of methyllithium in diethyl ether and exhibits remarkable thermal stability.[2] In contrast to the temperature- and light-sensitive complex Cp_2TiMe_2,[3] for which an autocatalytic, "catastrophic" decomposition is reported, **3** is stable for several days under inert gas atmosphere at room temperature, presumably due to a weak intramolecular coordination of the N^iPr_2 group to the titanium center, thus prohibiting an α-elimination decomposition. (III) The dichloride−hydrochloride **2** can be generated in quantitative yield by treatment of the dimethyl complex **3** with 3 equiv of HCl dissolved in methanol (decomposition products were not observed in this reaction). The parent compound Cp_2TiMe_2 reacts with aqueous HCl in methanol to give the Cp_2TiCl_2 in low yields only.[4]

Scheme 1



With regard to these unique results we now describe procedures which allow for efficient high-yield recycling of the titanocene precatalyst $Cp^NCp^STiCl_2\cdot HCl$ **(2)** after its use in the ethylene polymerization (a) and phenylsilane oligomerization reactions (b), by simple extraction with methanol and aqueous HCl.

(a) Complex **2** is treated with the cocatalyst MAO to give the active catalyst, which polymerizes ethylene at room temperature. The polymerization is quenched by the addition of methanol and aqueous HCl giving the titanocene dichloride $Cp^NCp^STiCl_2$ **(1)**, which is recycled to the precatalyst **2** by virtue of protonation by excess HCl (Scheme 1).

Compound **2** together with the hydrolyzed MAO is separated from polyethylene by filtration and further extraction of the polymer with water and acetone. After removal of all volatile products *in vacuo*, the precatalyst **2** can be separated from the hydrolyzed MAO (not soluble) by extraction with dichlormethane. Complex **2** is recovered as a red solid in excellent yield, which may be further optimized.

Until now, all known homogeneous catalysts contaminate the polymer (leave-in catalysts). In our case, the exceptional properties of the applied precatalyst, especially the excellent solubility and stability in polar protic solvents, allow an easy separation from the polymer.

(b) Reaction of $Cp^NCp^STiMe_2$ **(3)** with phenylsilane in toluene leads to the formation of oligophenylsilanes

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(1) Jutzi, P.; Redeker, T.; Neumann, B.; Stammler, H.-G. *Organometallics* **1996**, *15*, 4153.

(2) Jutzi, P.; Redeker, T.; Neumann, B.; Stammler, H.-G. *Chem. Ber.* **1996**, *129*, 1509.

(3) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am .Chem. Soc.* **1978**, *100*, 3611.

(4) Unpublished results of P.J. and T.R.

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in excellent yields. The oligomer products are separated by filtration through a Florisil column. By the addition of methanolic HCl, the hydrochloride **2** can be recycled in a fashion similar to that described above (Scheme 1); it is separated from the Florisil material by extraction with dichloromethane. In a second step complex **2** can be converted into the oligomerization catalyst **3** in nearly quantitative yield by the reaction with 3 equiv of methyllithium.[2] In all procedures so far published in the literature, the catalytic species or its decomposition products remain absorbed on the Florisil material.

In summary, efficient recycling of a versatile titanocene precatalyst has been described. The properties of the involved compounds, which are responsible for the simple recycling processes, are caused by the side-chain functionalization of the Cp ligand. Attempts to recycle the parent, nonfunctionalized complexes $\mathrm{Cp_2TiCl_2}$ and $\mathrm{Cp_2TiMe_2}$ have not been successful.[4] From this point of view the amino functionalization of Cp systems is taking on a special significance. We recommend further investigations into the recycling of other catalytically active complexes which possess (diisopropylamino)ethyl-functionalized Cp ligands.

Experimental Section

Ethylene (BASF AG) was used without further purification. Methylaluminoxane (MAO) was obtained from Witco (Bergkamen, Germany), as a 10 wt % toluene solution (4.9% wt % aluminium, density ~ 0.9 g/mL, average molar mass of the MAO oligomers 900−1100 g/mol). All polymerization reactions were performed in toluene solution at room temperature. The ethylene polymerization reactions took place under a pressure of 1 atm of ethylene.

Recycling of $\mathrm{Cp^NCp^STiCl_2\cdot HCl}$ (2). A 1.00 g (2.06 mmol) amount of **2** was dissolved in 40 mL of toluene. Under ethylene atmosphere 124 mL (0.21 mol) of MAO was introduced. After 5 min the clear yellow solution became turbid, and after 1 h the polymerzation was quenched by pouring the solution into 500 mL of methanol/aqueous HCl. The polyethylene was filtered off, washed with water and acetone, and dried to constant weight. Solvent was removed from the filtrate *in vacuo*. The residue was extracted for 5 h with 300 mL of $\mathrm{CH_2Cl_2}$ in a Soxhlet apparatus. After removal of the solvent in vacuo, the residue was washed with 40 mL of diethyl ether. The recycled precatalyst **2** was obtained in 73% yield (730 mg) as a red solid. Yield of polyethylene: 5.30 g.

Ethylene Polymerization Data for $\mathrm{Cp^NCp^STiCl_2}$ (1) and $\mathrm{Cp^NCp^STiCl_2\cdot HCl}$ (2) (2* = Recycled Precatalyst $\mathrm{Cp^NCp^STiCl_2\cdot HCl}$). **1**: 36.1 μmol in 10 mL of toluene, 18 mmol of cocatalyst MAO, 0.9 g of PE, M_r 15 237, M_n 5185, M_r/M_n 2.9, η value (dL/g) 0.38. **2**: 84.7 μmol in 20 mL of toluene, 42 mmol of cocatalyst MAO, 3.6 g of PE, M_r 24 163, M_n 7601, M_r/M_n 3.2, η value (dL/g) 0.34. **2***: 80.0 μmol in 20 mL of toluene, 40 mmol of cocatalyst MAO, 2.6 g of PE, M_r 14 356, M_n 4708, M_r/M_n 3.1, η value (dL/g) 0.33. Productivity of **1**, **2**, and **2*** $\approx$ 11 kg of PE (mol of Ti)$^{-1}$ ($\mathrm{C_2H_4}$)$^{-1}$ h^{-1}.

Recycling of $\mathrm{Cp^NCp^STiMe_2}$ (3). A 510 mg (1.25 mmol) amount of **3** was dissolved in 40 mL of toluene. Under argon atmosphere 2.03 g (18.76 mmol) of phenylsilane was added to this solution. An evolution of gas commenced, and stirring was continued for 20 h at room temperature. The oligophenylsilane was recovered by filtration trough a column of Florisil. Vacuum evaporation of the eluents toluene and diethyl ether affords the oligomer as a colorless, extremely viscous liquid. The residue on the column together with the Florisil material was treated with 50 mL of methanol/HCl. After removal of the solvents the remaining red solid, which consists of the generated hydrochloride **2** and the Florisil material, was washed with 40 mL of diethyl ether. **2** was separated from this mixture by extraction with 30 mL of $\mathrm{CH_2Cl_2}$. The hydrochloride **2** was obtained in 53% yield (320 mg) in the form of a red solid. The Florisil material is also soluble in methanol/HCl. Therefore an extraction with $\mathrm{CH_2Cl_2}$ was necessary. Compound **2** can be converted to the catalyst **3** by the reaction with 3 equiv of methyllithum in quantitative yield.

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