

Sequential Immobilization of Ansa-Hafnocene Complexes for Propene Polymerization

Marius Arz, Tim Kratky, Sebastian Günther, Katia Rodewald, Thomas Burger, Manfred Heuberger, Bernhard Rieger

Submitted date: 23/10/2019 • Posted date: 25/10/2019

Licence: CC BY-NC-ND 4.0

Citation information: Arz, Marius; Kratky, Tim; Günther, Sebastian; Rodewald, Katia; Burger, Thomas; Heuberger, Manfred; et al. (2019): Sequential Immobilization of Ansa-Hafnocene Complexes for Propene Polymerization. ChemRxiv. Preprint.

We report the immobilization of the ultrarigid ansa-hafnocene complexes $[\text{Me}_2\text{Si}(\text{Ind}^*)_2\text{HfCl}_2]$ ($\text{Ind}^* = 7, (3',5'\text{-Di-tert-butylphenyl})\text{-4-methoxy-2-methylindenyl}$) on silica as heterogeneous catalysts for propene polymerization. A sequential three-step synthesis on the siliceous surface led to pre-catalysts of the generalized structure $\text{SiO}_2\text{-Si}(\text{Ind}^*)_2\text{HfCl}_2$, which possess the silylene bridge of the substituted bis(indenyl) ligand directly attached to the surface. The immobilized pre-catalysts show very poor performance in the polymerization of propene, independent on the reaction conditions and the employed silica. Based on the results, we suggest that the close proximity of the catalyst to the surface combined with the steric congestion provoked by the ligand prevents a continuous polymerization, most likely due to a blockage of the catalytically active sites with growing polymer.

File list (1)

Sequential Immobilization of ansa-Hafnocene Complexes f... (4.33 MiB) [view on ChemRxiv](#) • [download file](#)

Sequential Immobilization of *ansa*-Hafnocene Complexes for Propene Polymerization

Marius I. Arz,^{1,2} Tim Kratky,¹ Sebastian Günther,¹ Katia Rodewald,¹ Thomas Burger,^{1,2}
Manfred Heuberger,³ Bernhard Rieger^{1,*}

¹Technische Universität München, Department of Chemistry, Lichtenbergstraße 4, 85748 Garching bei München, Germany

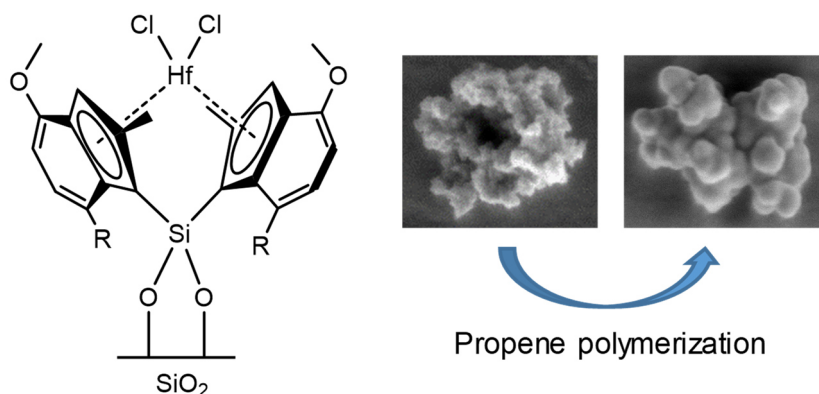
²Technische Universität München, Catalysis Research Center, Ernst-Otto-Fischer-Straße 1, 85748 Garching bei München, Germany

³Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Advanced Fibers, 9014 St. Gallen, Switzerland

*e-mail: rieger@tum.de

Abstract: We report the immobilization of the ultrarigid *ansa*-hafnocene complexes *rac*-[Me₂Si(Ind*)₂HfCl₂] (*rac*-**1**; Ind* = 7-(3',5'-Di-*tert*-butylphenyl)-4-methoxy-2-methylindenyl) on silica as heterogeneous catalysts for propene polymerization. A sequential three-step synthesis on the siliceous surface led to pre-catalysts of the generalized structure SiO₂-Si(Ind*)₂HfCl₂, which possess the silylene bridge of the substituted bis(indenyl) ligand directly attached to the surface. The immobilized pre-catalysts show very poor performance in the polymerization of propene, independent on the reaction conditions and the employed silica. Based on the results, we suggest that the close proximity of the catalyst to the surface combined with the steric congestion provoked by the ligand prevents a continuous polymerization, most likely due to a blockage of the catalytically active sites with growing polymer.

TOC:

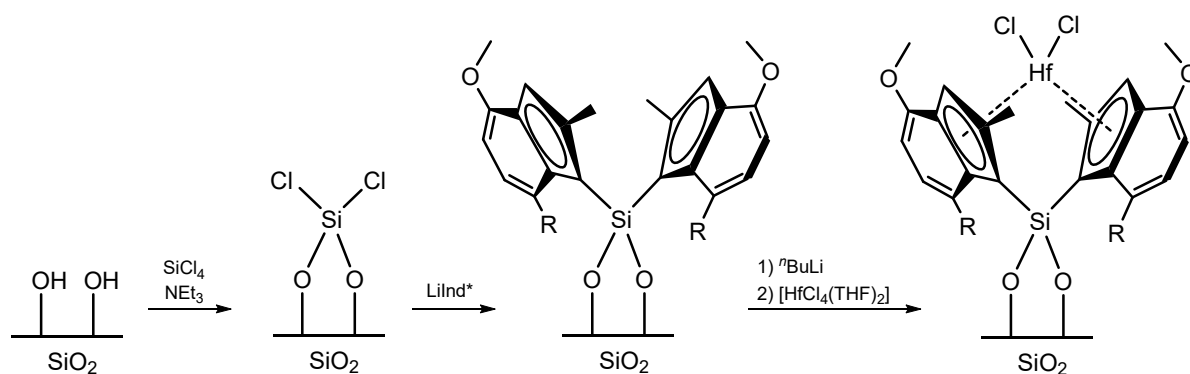


The immobilization of homogeneous catalysts onto heterogeneous carriers is an important approach to unify homogeneous with heterogeneous catalysis.^[1] Catalysts for α -olefin polymerization range amongst the most widely used catalysts due to the tremendous importance of polyolefins where polyethylene (PE), polypropylene (PP) and polystyrene (PS) alone contribute with >50 % to the overall global plastic production with ever-increasing demand.^[2] The immobilization of homogeneous α -olefin polymerization catalysts is appealing, because it potentially enables the unification of the high activity and control of the polymer microstructure as well as the molecular weight provided by homogeneous single-site catalysts with the unmatched operability of heterogeneous Ziegler-Natta catalysts at industrial process conditions.^[3] Consequently, a wide range of strategies were explored to immobilize these single-site polymerization catalysts, including physisorption, grafting and tethering of either the pre-catalyst or the activator reagent (co-catalyst).^[1,3]

The continuous optimization of Group 4 *ansa*-metallocenes has attracted considerable attention in the last ca. 30 years, which culminated in the rise of Zr and Hf metallocenes with tailored silylene-bridged substituted indenyl ligands to be one of the most frequently used homogeneous polymerization catalysts.^[4] More recently, significant progress was also achieved in the development of post-metallocene catalysts.^[5]

In 2012, we reported the synthesis of the ultrarigid hafnocene pre-catalyst *rac*-[Me₂Si(Ind*)₂HfCl₂] (*rac*-1; Ind* = 7-(3',5'-Di-*tert*-butylphenyl)-4-methoxy-2-methylindenyl), which produces isotactic polypropene (iPP) of ultrahigh molecular weight ($M_w > 5 \cdot 10^6$ g/mol) with nearly perfect stereocontrol ([*mmmm*] > 99.9 %), providing iPP with the so far highest melting point *ex reactor* of 171 °C.^[6]

Herein, we report our attempts to immobilize the catalyst *rac*-1 on silica particles using the sequential approach outlined in Scheme 1. This approach has been reported earlier for surface-tethering of zirconocene catalysts, but using only the unsubstituted indenyl (Ind, C₉H₇) as ligand, which induces no stereoselectivity in the metallation step and consequently leads to an undesired mixture of atactic (aPP) and isotactic polypropene (iPP) after propene polymerization.^[7] By contrast, the particular substitution pattern of the Ind* ligand favours a *racemo*-selective formation of *rac*-1,^[6] which is why we set out to explore the suitability of this rather simple approach to support *rac*-1 on silica.



Scheme 1. Sequential approach for supporting the pre-catalyst *rac*-1 onto silica; R = 3,5-*t*Bu₂-C₆H₃.

Two commercially available silicas were used in this study, namely Sipernat® 50 from Evonik ($a_{\text{BET}} = 450 \text{ m}^2/\text{g}$, cumulative pore volume = 1.75 mL/g; a_{BET} = surface area determined by BET analysis) and Sylopol® 2408 HT from Grace ($a_{\text{BET}} = 310 \text{ m}^2/\text{g}$, cumulative pore volume = 1.51 mL/g). The silica materials were calcined at 300 °C for 16 h under air, followed by at 100 °C under vacuum for 1 h and the calcined silicas are hereafter abbreviated with **EV**₃₀₀ (Sipernat® 50) and **GR**₃₀₀ (Sylopol® 2408 HT).

A mild chlorination of the silicas was achieved at ambient temperature in DCM suspension by the addition of an excess SiCl₄ and NEt₃ (Scheme 1).^[8] This method yielded the chlorinated silicas SiO₂-SiCl₂ with chlorine surface concentrations β_{Cl} of 6.02 $\mu\text{mol}/\text{m}^2$ (**EV**₃₀₀) and 6.01 $\mu\text{mol}/\text{m}^2$ (**GR**₃₀₀). By comparison, this approach leads to higher β_{Cl} values than the chlorination of silica with excess SiCl₄ in refluxing toluene [$\beta_{\text{Cl}} = 2.32 \mu\text{mol}/\text{m}^2$ (**EV**₃₀₀)],^[7] but lower β_{Cl} values than reached with the gas phase chlorination of silica with neat SiCl₄ at high temperature ($T > 200 \text{ }^\circ\text{C}$, $\beta_{\text{Cl}} > 7 \mu\text{mol}/\text{m}^2$).^[9]

Treatment of SiO₂-SiCl₂ with LiInd* in a 1:1 solvent mixture of 1,4-dioxane / toluene and moderate heating to 60 °C for 24 h led to the indenyl-modified silicas SiO₂-Si(Ind*)₂. Subsequent lithiation of SiO₂-Si(Ind*)₂ with *n*-butyllithium and treatment with [HfCl₄(THF)₂] in THF at -60 °C yielded the supported pre-catalyst SiO₂-Si(Ind*)₂HfCl₂ as a yellow powder. The hafnium contents of the materials were determined by ICP-OES analysis to be $\beta_{\text{Hf}} = 0.76 \mu\text{mol}/\text{m}^2$ (**EV**₃₀₀ and **GR**₃₀₀). These values are lower than the Zr content reported by Soga and coworkers in their original report using unsubstituted indenyl and ZrCl₄ ($\beta_{\text{Zr}} = 1.99 \mu\text{mol}/\text{m}^2$),^[7e] which likely reflects the higher steric congestion of the silica surface with the bulky indenyl ligand Ind*.

The successful synthesis of the supported pre-catalyst SiO₂-Si(Ind*)₂HfCl₂ was followed by X-ray photoelectron spectroscopy (XPS). The Hf 4d, Cl 2p and C 1s spectra displayed in Figure 1 confirm the chlorination of the bare SiO₂ support surface and the final assembly of the hafnocene complex at the anchoring sites. Starting from the clean SiO₂ surface the

appearance of the Cl 2p_{3/2} at 200.3 eV indicates the formation of Si-Cl species in agreement with literature.^[10] The final formation of the pre-catalyst is confirmed by a substantial C 1s and Hf 4d emission as well as a shifted Cl 2p_{3/2} signal at 199.3 eV reported for chlorinated hafnocene complexes.^[11] The Hf 4d/Cl 2p intensity ratio converts to the expected stoichiometry of 1:2. Note, that the Cl 2p intensity decrease from the chlorinated SiO₂ surface to the pre-catalyst reflects the loss of anchoring sites during synthesis of the hafnocene complex in agreement with chlorine and hafnium concentrations β_{Cl} and β_{Hf} observed with elemental analysis.

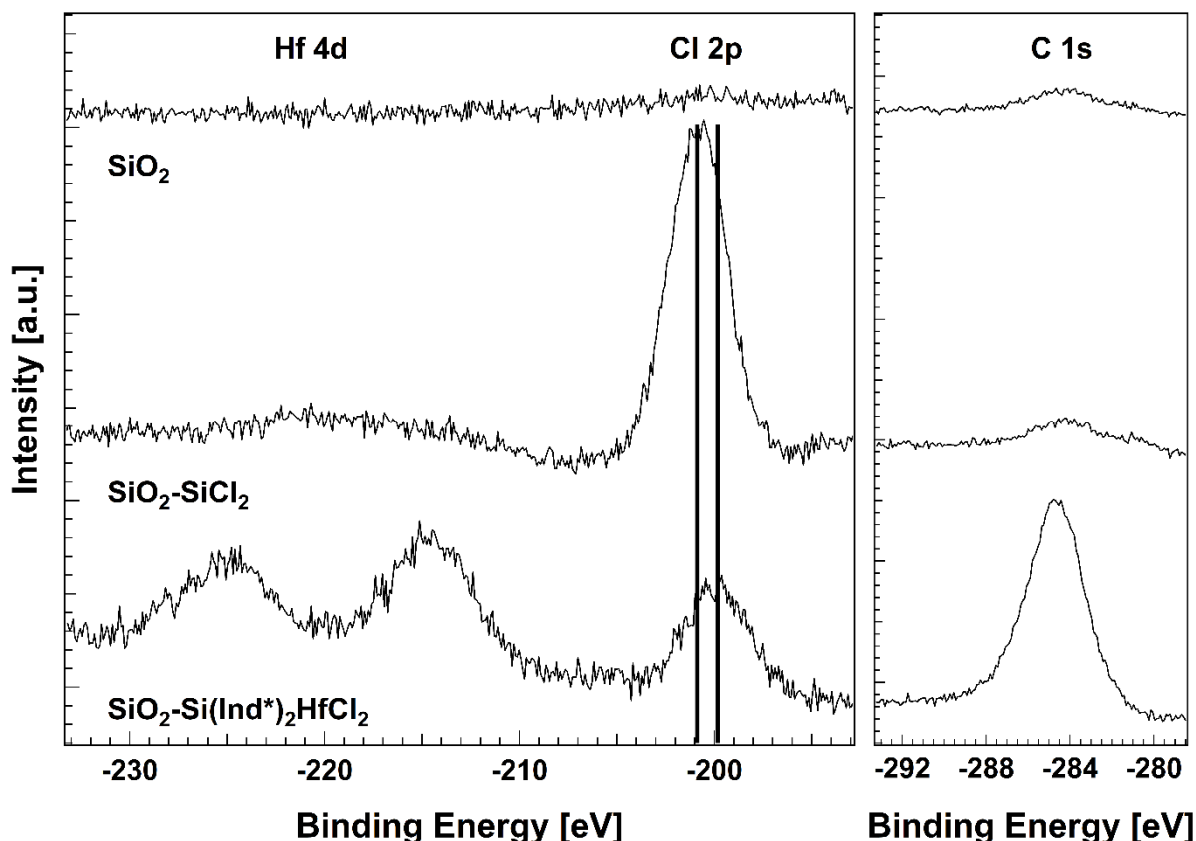


Figure 1. Hf 4d/Cl 2p as well as C 1s photoemission spectra obtained from SiO₂, SiO₂-SiCl₂ and SiO₂-Si(Ind*)₂HfCl₂. All spectra have been scaled to the Si 2p peak area originating from the support so that peak intensities reflect the amount of surface atoms.

We tested the slurry-phase polymerization of propene using the immobilized SiO₂-Si(Ind*)₂HfCl₂ pre-catalyst in toluene. For this purpose, the immobilized pre-catalyst was activated with an excess of triisobutylaluminium (TIBA) in toluene at 60 °C for 1 h and the polymerization initiated with CPh₃[B(C₆F₅)₄]. Only minor quantities of polymer formed and the attempted extraction of the polymer with 1,2,4-trichlorobenzene (TCB) at 160 °C yielded only traces of polymeric material for both used silica materials (< 5 mg). All further attempts to increase the amount of polymer by increasing either the catalyst loading, the polymerization time, the pressure, the temperature, or the time of pre-catalyst activation showed no

improvement of the polymer yield. Thus, the catalytic productivity of $\text{SiO}_2\text{-Si(Ind}^*\text{)}_2\text{HfCl}_2$ is markedly lower than that of the indenyl-substituted supported catalyst $\text{SiO}_2\text{-Si(Ind)}_2\text{ZrCl}_2$, for which already low productivities of 2.2 – 3.6 gram of polymer per gram of catalyst component were reported.^[7d,e] GPC analysis indicated the presence of polypropylene with a weight average molecular weight M_w of 113,000 g/mol and a broad dispersity ($D = 5.4$). Unfortunately, a further analysis of the polymer microstructure by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy or thermal analysis was hampered by the only very small quantities of isolated polymer.

Analysis of the supported pre-catalyst before and after polymerization by SEM imaging revealed that agglomerated silica particles are present before the polymerization with individual particle sizes below ca. 25 nm (Figure 2, left). After the polymerization, the presence of polymer could be clearly confirmed by the SEM images, showing agglomerates of particles with only marginally increased diameters up to a maximum value of roughly 65 nm (Figure 2, right). No significant differences were found for the two different silica materials **EV**₃₀₀ and **GR**₃₀₀.

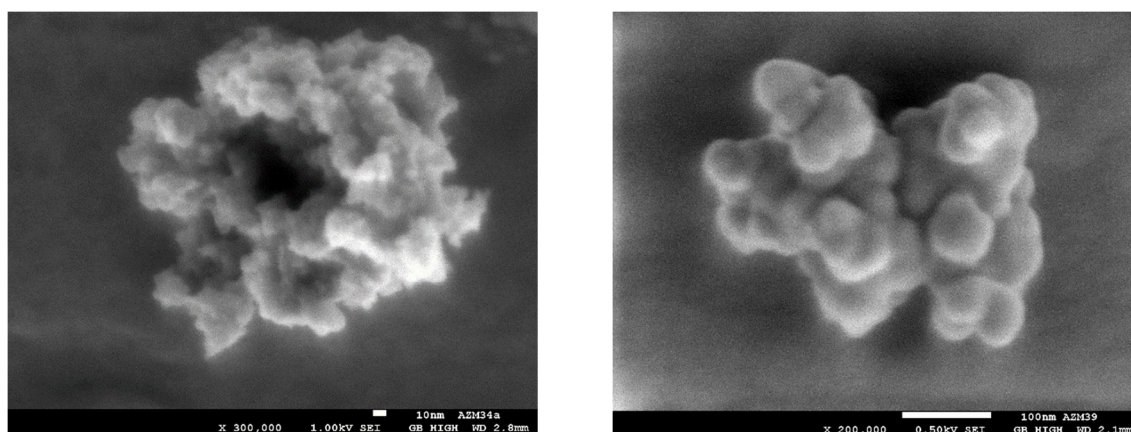


Figure 2. SEM images of $\text{SiO}_2\text{-Si(Ind}^*\text{)}_2\text{HfCl}_2$ before (left) and after (right) the polymerization of propene; used silica: **EV**₃₀₀ (qualitatively similar images were acquired for **GR**₃₀₀).

We conclude that although XPS and elemental analysis indicate that the supported pre-catalyst $\text{SiO}_2\text{-Si(Ind}^*\text{)}_2\text{HfCl}_2$ can be synthesized by the sequential approach employed herein, the material is highly inefficient in polymerizing propene, leading to only minor quantities of polypropylene, regardless of the reaction conditions and the used silica. SEM imaging shows that the particle diameter only slightly increases after the polymerization, suggesting that any catalytic activity shuts down after initial polymer formation. Presumably, this is a result of the poor accessibility of the catalytically active sites resulting from the steric congestion of the bulky Ind^* ligands and the close proximity of the catalyst to the surface, leading to a complete absence of catalytically active sites after the particles are covered with small amounts of polymer. Future studies will now focus on strategies to tether the ultrarigid hafnocene catalyst

rac-1 which allow for an adjustment of the distance of the catalytically active center and the surface by alteration of the length of the tether.^[12]

Acknowledgements: M.I.A. thanks the Alexander von Humboldt foundation for a Feodor Lynen return fellowship. We thank Evonik Industries AG and W. R. Grace & Co. for supply with silica samples and Dr. Asad Asadujjaman for experimental support.

-
- [1] a) X. Cui, W. Li, P. Ryabchuk, K. Junge, M. Beller, *Nat. Catal.* **2018**, *1*, 385; b) M. K. Samantaray, E. Pump, A. Bendjeriou-Sedjerari, V. D'Elia, J. D. A. Pelletier, M. Guidotti, R. Psaro, J.-M. Basset, *Chem. Soc. Rev.* **2018**, *47*, 8403; c) C. Copéret, A. Comas-Vives, M. P. Conley, D. P. Estes, A. Fedorov, V. Mougel, H. Nagae, F. Núñez-Zarur, P. A. Zhizhko, *Chem. Rev.* **2016**, *116*, 323; d) C. Li, Y. Liu (Eds.), *Bridging Heterogeneous and Homogeneous Catalysis. Concepts, Strategies, Applications*, Wiley-VCH, Weinheim, **2014**; e) P. Barbaro, F. Liguori (Eds.), *Heterogenized Homogeneous Catalysts for Fine Chemicals Production*, Springer, Dordrecht, Heidelberg, London, New York, **2010**; f) R. Anwander, in: *Handbook of Heterogeneous Catalysis*, 2nd ed. (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH, Weinheim, **2008**, chapter 2.4.9, pp. 583-614; g) G. M. Thomas, R. Raja, D. W. Lewis, *Angew. Chem. Int. Ed.* **2005**, *44*, 6456.
- [2] R. Geyer, J. R. Jambeck, K. L. Law, *Sci. Adv.* **2017**, *3*, e1700782.
- [3] a) R. Hoff (Ed.), *Handbook of Transition Metal Polymerization Catalysts*, 2nd ed., John Wiley & Sons, Hoboken, NJ, **2018**; b) M. M. Stalzer, M. Delferro, T. J. Marks, *Catal. Lett.* **2015**, *145*, 3; c) I. V. Sedov, V. D. Makhaev, P. E. Matkovskii, *Catal. Ind.* **2012**, *4*, 129; d) J. R. Severn, J. C. Chadwick (Eds.), *Tailor-Made Polymers. Via Immobilization of Alpha-Olefin Polymerization Catalysts*, Wiley-VCH, Weinheim, **2008**; e) J. R. Severn, J. C. Chadwick, R. Duchateau, N. Friederichs, *Chem. Rev.* **2005**, *105*, 4073; f) G. G. Hlatky, *Chem. Rev.* **2000**, *100*, 1347; g) G. Fink, B. Steinmetz, J. Zechlin, C. Przybyla, B. Tesche, *Chem. Rev.* **2000**, *100*, 1377.
- [4] a) V. Busico, *Dalton Trans.* **2009**, 8794; b) B. Wang, *Coord. Chem. Rev.* **2006**, *250*, 242; c) A. Razavi, U. Thewalt, *Coord. Chem. Rev.* **2006**, *250*, 155; d) R. Mülhaupt, *Macromol. Chem. Phys.* **2003**, *204*, 289; e) R. Blom, A. Follstad, E. Rytter, M. Tilset, M. Ystenes, *Organometallic Catalysts and Olefin Polymerization*, Springer-Verlag, Berlin, Heidelberg, **2001**; f) J. A. Gladysz, *Chem. Rev.* **2000**, *100*, 1167; g) L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, *Chem. Rev.* **2000**, *100*, 1253; h) W. Kaminsky (Ed.), *Metalorganic Catalysts for Synthesis and Polymerization*, Springer-Verlag, Berlin, Heidelberg, **1999**; i) H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. M. Waymouth, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143;
- [5] a) C. Chen, *Nat. Rev.* **2018**, *2*, 6; b) J. Klosin, P. P. Fontaine, R. Figueroa, *Acc. Chem. Res.* **2015**, *48*, 2004; c) M. C. Baier, M. A. Zuideveld, S. Mecking, *Angew. Chem. Int. Ed.* **2014**, *53*, 9722; d) M. Delferro, T. J. Marks, *Chem. Rev.* **2011**, *111*, 2450; e) T. Matsugi, T. Fujita, *Chem. Soc. Rev.* **2008**, *37*, 1264;
- [6] a) M. R. Machat, D. Lanzinger, A. Pöthig, B. Rieger, *Organometallics* **2017**, *36*, 399; b) D. Tranchida, D. Mileva, L. Resconi, B. Rieger, A. Schöbel, *Macromol. Chem. Phys.* **2015**, *216*, 2171; c) A. Schöbel, E. Herdtweck, M. Parkinson, B. Rieger, *Chem. Eur. J.* **2012**, *18*, 4174;
- [7] a) R. Spitz, T. Saudemont, J. Malinge, U.S. patent 6,057,258, **2000**; b) K. Soga, *Macromol. Symp.* **1996**, *101*, 281; c) K. Soga, *Macromol. Symp.* **1995**, *97*, 53; d) K. Soga, H. J. Kim, T. Shiono, *Macromol. Rapid Comm.* **1994**, *15*, 139; e) K. Soga, H. J. Kim, T. Shiono, *Macromol. Chem. Phys.* **1994**, *195*, 3347.
- [8] a) Y. Asakura, Y. Sakamoto, K. Kuroda, *Chem. Mater.* **2014**, *26*, 3796; b) P. van der Voort, E. F. Vansant, *J. Liq. Chrom. & Rel. Technol.* **1996**, *19*, 2723; c) C. P. Tripp, M. L. Hair, *J. Phys. Chem.* **1993**, *97*, 5693.
- [9] K. Unger, W. Thomas, P. Adrian, *Kolloid-Z. u. Z. Polymere*, **1973**, *251*, 45.
- [10] Y. Paz, S. Trakhtenberg, R. Naaman, *J. Phys. Chem.* **1994**, *98*, 13517.
- [11] P. Gassman, C. Winter, *Organometallics* **1991**, *10*, 1592.
- [12] a) C. J. Miller, D. O'Hare, *Chem. Comm.* **2004**, 1710; b) N. Suzuki, J. Yu, N. Shioda, H. Asami, T. Nakamura, T. Huhn, A. Fukuoka, M. Ichikawa, M. Saburi, Y. Wakatsuki, *Appl. Catal., A* **2002**, *224*, 63.

Sequential Immobilization of *ansa*-Hafnocene Complexes for Propene Polymerization

*Marius I. Arz,^{1,2} Tim Kratky,¹ Sebastian Günther,¹ Katia Rodewald,¹ Thomas Burger,^{1,2}
Manfred Heuberger,³ Bernhard Rieger^{1,*}*

¹Technische Universität München, Department of Chemistry, Lichtenbergstraße 4, 85748 Garching bei München, Germany

²Technische Universität München, Catalysis Research Center, Ernst-Otto-Fischer-Straße 1, 85748 Garching bei München, Germany

³Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Advanced Fibers, 9014 St. Gallen, Switzerland

*e-mail: riege@tum.de

Supporting Information

Content

1. General considerations	S2
2. Synthesis of the immobilized pre-catalyst	S4
2.1 Synthesis of SiO ₂ -SiCl ₂	S4
2.2 Synthesis of SiO ₂ -Si(Ind*) ₂	S5
2.3 Synthesis of SiO ₂ -Si(Ind*) ₂ HfCl ₂	S5
3. X-ray photoelectron spectroscopy (XPS)	S7
4. Polymerization of propene	S8
5. References	S9

1. General considerations

All manipulations were unless otherwise stated carried out under an atmosphere of argon using standard inert gas techniques or an argon-filled MBraun glovebox.^[S1] All chemicals unless otherwise stated were purchased from Sigma Aldrich, Acros or VWR and used as received. Sipernat® 50 silica was obtained from Evonik [a_{BET} : 450 m²/g, cumulative pore volume: 1.75 mL/g; a_{BET} = surface area determined by BET analysis] and Sylopol® 2408 HT silica was obtained from Grace [a_{BET} = 310 m²/g, cumulative pore volume: 1.51 mL/g]. The silicas were calcined at 300 °C for 16 h under air in a muffle furnace, followed by at 100 °C under vacuum for 1 h and stored under argon. The following abbreviations are used for the calcined silicas: **EV**₃₀₀ (Sipernat® 50) and **GR**₃₀₀ (Sylopol® 2408 HT). Propene 2.8 (Gerling, Holz+Co.) was purified by passage through two consecutive columns filled with BASF catalyst (R3-11) and molecular sieves (4 Å), which were heated to 60 °C and 40 °C, respectively. 7-(3',5'-Di-*tert*-butylphenyl)-4-methoxy-2-methylindene (Ind*H)^[S2] and [HfCl₄(THF)₂]^[S3] were prepared following the literature procedure. Dry toluene, dichloromethane (DCM), tetrahydrofuran (THF), diethyl ether (Et₂O) and *n*-pentane were obtained from an MBraun MB-SPS-800 solvent purification system and stored in the glovebox over molecular sieves (4 Å). 1,4-Dioxane was passed over activated neutral alumina, stirred 4 days over CaH₂, distilled under argon and stored in the glovebox over molecular sieves (4 Å).

Gel permeation chromatography (GPC) was performed on a PL-GPC 220 instrument equipped with 2 × Olexis 300 mm × 7.5 mm columns and triple detection via a differential refractive index detector, a PL-BV 400 HT viscometer and light scattering (Precision detectors model 2040; 15°, 90°). Measurements were performed at 160 °C in 1,2,4-trichlorobenzene (TCB; stabilized with 30 mg BHT/L) with a constant flow rate of 1 mL/min and a calibration set with narrow MWD polystyrene (PS) and polyethylene (PE) standards. The crude polymer (20 mg) was suspended in TCB (4 mL), the suspension heated for 1 h on a heated vibrating plate (140 °C) and filtered at 140 °C prior to the GPC measurement.

Elemental analyses (CHNS and chlorine) were performed by the microanalytical laboratory of the Department of Chemistry of the Technical University of Munich. The hafnium content of the supported pre-catalysts was determined by ICP-OES analysis on an Agilent 700. The samples for the ICP-OES analysis were prepared by stirring a suspension of the supported pre-catalyst in a mixture of 1 mL HCl (37 %), 1 mL HNO₃ (65 %) and 2 mL water for 48 h and subsequent filtration. Hf standards (Merck) were prepared for 50, 10, 1, and 0.1 ppm metal ion concentration. Signal superpositions and matrix effects were excluded. The wavelengths tracked for data evaluation were 232.25 and 277.34 nm. All data were collected 5 times.

N₂ physisorption measurements of the untreated silicas were performed on a Quantachrome NOVAtouch LX-4 instrument. Approximately 100 mg of the silica were

degassed at 120 °C for 3 h prior to analysis. The BET surface area a_{BET} was calculated with the multi-point BET method with seven data points in the p/p_0 range of 0.074 – 0.28. The cumulative pore volume was determined via the N_2 adsorption at a p/p_0 value of 0.99.

The SEM images were recorded with a Jeol JSM 7500F field emission scanning electron microscope. The samples were sonicated in diethyl ether for ca. 30 minutes, the solvent evaporated slowly under air and the samples mounted on an adhesive carbon tape, which was affixed on a copper specimen carrier. An acceleration voltage of either 1 kV or 0.5 kV was used for the measurements.

2. Synthesis of the immobilized pre-catalyst

2.1 Synthesis of SiO₂-SiCl₂

2.000 g of silica (**EV**₃₀₀ or **GR**₃₀₀) were suspended in 40 mL of DCM. 3.0 mL (21.5 mmol) of NEt₃ were added and the resulting yellow suspension was stirred for 30 minutes at ambient temperature. Subsequently, 3.0 mL (26.1 mmol) of SiCl₄ were added to give a dark yellow suspension. The suspension was stirred for 24 h at ambient temperature. The volatiles were removed under vacuum and the resulting colourless solid was dried under vacuum for 2 h. The solid was transferred to a frit (G4 porosity) and washed with 5 × 15 mL of DCM. Subsequently, the colourless solid was dried for 16 h at 100 °C under vacuum. Yield: 1.967 g (**EV**₃₀₀); 1.981 g (**GR**₃₀₀). A ¹H NMR spectrum recorded after agitating the solid in CDCl₃ and subsequent filtration showed no signals of residual [HNEt₃]Cl.

Alternative chlorination of silica

The chlorination of silica following the report from Soga and coworkers^[S4] was also tested. 1.000 g of silica (**EV**₃₀₀) was suspended in 10 mL toluene and 1.0 mL of SiCl₄ (8.7 mmol) was added. The slightly yellow suspension was refluxed for 24 h. A further amount of 0.5 mL of SiCl₄ (4.4 mmol) was added and the suspension further refluxed for 24 h. The mixture was filtered and the residue washed with 3 × 4 mL Et₂O. The colourless solid was dried under vacuum at 100 °C for 16 h. Yield: 1.013 g.

Table S1: Results of the chlorine analyses of SiO₂-SiCl₂.^[a]

silica	w-%(Cl)	α(Cl) [mmol/g]	β(Cl) [μmol/m ²]
EV ₃₀₀	9.6 ^[b]	2.71	6.02
EV ₃₀₀ ^[c]	3.7 ^[c]	1.04	2.32
GR ₃₀₀	6.6 ^[d]	1.86	6.01

[a]: The mass concentration α(Cl) was calculated via $\alpha(\text{Cl}) = w\text{-(Cl)}/[100 \cdot M(\text{Cl})]$ with $M(\text{Cl}) = 35.45 \text{ g/mol}$. The surface concentration β(Cl) was calculated via $\beta(\text{Cl}) = \alpha(\text{Cl})/a_{\text{BET}}$, where a_{BET} is the surface area of the specific silica determined by BET analysis [$a_{\text{BET}}(\text{EV}_{300}) = 450 \text{ m}^2/\text{g}$, $a_{\text{BET}}(\text{GR}_{300}) = 310 \text{ m}^2/\text{g}$]. [b]: Median of three independent determinations. [c]: Prepared by the alternative chlorination route with SiCl₄ in toluene. [d]: Median of two independent determinations.

2.2 Synthesis of SiO₂-Si(Ind*)₂

For the preparation of the LiInd* solution, 1.743 g of Ind*H (5.0 mmol) were dissolved in a mixture of 10 mL toluene / 10 mL 1,4-dioxane and the yellow solution was cooled to 0 °C. 2.2 mL (5.5 mmol, 1.1 eq.) of a 2.5 M *n*-butyllithium solution in *n*-hexane were added dropwise to give a red-orange solution, which was slowly warmed to ambient temperature within 30 minutes and stirred for additional 2 h. This solution of LiInd* was added dropwise to a suspension of 1.000 g of SiO₂-SiCl₂ (**EV**₃₀₀ or **GR**₃₀₀) in 10 mL toluene / 10 mL 1,4-dioxane via cannula at 0 °C to yield an orange-red suspension. The suspension was slowly warmed to ambient temperature and stirred for 16 h. Afterwards, the mixture was heated to 60 °C for additional 48 h. The volatiles of the resulting red suspension were removed under vacuum and the red solid was dried for 2 h under vacuum. The solid was transferred to a frit (G4 porosity) and washed with 3 × 12 mL toluene and 6 × 12 mL Et₂O, whereupon the initially dark red filtrate became colourless. The resulting off-white solid was dried under vacuum at 80 °C for 16 h. Yield: 1.020 g (**EV**₃₀₀); 1.047 g (**GR**₃₀₀). A ¹H NMR spectrum recorded after agitating the solid in CDCl₃ and subsequent filtration showed no signals of residual Ind*H.

Table S2: Results of the CHN analyses of SiO₂-Si(Ind*)₂.^[a]

silica	w-%(C)	w-%(H)	w-%(N)	α(Ind*) [mmol/g]	β(Ind*) [μmol/m ²]
EV ₃₀₀	11.84 ^[b]	1.99 ^[b]	<0.1	0.39	0.88
GR ₃₀₀	9.79 ^[b]	1.79 ^[b]	<0.1	0.33	1.05

[a]: The mass concentration α(Ind*) was calculated via $\alpha(\text{Ind}^*) = \text{w-\%}(\text{Ind}^*) / [100 \cdot M(\text{C in Ind}^*)]$ with $M(\text{C in Ind}^*) = 300.27 \text{ g/mol}$. The surface concentration β(Ind*) was calculated via $\beta(\text{Ind}^*) = \alpha(\text{Ind}^*) / a_{\text{BET}}$, where a_{BET} is the surface area of the specific silica determined by BET analysis [$a_{\text{BET}}(\text{EV}_{300}) = 450 \text{ m}^2/\text{g}$, $a_{\text{BET}}(\text{GR}_{300}) = 310 \text{ m}^2/\text{g}$]. [b]: Median of three independent determinations.

2.3 Synthesis of SiO₂-Si(Ind*)₂HfCl₂

600 mg of SiO₂-Si(Ind*)₂ (**EV**₃₀₀ or **GR**₃₀₀) were suspended in a mixture of 10 mL toluene / 10 mL 1,4-dioxane and the suspension was sonicated for 5 minutes. The yellow suspension was cooled to 0 °C and 0.32 mL (0.80 mmol) of a 2.5 M solution of *n*-butyllithium in *n*-hexane was added to give a red suspension, which was slowly warmed to ambient temperature and stirred for 24 h. The solid was filtered off with a filter cannula, washed with 2 × 10 mL *n*-pentane and dried under vacuum for 1 h at ambient temperature. The off-white solid was suspended in 10 mL THF and a solution of 372 mg (0.80 mmol) [HfCl₄(THF)₂] was added dropwise at −78 °C. The suspension was slowly warmed to ambient temperature and stirred for 16 h. Afterwards it was sonicated for 15 minutes. The volatiles were removed under vacuum and off-white solid was transferred to a frit with G4 porosity and washed with 2 × 5 mL THF, 2 × 5 mL Et₂O and 2 × 5 mL *n*-pentane. Drying under vacuum at 80 °C for 16 h yielded the pre-catalyst as an off-white solid. Yield: 534 mg (**EV**₃₀₀); 550 mg (**GR**₃₀₀). A ¹H NMR spectrum recorded after

agitating the solid in CDCl_3 and subsequent filtration showed no signals of any soluble impurities.

Table S3: Results of the ICP-OES analyses of $\text{SiO}_2\text{-Si(Ind}^*)_2\text{HfCl}_2$.^[a]

silica	w-%(Hf)	$\alpha(\text{Hf})$ [mmol/g]	$\beta(\text{Hf})$ [$\mu\text{mol/m}^2$]
EV₃₀₀	6.09 ^[b]	0.34	0.76
GR₃₀₀	6.09 ^[b]	0.34	0.76

[a]: The mass concentration $\alpha(\text{Hf})$ was calculated via $\alpha(\text{Hf}) = \text{w}-(\text{Hf})/[100 \cdot \text{M}(\text{Hf})]$ with $\text{M}(\text{Hf}) = 178.49$ g/mol. The surface concentration $\beta(\text{Hf})$ was calculated via $\beta(\text{Hf}) = \alpha(\text{Hf})/a_{\text{BET}}$, where a_{BET} is the surface area of the specific silica determined by BET analysis [$a_{\text{BET}}(\text{EV}_{300}) = 450$ m²/g, $a_{\text{BET}}(\text{GR}_{300}) = 310$ m²/g]. [b]: Median of two independent determinations.

Table S4: Results of the CHN analyses of $\text{SiO}_2\text{-Si(Ind}^*)_2\text{HfCl}_2$.^[a]

silica	w-%(C)	w-%(H)	w-%(N)	$\alpha(\text{Ind}^*)$ [mmol/g]	$\beta(\text{Ind}^*)$ [$\mu\text{mol/m}^2$]
EV₃₀₀	11.25 ^[b]	1.63 ^[b]	<0.1	0.37	0.83
GR₃₀₀	8.12 ^[b]	1.52 ^[b]	<0.1	0.27	0.87

[a]: The mass concentration $\alpha(\text{Ind}^*)$ was calculated via $\alpha(\text{Ind}^*) = \text{w}-(\text{Ind}^*)/[100 \cdot \text{M}(\text{C in Ind}^*)]$ with $\text{M}(\text{C in Ind}^*) = 300.27$ g/mol. The surface concentration $\beta(\text{Ind}^*)$ was calculated via $\beta(\text{Ind}^*) = \alpha(\text{Ind}^*)/a_{\text{BET}}$, where a_{BET} is the surface area of the specific silica determined by BET analysis [$a_{\text{BET}}(\text{EV}_{300}) = 450$ m²/g, $a_{\text{BET}}(\text{GR}_{300}) = 310$ m²/g]. [b]: Median of two independent determinations.

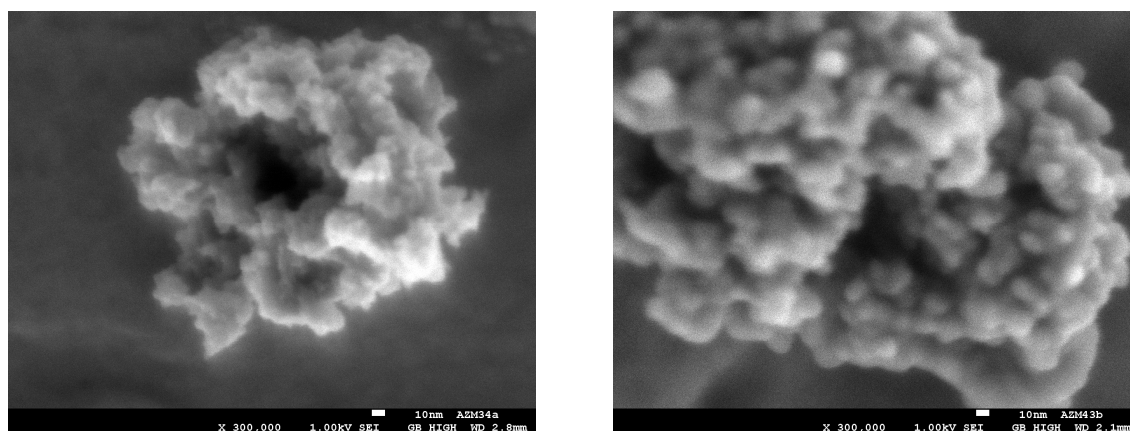


Figure S1. SEM images of the supported pre-catalyst $\text{SiO}_2\text{-Si(Ind}^*)_2\text{HfCl}_2$ prepared with **EV₃₀₀** (left) and **GR₃₀₀** (right).

3. X-ray photoelectron spectroscopy (XPS) studies

X-ray photoelectron spectra were recorded on a Leybold-Heraeus LHS 10 spectrometer using a non-monochromatized Mg K_{α} source (1253.6 eV). The powder samples were pressed into cavities and measured as pellets. Sample preparation and transfer into the XPS spectrometer were carried out under argon atmosphere. All spectra were recorded in an ultra-high vacuum chamber at a pressure below 5×10^{-8} mbar. The analyzer was operated at a constant pass energy of 100 eV leading to an energy resolution with a full width at half-maximum (fwhm) of ~ 1.1 eV. The energy scale of the spectra was corrected for sample charging by using the Si 2p signal at 103.3 eV. The intensity of all spectra was scaled to the total peak area of Si 2p. Core level spectra were deconvoluted by using Voigt functions and linear background subtraction.

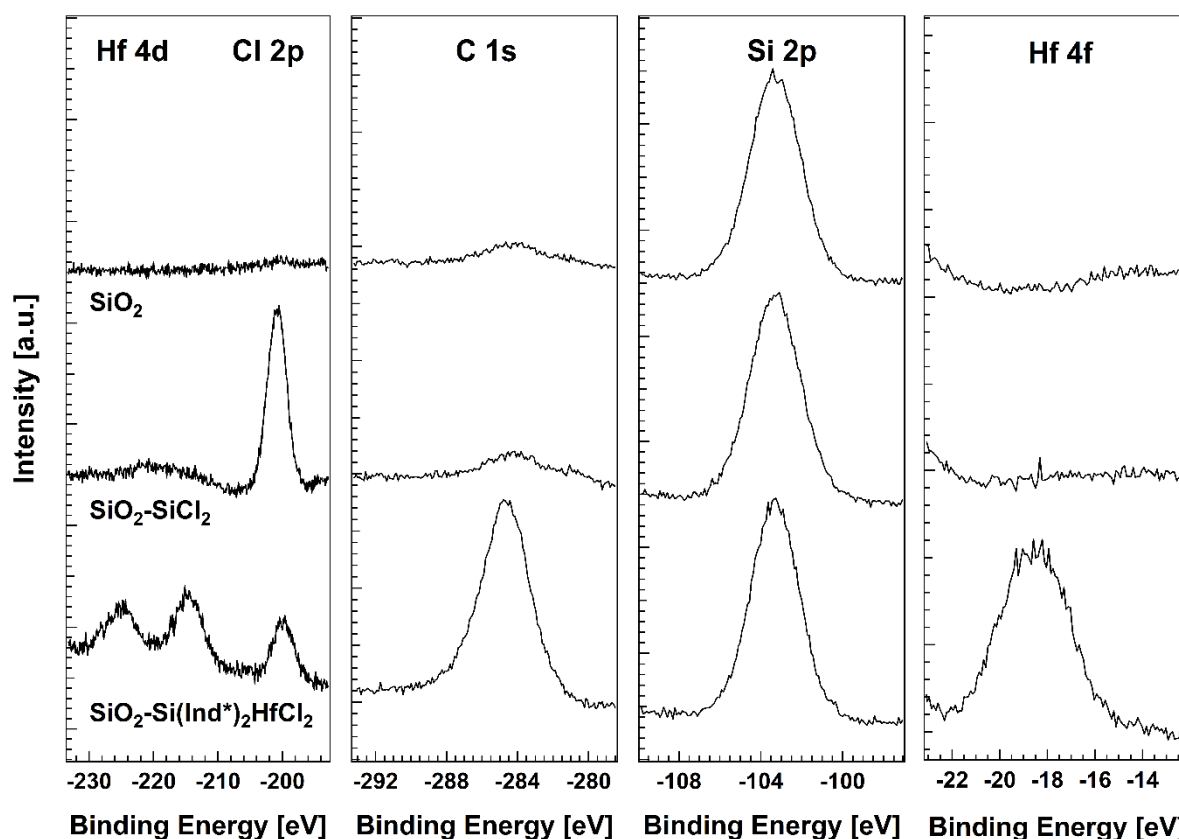


Figure S2. Hf 4d/Cl 2p, C 1s, Si 2p and Hf 4f photoemission spectra obtained from SiO₂, SiO₂-SiCl₂ and SiO₂-Si(Ind*)₂HfCl₂. All spectra have been scaled to the Si 2p peak area originating from the support so that peak intensities reflect the amount of surface atoms.

4. Polymerization of propene

The polymerizations were carried out in a stain-less steel jacketed high-pressure reactor (100 mL total volume), which was equipped with a gas inlet, a gas burette and a mechanical stirrer. The polymerization temperature was adjusted by means of a cryostat. Before the reactor was charged, it was stirred with a solution of 50 mL toluene containing 0.2 mL of a 1.1 M solution of triisobutylaluminium (TIBA) in toluene at 60 °C for 1 h for inertization; the cleaning solution was drained from the reactor before the polymerization.

The supported pre-catalyst (50 mg) was suspended in toluene (10 mL) and 0.2 mL (0.5 mL) of a 1.1 M TIBA solution in toluene were added. The suspension was stirred for 1 h at 60 °C. After cooling to ambient temperature, the suspension containing the activated pre-catalyst was transferred into the reactor with a cannula. Subsequently, a solution of 30 mL containing 0.3 mL of a 1.1 M TIBA solution in toluene was added to the reactor. The gas burette was charged with a solution of $\text{CPh}_3[\text{B}(\text{C}_6\text{F}_5)_4]$ (20 mg, 21.7 mmol) in 10 mL of toluene. The reactor was pressurized with propene for 15 minutes. Afterwards, the initiator solution of $\text{CPh}_3[\text{B}(\text{C}_6\text{F}_5)_4]$ was added via the gas burette and the polymerization was carried out under a constant propene feed. The reaction was stopped by the releasing the propene and adding 1 mL of acidified methanol to the reactor. The reaction mixture was poured into 200 mL of acidified methanol (containing ca. 0.1 mL of 37 % HCl solution) and the precipitate was collected and washed extensively with methanol. The colourless solid was dried for 24 h under vacuum. The reaction conditions and the crude yields of the isolated materials are given in Table S5. SEM images of the crude materials of runs 4 and 5 are shown in Figure S3. The extraction of the crude materials isolated in run 6 and 7 (Table S5) was attempted by extraction with 1,2,4-trichlorobenzene (TCB) at 160 °C and by Soxhlet extraction with boiling TCB under static vacuum. In both cases only minor quantities (<5 mg) of polymer were recovered. The GPC results are reported for the material isolated in run 6.

Table S5. Propene polymerization conditions and isolated crude yields (total solid weights).

run	Silica	m(pre-catalyst) [mg]	pressure [bar]	temperature [°C]	time [h]	crude yield [mg]
1	EV₃₀₀	50	4	25	1	63
2	EV₃₀₀	50	7	40	5	60
3	EV₃₀₀	50 ^[a]	6	40	4	64
4	EV₃₀₀	50	6	40	2	59
5	GR₃₀₀	50	6	40	2	63
6	EV₃₀₀	250 ^[b]	6	40	2	253
7	GR₃₀₀	400 ^[c]	6	40	2	401

[a]: Pre-catalyst activated with TIBA in toluene at 60 °C for 16 h instead of 1 h. [b]: Activated in toluene with 0.5 mL of 1.1 M TIBA solution in toluene; 30 mg (32.5 mmol) of $\text{CPh}_3[\text{B}(\text{C}_6\text{F}_5)_4]$ used in this run. [c]: Activated in toluene with 0.6 mL of 1.1 M TIBA solution in toluene; 35 mg (37.9 mmol) of $\text{CPh}_3[\text{B}(\text{C}_6\text{F}_5)_4]$ used in this run.

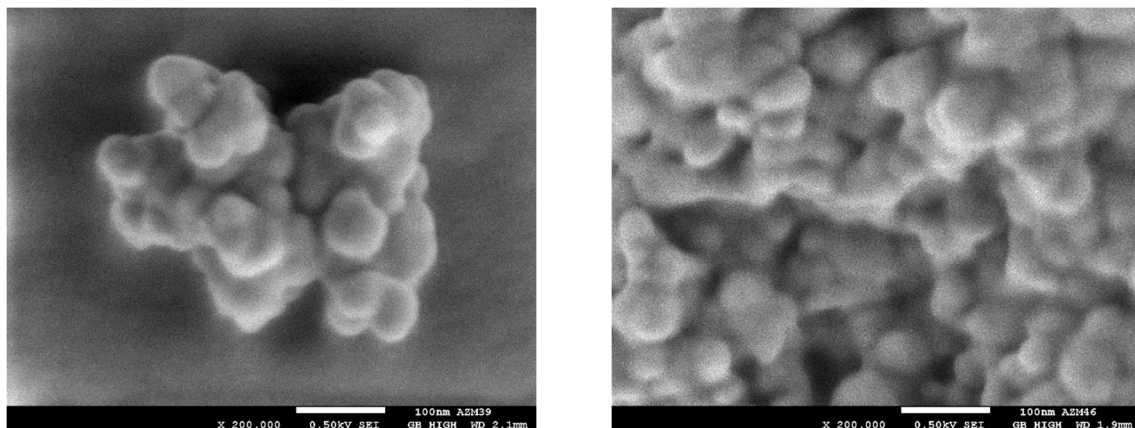


Figure S3. SEM images after polymerization of propene with the supported pre-catalyst $\text{SiO}_2\text{-Si(Ind}^*\text{)}_2\text{HfCl}_2$ prepared with **EV**₃₀₀ (left) and **GR**₃₀₀ (right).

5. References

- [S1] D. F. Shriver, M. A. Drezdson, *The manipulation of air-sensitive compounds*, 2nd ed., John Wiley & Sons, New York, **1986**.
- [S2] A. Schöbel, E. Herdtweck, M. Parkinson, B. Rieger, *Chem. Eur. J.* **2012**, *18*, 4174.
- [S3] L. E. Manzer, J. Deaton, P. Sharp, R. R. Schrock, *Inorg. Synth.* **1982**, *21*, 136.
- [S4] a) K. Soga, H. J. Kim, T. Shiono, *Macromol. Rapid Comm.* **1994**, *15*, 139; b) K. Soga, H. J. Kim, T. Shiono, *Macromol. Chem. Phys.* **1994**, *195*, 3347.

Sequential Immobilization of ansa-Hafnocene Complexes f... (4.33 MiB) [view on ChemRxiv](#) • [download file](#)
