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Switched Stereocontrol in Grubbs−Hoveyda Complex Catalyzed ROMP Utilizing Proton-Switched NHC Ligands†

Lars H. Peeck, Steffen Leuthäusser, and Herbert Plenio*

Organometallic Chemistry, Petersenstrasse 18, Technische Universität Darmstadt, 64287 Darmstadt, Germany

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Grubbs−Hoveyda and Grubbs III type complexes with ferrocenyl- or $-NEt_2$-substituted NHC ligands were synthesized according to standard procedures. The electron donation of the NHC ligands in the respective ruthenium complexes can be modulated by oxidation of the ferrocenyl moiety or by protonation of the amino group. The neutral and the respective cationic (oxidized or protonated) ruthenium complexes were tested in the ROMP of norbornene. The change in the electron donation of the NHC ligands upon protonation leads to a significant change in the double-bond geometry (from E/Z ratio = 0.78 to E/Z = 1.04) and in the microstructure of the resulting polynorbornene. Consequently, addition of acid and protonation of the living catalyst attached to the polymer chain during the polymerization reaction allows fine-tuning the E/Z ratio of the resulting polynorbornene.

Introduction

The microstructure of a polymer has a significant influence on the properties and consequently the application of such materials.[1] This was convincingly demonstrated for various zirconocenes in stereoselective propene polymerization reactions.[2] Different zirconocenes render different polymer microstructures such as atactic, isotactic, or syndiotactic polyolefins, resulting in very different materials properties.[3] Even more exciting are metal complexes, which are able to exert an oscillating stereocontrol during the polymerization process. Coates and Waymouth demonstrated that shuttling a catalyst complex between two different conformations allows switching the stereocontrol during propene polymerization, resulting in stereoblock copolymers composed of isotactic and atactic blocks,[4] even though Busico et al. later suggested a more complicated explanation.[5] A special block copolymer can also be obtained by a chain shuttling polymerization, in which the growing polymer chain oscillates between two different catalytic metals through the use of chain transfer agents.[6] The facile switching of polymer microstructure between a linear, highly branched or even dendritic structure depending on the ethene pressure and the different degree of chain-walking was demonstrated by the Guan group.[7]

Ring-opening metathesis polymerization (ROMP) is a highly useful method for the synthesis of numerous polymers.[8] Consequently, it appeared to be an interesting target to synthesize functionally related catalyst complexes, which enable reversible control over the stereochemical outcome of a polymerization reaction by manipulating the catalytically active center in the course of the chain-growth reaction.

We wish to report our initial attempts to bring about switchable stereocontrol in ROMP reactions. A ROMP monomer such as norbornene can approach the metal center in four different orientations to potentially result in four different stereoregular polymers.[9] A suitable catalyst has the ability to control E/Z selectivity as well as the relative stereochemistry between monomer units (tacticity control).[10] However, attaining efficient stereochemical control in olefin metathesis reactions remains a challenging problem. The stereospecific polymerization of various ROMP monomers was realized with Schrock-type molybdenum complexes, to result in polynorbornenes with excellent stereoregularity.[11] However, due to the high oxophilicity of the high-valent

† Dedicated to Dietmar Seyferth in recognition of his tremendous contributions to organometallic chemistry and Organometallics.

*To whom correspondence should be addressed. E-mail:plenio@tu-darmstadt.de.

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molybdenum center, the application of such catalysts is limited to certain substrates and anhydrous reaction conditions. Work from Noels et al. on $[RuCl_2(p\text{-cymene})]_2$ established that stereocontrol led to an all-*trans*, highly isotactic polymer after hydrogenation of a polymeric norbornadiene.[12] Attempts to realize stereoregular polymers with highly active Grubbs-type complexes have seen only limited success.[8a,13] However, several complexes were published that are (potentially) able to exert stereocontrol by utilizing steric effects.[14]

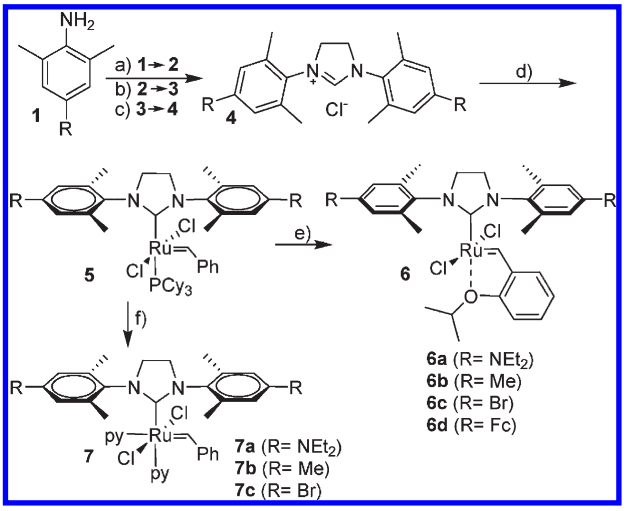
Our target is a switchable ruthenium complex, whose stereochemical preferences in the ROMP process can be changed upon applying an external stimulus. It appears much easier to switch the electronic situation at a catalytic center rather than the steric environment. Therefore we became interested in whether it is possible to create a ruthenium-based olefin metathesis catalyst whose *E*/*Z* preference in the ROMP reaction can be modulated by switching the electronic situation of the catalytic center.

Results and Discussion

We recently synthesized several [*N*,*N*′-bis(2,6-dimethyl-4-R-phenyl)imidazolidene]-2-ylidene-type NHC ligands with different 4-R substituents, whose electron-donating properties were systematically varied.[15] This led to a series of NHC ligands with tunable electron-donating properties. We were motivated to learn whether the variable donor properties of such ligands have an influence on the catalytic properties of the respective Grubbs-type complexes. It is well known that the activity of different (NHC)Ru complexes in olefin metathesis reactions improves on increasing the electron-releasing capacity of the NHC ligands.[16] For the synthesis of polymers the activity of a given complex is important, but especially with living polymerization reactions such as ROMP, many catalysts provide very good activity.

ROMP Reactions of Complexes 6a−6d. We first studied the influence of the variable NHC electron donation of complexes **6a** (R = −NEt_2), **6b** (R = −Me), and **6c** (R = Br) (which were available from previous studies, Scheme 1)[15,17] on the stereochemistry of ROMP-generated polynorbornene. The molecular weight of the monomodal polymers obtained in nearly quantitative yields is around 40.000 g/mol with relatively high polydispersities ranging between 1.53−1.91

Scheme 1. Synthesis of New Ferrocenyl-Substituted (d stands for R = Fc) NHC·HCl 4d, Grubbs−Hoveyda Complex 6d, and New Grubbs III Complexes 7a and 7c as Well As the List of Complexes Used for Polymerization Reactions[a]



[a] Reagents and conditions: (a) glyoxal(aq), formic acid, EtOH, yield **2d** 87%; (b) $LiAlH_4$, thf, yield **3d** 95%; (c) $HC(OEt)_3$, HCOOH, 120 °C, yield **4d** 77%; (d) Grubbs I complex, KO*t*Bu, toluene, 50 °C, yield **5d** 36%; (e) isopropoxystyrene, CuCl, toluene, 40 °C, yield **6d** 80%; (f) pyridine, 5 min, rt, yield **7c**−**7a**: 68−94%.

Table 1. Summary of Polynorbornene Properties Produced via ROMP[a]

entry	catalyst	yield [%]	*E*/*Z*[c]	M_n (GPC)[d]	PDI[e]
1[b]	**6a**	99	0.78	48 500	1.65
2[b]	**6b**	99	0.68	42 000	1.74
3[b]	**6c**	99	0.64	42 500	1.91
4[b]	**6d**	99	0.71	38 800	1.53
5[b]	$\mathbf{6d}^{2+}$	99	0.73	35 600	1.61
6[b]	**6a**·$2H^+$	99	1.04	41 900	1.55
7[b]	**7a** + 2 HCl	99	0.88	28 000	1.28
8[b]	**7a** + 4 HCl	99	1.09	31 300	1.57
9[b]	**7a**	99	0.78	21 700	1.57
10[b]	**7b**	99	0.68	20 000	1.40
11[b]	**7c**	99	0.64	23 600	1.22

[a] Catalyst: 1.0 mol % [Ru], solvent: CH_2Cl_2, T = 293 K. [b] Polynorbornene M_n (theory) 9400. [c] Ratio of *cis* and *trans* double bonds from ^1H NMR measurements. [d] GPC in 1,2,4-trichlorobenzene at 140 °C relative to polystyrene standard. [e] Polydispersity index.

(Table 1, entries 1−3). Grubbs−Hoveyda-type complexes are known to undergo slow initiation reactions.[18] Consequently, the M_n for polynorbornene is much higher than expected (100% initiation should correspond to 9400 g/mol).[19] In our experiments, and in contrast to observations by Schanz et al., the polymer weight is not strongly correlated with the electron richness of the ruthenium catalyst.[20] However, depending on the electron-releasing capacity of the R-substituted NHC ligand, the *E*/*Z* ratio of the double bonds in the polymer changes in a systematic manner. For the most electron-rich ruthenium complex **6a** (R = NEt_2) the *E*/*Z* ratio of double bonds is 0.78. With successively less electron-releasing NHC ligands this ratio changes with reduced electron donation (Table 1). The change in the *E*/*Z* ratio across the series of complexes **6a**−**6c** is not large, but it should be

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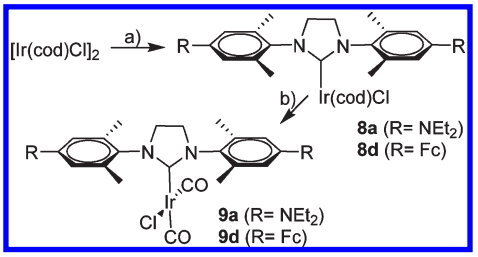
noted that with a given complex the E/Z ratio is highly reproducible (to within 1%). Therefore the differences observed by us are significant.

We were next interested in the synthesis of ruthenium complexes with substituted NHC ligands whose electron-donating properties can be switched reversibly.[21] The obvious idea was to create ROMP catalysts with switchable stereocontrol via switchable electron donation. Ferrocenes are well known as electrochemically switchable groups with a high degree of reversibility,[22] which have been used previously in molecular switches.[23] Consequently, it was decided to first synthesize a ferrocene-substituted NHC ligand, aiming for the redox switching of this substituent from an electron-releasing ferrocenyl to an electron-withdrawing ferrocenium group. The $-NEt_2$ group in **6a** is potentially equally useful, since protonation converts a strongly electron-donating amine into a strongly electron-withdrawing ammonium.

Synthesis of the Ferrocenyl-Substituted Grubbs−Hoveyda Complex. The new ferrocenyl-tagged Grubbs−Hoveyda complex **6d** (R = Fc) (Scheme 1) was prepared analogously to published procedures.[15,17,24] In order to enhance the switching effect, the ferrocenyl group was directly attached to the mesityl ring and thus closer to the ruthenium than in the ethinylferrocene-substituted NHC reported previously.[23b] In order to retain sufficient catalytic activity in the Grubbs-type complex **6d**, it was decided to preserve the "ideal" dimesityl NHC structure for catalysis, and other ferrocenyl-tagged NHC ligands were not tested.[21d,23c,25] The known aniline **1d**[26] was converted to the dimine **2d**, $LiAlH_4$ reduction gave the diamine **3d**, ring closing provided the imidazolinium salt **4d**, and finally via the Grubbs II complex **5d** the desired Grubbs−Hoveyda complex **6d** was obtained (Scheme 1). **6d**$^{2+}$ was synthesized by addition of two equivalents of acetylferrocenium tetrafluoroborate to **6d** prior to the polymerization reaction.

In order to probe the electron-releasing capacity of the ferrocenyl group, the respective iridium NHC complexes **8d** and **9d** were synthesized according to a published procedures.[15] In the electrochemical experiment the Fe(II/III) oxidation (**8d** → **8d**$^{2+}$, $E_{1/2} = +0.447$ V) was observed and at a more anodic potential the Ir(I/II) redox potential (**8d**$^{2+}$ → **8d**$^{3+}$, $E_{1/2} = +0.858$ V). The Ir(I/II) redox potential in **8d** is close to that of the Ir(I/II) potential in **8c** (R = Br) ($E_{1/2} = +0.838$ V).[15] The redox potentials of **6d** were determined as $E_{1/2} = 0.474$ V for Fe(II/III) and $E_{1/2} = +0.951$ V for Ru(II/III). Again the Ru(II/III) redox potential of **6d**$^{2+}$ is close to that of the bromo-substituted complex **6c** (Ru(II/III) $E_{1/2} = +0.935$ V).[17] Since the iron of the ferrocene unit is oxidized prior to the iridium in **8d** and to the ruthenium in **6d**, it is not possible to determine the electron-releasing capacity of the ferrocenyl-substituted NHC using this technique. We therefore synthesized (NHC)IrCl(CO)$_2$ (**9d**) and determined the ν(CO) = 1982, 2070 cm^{-1} (TEP (Tolman electronic parameter) = 2055.8 cm^{-1}). This is indicative of an electron-releasing capacity of the ferrocenyl group close to that of the methyl group in **9b** and is in agreement with the Hammett parameters of the ferrocenyl substituent.[27] Since neither the Grubbs−Hoveyda complex **6a**·2H$^+$ nor the iridium complex **8a**·2H$^+$ displays reversible redox behavior, the electron-releasing capacity of the $-NEt_2H^+$-substituted NHC ligand was determined via infrared spectroscopy. With a ν(CO) for **9a**·2H$^+$ (1986, 2072 cm^{-1}, TEP = 2058 cm^{-1}) the electron-releasing ability of $-NEt_2H^+$ is comparable to that of −SOAr (TEP = 2058 cm^{-1}).[9]

Scheme 2. Synthesis of (NHC)IrCl(cod) (8d) and (NHC)IrCl(CO)$_2$ (9d)[a]



[a] Reagents and conditions: (a) KOtBu, imidazolium salt, thf, rt, yield 66%; (b) CO, CH_2Cl_2, rt, yield 96%.

Switched ROMP Reactions Utilizing Complexes 6d/6d^{2+} and 6a/6a·2H$^+$. It was first tested whether the oxidation of the ferrocene unit in **6d** has a significant effect on the stereochemistry of the polymer resulting from the norbornene ROMP. However, both **6d** and **6d**$^{2+}$ render polymers with nearly the same E/Z ratio (0.71 vs 0.73) (Table 1, entries 4, 5). We believe that the difference in the electron donation of the NHC ligand in **6d** and in **6d**$^{2+}$ is too small for a significant change in the polymer stereochemistry and went on to study the much larger effect of the NHC protonation in **6a** for ROMP reactions of norbornene. On comparing the microstructure produced in the norbornene polymerization using **6a** with that obtained using the protonated complex **6a**·2H$^+$, the E/Z ratio changes significantly from 0.78 to 1.04 (Table 1). The molecular weight of the polynorbornene obtained from **6a** is higher than that from **6a**·2H$^+$ (Table 1). This may be due to the lower propagation rate (k_{prop}) for the protonated and thus less electron-rich ruthenium center, which leads to a larger ratio k_{init}/k_{prop}. This is in agreement with observations made by Schanz.[20]

It was next tested whether the addition of acid to a nonprotonizable Grubbs−Hoveyda complex has an influence on the polymer microstructure. Two equivalents of HCl (in dioxane) was added to complex **6b** prior to the polymerization experiments. This did not have a measurable effect on the E/Z ratio of the resulting polynorbornene. Next the acid

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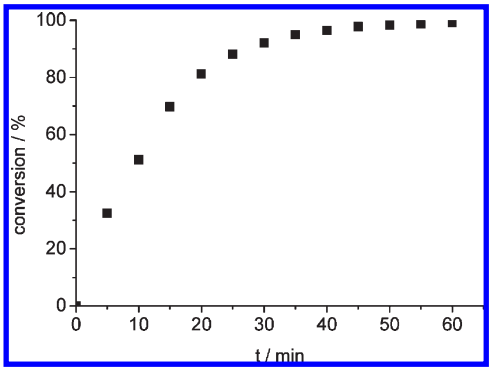
Scheme 3. Conversion−Time Curve for the ROMP of Norbornene at −50 °C



was changed, to learn whether the nature of the counterion has any effect. Two equivalents of HBF_4 was added to **6a** and the resulting protonated complex **6a**·2HBF_4 applied in the norbornene ROMP. The *E*/*Z* ratio observed in this polynorbornene was exactly the same as observed for **6a**·2HCl. These important experiments allow excluding medium as well as counterion effects on the switched stereochemistry.

Finally, the effect of catalyst loading on the stereochemistry of the ROMP polymer was probed. It is important to check this, since with a 1 mol % [Ru] loading only a small amount of the Grubbs−Hoveyda complex **6a** is activated for the ROMP reaction. In order to exclude whether this has an influence on the *E*/*Z* ratio in the resulting polynorbornenes, the amount of precatalyst in the ROMP reactions was varied. Instead of the 1 mol % [Ru] normally employed here for the polymerization of norbornene, the ROMP reactions were carried out using a 0.1 mol % loading of **6a** and **6a**·2H^+. However, the variable catalyst loading did not have any effect on the *E*/*Z* ratio in the resulting norbornene.

We were next interested to find out whether the amine/ammonium-induced change of the polynorbornene stereochemistry can be exploited to switch the stereochemistry of the resulting polymer during the polymerization reaction. The interception of the very fast ROMP reaction of norbornene at room temperature for pH switching is difficult, and the polymerization with **6a** had to be slowed by lowering the reaction temperature to −50 °C. Under these conditions this specific ROMP reaction requires ca. 60 min until completion (Scheme 3).

Under the assumption that the stimulus change is fast enough, the active polymerization catalyst can be intercepted to enable the switching of the double-bond stereochemistry. Fortunately for the very fast protonation reactions, this should not pose a problem. Starting with **6a** at −50 °C, a polynorbornene with an *E*/*Z* ratio of 0.64 was obtained; under the same reaction conditions **6a**·2H^+ provides an *E*/*Z* ratio of 0.85 (Table 2). After starting the polymerization with **6a**, two equivalents of HCl were added after 10 min reaction time to protonate the active catalyst with the attached growing polymer chain during the polymerization reaction. This led to an increase (relative to the *E*/*Z* with **6a**) in the *E*/*Z* ratio to 0.73 (Table 2). Successively earlier additions of acid result in a more pronounced increase in the *E*/*Z* ratio of the final polymer due to the earlier formation of the protonated catalyst, with its preference for a higher *E*/*Z* ratio. These results provide clear evidence for the ability to control the resulting stereochemistry of the polymer by the addition of acid.

Table 2. Polynorbornene ROMP at $T = -50$ °C Using Precatalyst 6a and with the Addition of Acid after the Specified Reaction Times[a]

complex	HCl addition after	*E*/Z[b]	M_n (GPC)[c]	PDI[d]
6a		0.64	37 600	1.71
6a	10 min	0.73	35 900	1.69
6a	5 min	0.79	35 100	1.73
6a	3 min	0.82	34 700	1.71
6a·2H^+		0.85	31 300	1.70

[a] Yield 99% for all reactions. [b] Ratio of *cis* and *trans* double bonds from ^{1}H NMR measurements. [c] GPC in 1,2,4-trichlorobenzene at 140 °C relative to polystyrene standard. [d] Polydispersity index.

In order to determine whether the variable *E*/*Z* ratio has an influence on the material properties, the glass transition temperatures (polymer from **6a** $T_g = 55$ °C, **6a**·2H^+ 52 °C, **6c** 58 °C) were determined. The effect on the polynorbornene T_g is small, but it is significant.

The origin of the effect of the R substituent on the polymer microstructure is unclear. Normally two factors, enantiomorphic site control and chain-end control, are considered to be responsible for stereocontrol in transition metal-catalyzed reactions.[3] Both modes of action can be distinguished in polymers with a high degree of stereocontrol via the response of the active metal−polymer complex following adventitious stereodefects.[3] However, with a view to the large distance between the R substituents and the ruthenium, a steric effect of the variable R substituents in the ligand on the ROMP reaction, and thus enantiomorphic site control, seems unlikely. For a chain-end control mechanism the observed switched stereochemistry upon protonation is difficult to explain. A significant steric influence on the polymer stereochemistry is also unlikely, since the use of R groups of comparable steric bulk (−CH_3 and Br) but significantly different electronic properties leads to different polymer microstructures. The correlation of the polynorbornene microstructure and the electron-donating ability of the R substituent clearly favors an electronic effect. An electronic effect of a stereogenic metal center on the ROMP was recently also postulated by Schrock et al. to occur for a molybdenum hexaisopropylterphenoxide monopyrrolide complex.[11a]

It may be surprising that the remote R substituent exerts a significant electronic effect on the properties of the ROMP catalysts. The transfer of electronic information via the bonds between the R group and ruthenium appears less likely, also with a view to the orthogonality of the five- and six-membered rings. However, we recently demonstrated conclusively that apart from the established σ-donor/π-acceptor abilities of NHC ligands via the carbene carbon in [*N*,*N*′-bis(2,6-dialkylphenyl)imidazolidene]-2-ylidene-type carbenes,[28] electron density can also be transferred directly via π-face donation between the Ru=CHPh unit and the mesityl ring carrying the R substituent.[17,24,29] We therefore believe that the transfer of electron density directly from the mesityl ring to the ruthenium enables an electronic control in the polymerization process. Recent results by Lavigne et al.[30] and Bielawski et al.[21i] lend further support, concerning the possibility of a direct interaction of certain NHC ligands and a NHC-bound

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transition metal. With respect to the influence of NHC donation on reactivity, Fürstner et al. recently reported on the consequences of variable π-acceptor properties of NHC ligands in gold-catalyzed cycloisomerization reaction;[31] Bielawski et al. observed an influence of σ-donor/π-acceptor effects in palladium-catalyzed cross-coupling reactions.[32] An open question remains concerning the change of the E/Z ratio with changing NHC donicity. The data in Table 1 for complexes **6a**−**6c** show that decreasing NHC donation translates into a decreasing E/Z ratio in the polymers produced via the respective complex. On the other hand, upon protonation of **6a** the E/Z ratio of the polynorbornene is increasing. This was unexpected: a decrease of donation upon protonation of the NHC, viz., a lower electron density at the ruthenium, was expected. This understanding of an amino substituent is based on the respective Hammett parameters, but the partitioning of the σ- and π-components clarifies that upon protonation a strong π-donor is converted into a strong σ-acceptor.[27] Kennepohl et al.[33] and Schanz et al.[20] point out that the charge density at the ruthenium has a strong influence on the olefin metathesis rate. On the basis of DFT-derived Mulliken charges Schanz argues that the protonation of an amine leads to a decrease in the positive charge at ruthenium.[20] This appears to be counterintuitive, but might help to explain the observed trends in the E/Z ratio of the ROMP polymerization of **6a** vs **6a**·$2H^+$.

Switched ROMP Reactions Utilizing Complexes 7a/7a·$2H^+$. In order to lend additional support to the hypothesis that switched stereocontrol results from the switched electron donation of the NHC ligand, we also tested different precatalysts for the ROMP of norbornene. The Grubbs III complexes **7a**−**c** (synthesized from the respective Grubbs II complex **5a**−**c** and pyridine, Scheme 1) afford exactly the same E/Z ratio as complexes **6a**−**c** (Table 1, entries 1−3 and 9−11). This is reasonable, since following activation complexes **7** provide the same active species as the one originating from the Grubbs−Hoveyda complexes **6**. This experiment also shows that the different initiation rates in **6** and in **7** do not influence the polymer stereochemistry. However, as a result of the faster initiation rates, the M_n for the polynorbornene produced with complexes **7** are lower than those with the Grubbs−Hoveyda complexes **6** (Table 1), while the polydispersities are lower. Next the proton-induced switching experiment was repeated using **7a** and variable amounts of HCl. This reaction is more complex for complex **7a** than **6a**, since in addition to the $-NEt_2$ substituents at the NHC, the pyridine ligands are also available for protonation, which should have an effect on the initiation rates as reported by Schanz.[34] Upon protonation of complex **7a** with two and four equivalents of acid, respectively, the E/Z ratio increases to 0.88 (Table 1, entry 7) and finally to 1.09 (Table 1, entry 8), which is very close to $E/Z = 1.04$ observed for the related Grubbs−Hoveyda complex. Using four equivalents of acid the two $-NEt_2$ groups and the two pyridines should be protonated. We note that the nature of the precatalyst is not important for the E/Z ratio of the polynorbornenes (as long as the same active species is generated!). This again underlines that changes in the electronic nature of the active species upon protonation seem to be responsible for the observed switch in the stereochemistry of polynorbornene.

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Summary and Conclusions

The variation of the electron-donating ability of the NHC ligand in Grubbs−Hoveyda complexes can lead to significant changes in the double-bond geometry (E/Z ratio) of ROMP-generated polynorbornene. Specifically, the protonation of amino-substituted NHC ligands in Grubbs−Hoveyda and Grubbs III-type complexes enables the switchable control over the microstructure of ROMP polymers. The fast protonation of the catalytically active species during the ROMP reaction constitutes this switch, which relies on variable electron donation. Further improvements of the switching efficiency, as well as a better understanding of the observed effects, are warranted, but nonetheless this work opens the door to switchable stereocontrol producing ROMP stereoblock-copolymers with distinct properties.

Experimental Section

For general experimental details see the Supporting Information.

***N,N′*-Bis(2,6-dimethyl-4-ferrocenylphenyl)ethylenediimine, 2d.** A solution of 2,6-dimethyl-4-ferrocenylaniline (1.66 g, 5.46 mmol) in EtOH (12 mL) was treated with aqueous glyoxal solution (40 wt %, 313 μL, 2.73 mmol) and three drops of formic acid. The reaction mixture was stirred overnight. The orange precipitate was filtered off, washed with MeOH, and dried *in vacuo*. *N,N′*-Bis(2,6-dimethyl-4-ferrocenylphenyl)ethylenediimine was obtained as an orange powder. Yield: 1.50 g (87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (s, 2H, N=C*H*-C*H*=N), 7.21 (s, 4H, *m*-H_{aryl}), 4.62 ("t", $J = 1.9$ Hz, 4H, C_5H_4), 4.30 ("t", $J = 1.9$ Hz, 4H, C_5H_4), 4.08 (s, 10H, C_5H_5), 2.17 (s, 12H, *o*-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.3, 147.9, 135.8, 126.8, 126.2, 85.4, 69.6, 68.7, 66.3, 18.5. HRMS: *m*/*z* calcd for $C_{38}H_{36}N_2Fe_2$ 632.15770; found 632.15668.

***N,N′*-Bis(2,6-dimethyl-4-ferrocenylphenyl)ethylenediamine Dihydrochloride, 3d.** *N,N′*-Bis(2,6-dimethyl-4-ferrocenylphenyl)-ethylenediimine (**2d**) (1.50 g, 2.38 mmol) was dissolved in dried, degassed THF (25 mL). The solution was cooled to 0 °C, and $LiAlH_4$ pellets (0.23 g, 5.95 mmol) were added. The reaction mixture was stirred overnight at room temperature and poured carefully into a mixture of concentrated HCl (50 mL) and ice (150 g). The yellow precipitate was collected by filtration, washed with water (3 × 50 mL), and dried *in vacuo*. Yield: 1.61 g (95%). Since the dihydrochloride was not soluble in [D_6]-DMSO, 50 mg (0.070 mmol) of this compound was dissolved in 2 N NaOH (10 mL). The reaction mixture was extracted with MTBE (3 × 10 mL). The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated *in vacuo* to obtain the corresponding free diamine as an orange solid. Yield: 43 mg (95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12 (s, 4H, *m*-H_{aryl}), 4.55 ("t", $J = 1.8$ Hz, 4H, C_5H_4), 4.25 ("t", $J = 1.8$ Hz, 4H, C_5H_4), 4.05 (s, 10H, C_5H_5), 3.22 (s, 4H, NCH_2CH_2N), 2.34 (s, 12H, *o*-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.2, 132.4, 129.4, 126.9, 86.3, 69.5, 68.4, 66.2, 48.9, 18.8. HRMS: *m*/*z* calcd for $C_{38}H_{40}N_2Fe_2$ 636.1890; found 632.19120.

***N,N′*-Bis(2,6-dimethyl-4-ferrocenylphenyl)imidazolinium Chloride, 4d.** *N,N′*-Bis(2,6-dimethyl-4-ferrocenylphenyl)ethylenediamine dihydrochloride (**3d**) (0.70 g, 0.99 mmol) was suspended in $HC(OEt)_3$ (5 mL). Three drops of formic acid were added. The reaction mixture was stirred at 120 °C overnight. The brown precipitate was filtered off, washed with MTBE (5 × 30 mL), and dried *in vacuo*. Yield: 0.52 g (77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.10 (s, 1H, $H_{imidazolinium}$),

7.45 (s, 4H, *m-H*$_{aryl}$), 4.83 (s, 4H, C_5H_4), 4.51 (s, 4H, NCH_2CH_2N), 4.40 (s, 4H, C_5H_4), 4.07 (s, 10H, C_5H_5), 2.43 (s, 12H, *o*-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.6, 141.5, 135.9, 131.4, 126.5, 83.6, 69.8, 69.7, 67.0, 51.3, 17.8. HRMS: *m*/*z* calcd for $C_{39}H_{39}N_2Fe_2$ 647.18120; found 647.18014.

Complex 5d. *N,N*′-Bis(2,6-dimethyl-4-ferrocenylphenyl)imidazolinium chloride (**4d**) (350 mg, 0.51 mmol) and KO*t*Bu (57 mg, 0.51 mmol) were weighed in a Schlenk flask under an atmosphere of argon. Dried and degassed toluene (20 mL) was added and the mixture stirred for 15 min. Next dichlorobenzylidenebis-(tricyclohexylphosphine)ruthenium(II) (210 mg, 0.26 mmol) was added. The mixture was stirred at 50 °C for 1 h, and the volatiles were evaporated *in vacuo*. The remaining solid was purified by column chromatography (cyclohexane/ethyl acetate, 15:1 v/v) and the desired product obtained as a brown solid. Yield: 111 mg (36%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 19.09 (s, 1H, Ru=C*H*), 8.00−5.60 (m, 6H, *m-H*$_{aryl}$ + $H_{benzylidene}$), 7.28 (s, 2H, m-H_{aryl}), 7.21 (t, *J* = 7.3 Hz, 1H, $H_{benzylidene}$), 4.62 ("t", *J* = 1.7 Hz, 4H, C_5H_4), 4.36 (bs, 2H, C_5H_4), 4.31("t", *J* = 1.7 Hz, 2H, C_5H_4), 4.27 ("t", *J* = 1.7, 2H, C_5H_4), 4.11 (s, 5H, C_5H_5), 4.10−4.04 (m, 2H, NCH_2CH_2N), 4.01 (s, 5H, C_5H_5), 4.00−3.86 (m, 2H, NCH_2CH_2N), 2.74 (bs, 6H, *o*-CH_3), 2.50−2.20 (m, 6H, *o*-CH_3), 2.14 (q, *J* = 11.0 Hz, 3H, PC*H*), 1.58−1.19 (m, 15H, Cy), 1.12−0.69 (m, 15H, Cy). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 295.1, 220.7 (d, J_{C-P} = 78 Hz), 151.5, 139.8, 139.0, 138.9, 137.8, 137.0, 135.7, 128.1, 128.0, 126.9, 126.3, 85.5, 85.1, 69.7, 69.5, 68.9, 68.6, 66.8, 52.3, 51.4, 31.6 (d, J_{C-P} = 16 Hz), 29.1, 27.7 (d, J_{C-P} = 10 Hz), 26.3, 20.3, 19.0. ^{31}P NMR ($CDCl_3$, 81 MHz): δ 28.27. MS (ESI): *m*/*z* 1153.6 (M − Cl), 647.5 (M − $Cl_2RuCHPhPCy_3$).

Complex 6d. Grubbs second-generation complex **5d** (111 mg, 0.090 mmol) was placed in a Schlenk flask and dissolved in dried and degassed toluene (20 mL). CuCl (28 mg, 0.28 mmol) and isopropoxystyrene (35 μL, 0.19 mmol) were added, and the mixture was stirred for 2 h at 40 °C. The volatiles were removed *in vacuo*, and the residue was purified by column chromatography (cyclohexane/ethyl acetate, 6:1 v/v). The Hoveyda-type complex **6d** was obtained as a green crystalline solid. Yield: 72 mg (80%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 16.81 (s, 1H, RuC*H*), 7.44 (t, *J* = 7.4 Hz, 1H, $H_{benzylidene}$), 7.35 (s, 4H, *m-H*$_{aryl}$), 7.02 (dd, J = 7.9, 1.6 Hz, 1H, $H_{benzylidene}$), 6.85−6.78 (m, 2H, $H_{benzylidene}$), 4.91 (sept., *J* = 6.2 Hz, 1H, $(CH_3)_2CH$OAr), 4.67 (s, 4H, C_5H_4), 4.36 (s, 4H, C_5H_4), 4.19 (s, 4H, NCH_2CH_2N), 4.14 (s, 10H, C_5H_5), 2.55 (bs, 12 H, *o*-CH_3), 1.35 (d, *J* = 6.2 Hz, 6H, $(CH_3)_2$CHOAr). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 296.5, 211.7, 152.4, 145.4, 140.4, 139.4, 139.3, 129.7, 126.8, 123.0, 122.4, 113.0, 85.3, 75.1, 69.8, 69.1, 66.9, 51.7, 21.5, 19.4. MS (ESI): *m*/*z*: 966.1 (M), 931.1(M − Cl), 895.3 (M − 2 Cl), 853.5 (M − 2 Cl − C_3H_7).

Complex 6a. Grubbs second-generation complex **5a** (99 mg, 0.10 mmol) was placed in a Schlenk flask and dissolved in dry and degassed toluene (20 mL). CuCl (31 mg, 0.31 mmol) and isopropoxystyrene (34 mL, 0.21 mmol) were added, and the mixture was stirred for 1 h at 40 °C. The volatiles were removed *in vacuo* and the residue purified by column chromatography (cyclohexane/ethyl acetate, 2:1 v/v). The Hoveyda-type complex **6a** was obtained as a green crystalline solid. Yield: 55 mg (73%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 16.86 (s, 1H, Ru=CH), 7.46 (td, *J* = 8.0, 1.6 Hz, 1H, $H_{benzylidene}$), 7.03 (dd, *J* = 7.5, 1.6 Hz, 1H, $H_{benzylidene}$), 6.84 (t, *J* = 7.5 Hz, 1H, $H_{benzylidene}$), 6.79 (d, *J* = 8.2 Hz, 1H, $H_{benzylidene}$), 6.52 (s, 4H, *m-H*$_{aryl}$), 4.90 (sept., J = 6.1 Hz, 1H, $OCH(CH_3)_2$), 4.14 (s, 4H, NCH_2CH_2N), 3.42 (bs, 8H, $N(CH_2CH_3)_2$), 2.57 (bs, 6H, *o*-CH_3), 2.35 (bs, 6H, *o*-CH_3), 1.31 (d, 6 H, *J* = 6.1 Hz, $OCH(CH_3)_2$, 1.23 (bs, 12H, $N(CH_2CH_3)_2$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 299.3, 211.8, 152.3, 147.9, 147.8, 145.7, 141.3, 139.1, 129.3, 128.9, 124.7, 122.9, 122.3, 113.0, 111.5, 111.0, 74.9, 52.6, 51.3, 44.5, 21.3, 19.1, 12.8. HRMS: *m*/*z* calcd for $C_{37}H_{52}N_4OCl_2Ru$ 740.25530; found 740.25740.

Complex 6a·2HCl. Complex **6a** (50 mg, 0.067 mmol) was dissolved in dried and degassed toluene (20 mL). Then 34 μL of a HCl solution in dioxane (4 M, 0.134 mmol) was added and the reaction mixture stirred for 15 min. The light green precipitate was filtrated, washed with pentane (3 × 10 mL), and dried *in vacuo*. Yield: 49 mg (98%). ^{1}H NMR (CD_3OD, 500 MHz): δ 16.87 (s, 1H, RuC*H*), 7.62 (m, 1H, $H_{benzylidene}$), 7.49 (bs, 1H, *m-H*$_{aryl}$), 7.05 (d, *J* = 8.5 Hz, 1H, $H_{benzylidene}$), 7.03 (dd, *J* = 7.7, 1.4 Hz, 1H, $H_{benzylidene}$), 6.93 (t, *J* = 7.4 Hz, 1H, $H_{benzylidene}$), 5.03 (sept, *J* = 6.1 Hz, 1H, $OCH(CH_3)_2$), 4.24 (s, 4H, NCH_2CH_2N), 3.70 (bs, 8 H, $N(CH_2CH_3)_2$), 2.62 (bs, 12 H, *o*-CH_3), 1.34 (d, *J* = 6.1 Hz, 6H, $OCH(CH_3)_2$), 1.28 (t, J = 7.1 Hz, 12H, $N(CH_2CH_3)_2$). ^{13}C NMR (CD_3OD, 126 MHz): δ 293.3, 211.4, 153.9, 146.3, 143.8, 131.6, 123.8, 123.5, 123.1, 114.7, 76.6, 54.5, 53.1, 22.2, 22.1, 11.2.

Complex 7a. Complex **5a** (200 mg, 0.21 mmol) was dissolved in dried and degassed pyridine (2 mL). After 5 min the resulting green solution was transferred into cold pentane (10 mL) and the green precipitate was filtered and dried *in vacuo*. Yield: 120 mg (68%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 19.25 (s, 1H, RuC*H*), 8.64 (s, 2H, $H_{pyridine}$), 7.85 (s, 2H, $H_{pyridine}$), 7.75 (d, *J* = 7.6 Hz, 2H, $H_{benzylidene}$), 7.63 (s, 2H, $H_{pyridine}$), 7.43 (t, *J* = 7.3 Hz, 1H, $H_{benzylidene}$ + s, 1H, $H_{pyridine}$), 7.24 (s, 1H, $H_{pyridine}$), 7.03 (t, *J* = 7.7 Hz, 2H, $H_{benzylidene}$), 6.91 (s, 2H, $H_{pyridine}$), 6.47 (s, 2H, *m-H*$_{aryl}$), 6.21 (s, 2H, *m-H*$_{aryl}$), 4.30−3.90 (m, 4H, NCH_2CH_2N), 3.36 (m, 8H, NCH_2CH_3), 2.60 (s, 6H, *o*-CH_3), 2.21 (s, 6H, *o*-CH_3), 1.19 (m, 12H, NCH_2CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 312.8, 218.9, 152.1, 151.5, 150.0, 147.9, 147.4, 141.3, 138.5, 136.4, 135.9, 130.3, 129.6, 127.9, 124.9, 123.7, 111.1, 110.9, 52.3, 51.0, 44.3 (two signals), 21.3, 19.1, 12.9 (two signals). Decomposition upon attempted mass spectrometric characterization.

Complex 7c. Complex **5c** (200 mg, 0.20 mmol) was dissolved in dried and degassed pyridine (2 mL). After 5 min the resulting green solution was transferred into cold pentane (10 mL), and the green precipitate was filtered and dried *in vaccuo*. Yield: 130 mg (73%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 19.23 (s, 1H, RuC*H*), 8.71 (s, 4H, $H_{pyridine}$), 7.96 (s, 2H, $H_{pyridine}$), 7.76 (d, *J* = 7.7 Hz, 2H, $H_{benzylidene}$), 7.61 (s, 1H, $H_{pyridine}$), 7.44 (t, *J* = 7.4 Hz, 1H, $H_{benzylidene}$), 7.31 (s, 1H, $H_{pyridine}$), 7.17 (s, 2H, *m-H*$_{aryl}$), 7.10 (m, *J* = 2H, $H_{benzylidene}$), 7.08 (s, 2H, *m-H*$_{aryl}$), 6.81 (s, 2H, $H_{pyridine}$), 4.00 (s, 4H, NCH_2CH_2N), 2.10−2.90 (bs, 12H, *o*-CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 315.4, 219.4, 151.9, 150.0, 141.0 (bs),136.4, 135.8, 131.6, 130.5, 130.3, 128.2, 123.7, 51.5, 19.5 (bs). Decomposition upon attempted mass spectrometric characterization.

Complex 8d. [Ir(μ-Cl)(cod)]$_2$ (50 mg, 0.08 mmol) and KO*t*Bu (17 mg, 0.15 mmol) were placed in a Schlenk tube, dissolved in thf (5 mL) under an atmosphere of Ar, and stirred for 10 min at room temperature. To this mixture was added *N,N*′-bis(2,6-dimethyl-4-ferrocenylphenyl)imidazolinium chloride (**4d**) (93 mg, 0.14 mmol). The reaction mixture was stirred for 2 h at room temperature, the volatiles were evaporated *in vacuo*, and the residue was purified by column chromatography (cyclohexane/ethyl acetate (10:1 v/v)). The product was obtained as an orange solid. Yield: 97 mg (66%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.25 (s, 4H, *m-H*$_{aryl}$), 4.67 ("t", *J* = 1.7 Hz, 4H, C_5H_4), 4.33 ("t", *J* = 1.7 Hz, 4H, C_5H_4), 4.18−4.14 (m, 2H, CH_{COD}), 4.07 (s, 10H, C_5H_5), 3.96 (s, 4H, NCH_2CH_2N), 3.20−3.17 (m, 2H CH_{COD}), 2.63 (s, 6H, *o*-CH_3), 2.42 (s, 6H, *o*-CH_3), 1.72−1.68 (m, 4H, CH_{2COD}), 1.34−1.30 (m, 4H, CH_{2COD}). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 207.4, 139.1, 138.3, 136.6, 135.4, 126.6, 125.1, 84.5, 83.9, 69.7, 69.2, 66.8, 66.3, 51.6, 51.4, 33.7, 28.8, 20.1, 18.7. MS (EI): *m*/*z* 944 (M −C_3H_2), 918 (M − cp), 874 (M − cod).

Complex 9d. Complex **8d** (66 mg, 0.07 mmol) was dissolved in CH_2Cl_2 (20 mL) and CO bubbled through this solution for 15 min. The volatiles were evaporated, and the residue was washed with pentane (3 × 5 mL) and dried *in vacuo*. The product was obtained as an orange solid. Yield: 60 mg (96%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.24 (s, 4H, *m-H*$_{aryl}$), 4.64 ("t", *J* = 1.8 Hz, 4H, C_5H_4), 4.32 ("t", *J* = 1.8 Hz, 4H, C_5H_4), 4.09 (s, 4H, NCH_2CH_2N), 4.07 (s, 10H, C_5H_5), 2.50 (s, 12H, *o*-CH_3). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 202.0, 180.1, 168.7, 140.0, 136.0,

135.0, 126.3, 84.3, 69.7, 69.1, 66.7, 51.7, 18.9. MS (EI): m/z 930 (M), 916 (M − CH_3), 874 (M − 2 CO).

Complex 9a·2HCl. Complex **9a** (50 mg, 0.07 mmol) was dissolved in acetone and HCl in dioxane (36 μL, 4 M, 0.14 mmol) added. The light yellow precipitate was filtered, washed with acetone (3 × 5 mL), and dried *in vacuo*. Yield: 52 mg (94%). ^{1}H NMR ($CD_3OD/CDCl_3$, 3:1 v/v, 500 MHz): δ 7.40 (bs, 1H, *m*-H_{aryl}), 4.22 (s, 4H, NCH_2CH_2N), 3.62 (bs, 8H, $N(CH_2CH_3)_2$), 2.55 (bs, 12H, *o*-CH_3), 1.20 (t, J = 7.2 Hz, 12H, $N(CH_2CH_3)_2$). ^{13}C NMR ($CD_3OD/CDCl_3$, 3:1 v/v, 126 MHz): δ 202.2, 180.6, 169.1, 143.0 (bs), 123.0 (bs), 54.6 (bs), 52.6, 19.5, 10.9.

General Procedure for the ROMP of Norbornene at Room Temperature. According to the procedure of Leitner et al.,[13b] norbornene (94 mg, 1.0 mmol) was placed in a Schlenk flask and dissolved in dry and degassed CH_2Cl_2 (2.5 mL). The appropriate amount of complex **6** or **7** (1 mol %) was weighed into another Schlenk flask and dissolved in 0.5 mL of dry and degassed CH_2Cl_2. Only for pH-switching experiments was HCl in dioxane (5.0 μL, 2 equiv/10.0 μL, 4 equiv) added under an atmosphere of argon via pipet. The catalyst solution was added to the norbornene solution via pipet under an atmosphere of argon. The reaction mixture was stirred for 60 min at room temperature and then quenched with 400 μL of ethyl vinyl ether, diluted with CH_2Cl_2 (10 mL), and stirred for another 1 h. The mixture was then added dropwise to vigorously stirred methanol (100 mL). The precipitated polymer was filtered off and dried *in vacuo*.

ROMP of Norbornene Including *in Situ* Oxidation of Catalyst. Preparation of the catalyst solution: Acetylferrocenium tetrafluoroborate (2 mol %) was dissolved in dried and degassed CH_2Cl_2 (0.5 mL). **6d** (1 mol %) was added, and the mixture was stirred for 15 min. The catalyst solution was added to a solution of norbornene (94 mg, 1 mmol) in dried and degassed CH_2Cl_2 (2.5 mL), and the reaction mixture was stirred for 10 min at room temperature. After quenching with ethyl vinyl ether (400 μL), dilution with CH_2Cl_2 (10 mL), and stirring for another 2 h, the mixture was added dropwise to vigorously stirred methanol (100 mL). The precipitated polymer was filtered off and dried *in vacuo*.

General Procedure for the ROMP of Norbornene at −50 °C. Norbornene (94 mg, 1 mmol) was placed in a Schlenk flask and dissolved in dry and degassed CH_2Cl_2 (2.5 mL). The appropriate amount of catalyst (1 mol %) was weighed into another Schlenk flask and dissolved in dried and degassed CH_2Cl_2 (0.5 mL). Both catalyst and monomer solutions were cooled to −50 °C (2-propanol/liquid nitrogen), and the catalyst solution was added to the norbornene solution via pipet under an atmosphere of argon. The reaction mixture was stirred for 2 h at −50 °C. In the case of pH-switching experiments, HCl in dioxane (5.0 μL, 2 equiv) was added under an atmosphere of argon via pipet after polymerizing for 3, 5, or 10 min, respectively. Finally, the reaction mixture was quenched with ethyl vinyl ether (400 μL), diluted with CH_2Cl_2 (10 mL), and stirred for another 1 h. The mixture was then added dropwise to vigorously stirred methanol (100 mL). The precipitated polymer was filtered off and dried *in vacuo*.

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Supporting Information Available: Experimental procedures, copies of the full set of ^{1}H and ^{13}C NMR spectra for the new complexes, cyclic voltammograms, GPC traces, mass spectra, and DSC curves are available free of charge via the Internet at http://pubs.acs.org.