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The utility of Hoveyda-type catalysts in ADMET chemistry: Sterics versus electronics

Florence C. Courchay, John C. Sworen, Armando Coronado, Kenneth B. Wagener *

The George and Josephine Butler Polymer Research Laboratory, Department of Chemistry, University of Florida, Gainesville, FL 32611, United States

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Abstract

The influence of the ligand sphere's electronics/sterics on catalytic activity was investigated at various temperatures for complexes of the type $(L)(Cl)_2Ru=CH(o\text{-}i\text{PrO}C_6H_3X)$ (L = H_2IPr or H_2IMes, X = NO_2, Cl, H, CH_3, OCH_3). Their kinetic behavior was evaluated under ADMET polymerization conditions. At all temperatures the steric hindrance brought about by the *N*-heterocyclic carbene H_2IPr dominates any electronic effect as initial rates remain constant regardless of the X substituent. Nevertheless, complexes bearing electron donating groups seem to be more stable and result in higher DPs than complexes bearing electron withdrawing groups. In any case, catalysts containing larger NHC ligands are more efficient in ADMET chemistry than any modified Hoveyda–Grubbs catalyst. At 60 °C, the electronic factor becomes evident and the substituted catalysts exhibit significantly higher reactivity, resulting in the fastest initial rates ever witnessed in an ADMET reaction.

Keywords: Ruthenium catalyst; ADMET; Kinetic behavior

1. Introduction

Over the past decade, olefin metathesis has become a major synthetic method for the formation of C–C bonds [1], especially since the discovery of the Grubbs' functional group tolerant ruthenium carbene catalyst **1** [2]. Its reactivity was further enhanced by exchanging one phosphine with an *N*-heterocyclic carbene (NHC) ligand (complexes **2a** [3] and **2b** [4], Fig. 1). This phosphine mimic, being a strong σ-donor but a weak π-acceptor, favors the binding of olefinic substrates to ruthenium, which results in higher turnovers [3–5]. Since then, other modified complexes have been reported, among them the Hoveyda-type catalysts bearing an isopropoxystyrene ligand (**3a** and **3b**, Fig. 1) [6]. The chelating nature of the ligand provides an exceptional stability to this type of catalyst and allows its recovery after some ring-closing metathesis (RCM) and cross-metathesis (CM) reactions [7].

Even though these phosphine-free alkylidenes initiate more slowly than their phosphine analogs, they have gathered much interest for both their ease of use and their enhanced reaction rates with electron deficient olefins. In addition, the isopropoxystyrene ligand represents an ideal anchor point for modification studies involving the introduction of different steric and electronic groups [8] as well as ionic groups [9] and solid supports [10]. Fine tuning of the ligand structure can be achieved for a desired substrate, as the initiation rate and the overall activity of these catalysts have proven very sensitive to the nature of the isopropoxybenzylidene. As suggested by the dissociative mechanism, the catalytic activity can be enhanced by: (1) increasing the steric hindrance around the isopropoxy group, or (2) decreasing the electron density at both the chelating oxygen atom and the benzylidene carbon [8(e,f)].

Our laboratory routinely uses metathesis catalysts for the synthesis of unique macromolecules via acyclic diene metathesis (ADMET) polymerization [11,12]. The extended lifetime of this particular class of catalyst motivated our interest, since long-living catalysts are desirable considering the reaction times required by ADMET polycondensation. Typically, we evaluate the activity of a catalyst in ADMET through comparative kinetic experiments using standard catalysts **1** and **2a**, and 1,9-decadiene as the substrate [13]. This method has allowed us to find optimal conditions of temperature and concentration for a wide range of metathesis catalysts in ADMET chemistry [13(b,c)]. In addition, we have investigated the effect of

* Corresponding author.
E-mail address: wagener@chem.ufl.edu (K.B. Wagener).

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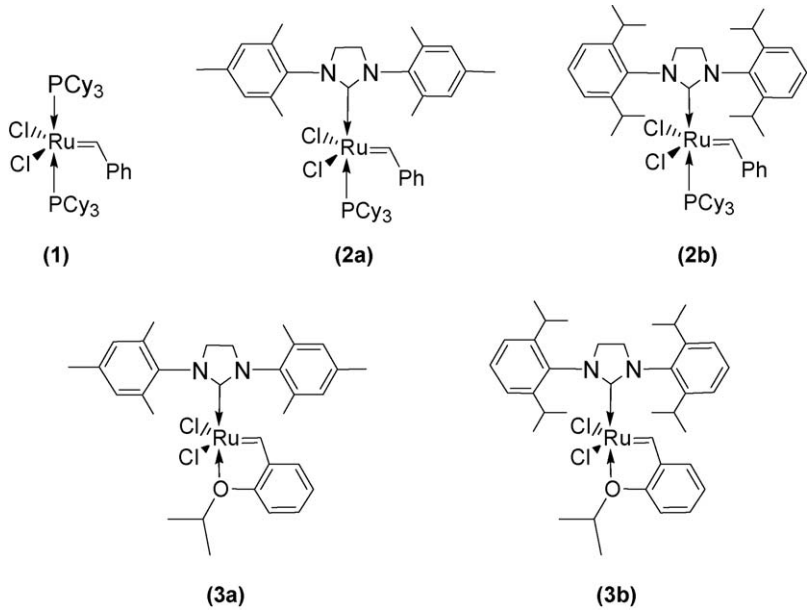

Fig. 1. Olefin metathesis catalysts.

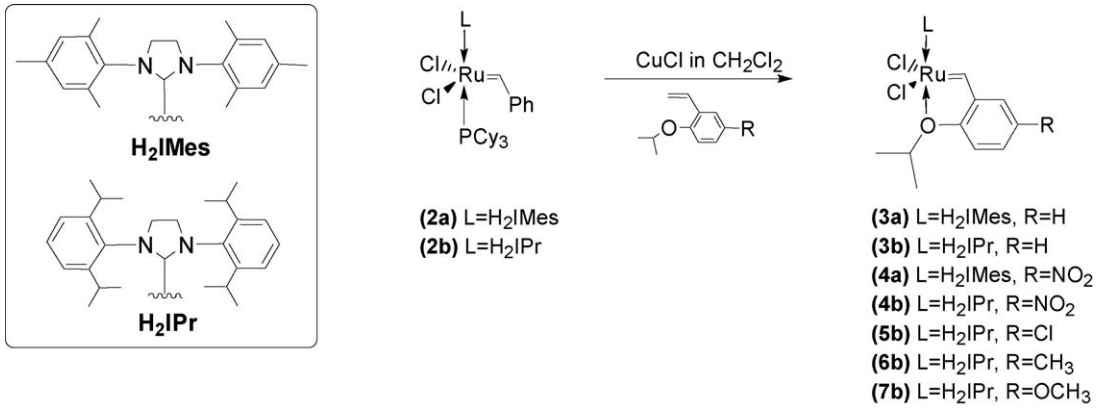

Fig. 2. Synthesis scheme for complexes **3**–**7**.

structural perturbations on catalytic activity in order to model more efficient catalyst systems. For instance, larger substituents around the NHC ligand (**2b** and **3b**) result in faster initial rates while incorporation of isopropoxybenzylidene expands the stability of the complex (**3a** and **3b**) [13(c)].

After developing complex **3b**, whose increased activity was more suitable to ADMET polymerization [13(c)], we began to examine the effect of electronics on the isopropoxy fragment of the catalyst. In this report we present a comprehensive study on a series of ruthenium catalysts bearing different isopropoxybenzilydene ligands and different NHC ligands (Fig. 2). Their catalytic activity is measured during the ADMET oligomerization of 1,9-decadiene at different temperatures, and their initial rates are compared to standard catalysts for ADMET.

2. Results and discussion

Following the introduction of faster initiators by increasing the NHC ligand bulk, we turned our attention to the isopropoxy fragment of the catalyst, the idea being to enjoy the inherent stability of the Hoveyda-type catalysts while improving their catalytic activity in ADMET. Although the influence of electronics and sterics has been studied in much detail in small molecule chemistry [8], the catalytic activity was only observed during monocoupling reactions such as CM or RCM. The polycondensation nature of ADMET renders the catalytic profile very different, hence the use of different parameters to measure catalytic activity in this study. For example, complex **3a** has been successful in many organic reactions but only results in low conversions in the ADMET oligomerization of 1,9-decadiene [13(c)]. Therefore, we have applied electronic modifications on complex **3b**, which has proven to be an efficient ADMET catalyst. The design of catalysts **4b**–**7b** was based on the idea that decreasing the electron density at the chelating *i*PrO fragment would result in even higher catalytic activities, the ultimate goal being the elaboration of a Hammett plot. The same modifications were applied to complex **3a** to control the influence of sterics on the NHC ligand.

Table 1
Initial rates in DP s^{-1} for catalysts **3a–4b**

Temperature (°C)	**3a**	**4a**	**3b**	**4b**
30	5 ± 3	10 ± 2	13 ± 2	21 ± 4
45	20 ± 5	22 ± 4	45 ± 4	48 ± 7
60	42 ± 4	42 ± 9	70 ± 10	117 ± 8

The ligands were obtained from the corresponding substituted *o*-hydroxybenzaldehyde which was subjected to a Williamson substitution followed by a Wittig reaction. The synthesis of complexes **4–7** then followed the same procedure as for complex **3a** and **3b**, affording good to excellent yields (83–95%) [6]. All complexes are stable in solution and in air.

Each catalyst was subjected to a systematic reaction with 1,9-decadiene using a 450:1 monomer:catalyst ratio to reproduce typical polymerization conditions. Reaction progress was followed by quantifying ethylene as it was released, and the degree of polymerization was plotted against time [13(a)]. The catalytic activity was evaluated in comparison with **3a** and **3b** at 30, 45 and 60 °C.

2.1. Steric effect

Table 1 shows the initial rates for catalysts **3** and **4** at different temperatures, calculated as the initial slope (DP versus time, Fig. 3) of each kinetic curve during the average dimerization (DP = 2) of the monomer [14]. Rates increase with temperature for all complexes, and a straight line is obtained when the log of the initial rate is plotted against $1/T$, verifying the Arrhenius law. The activation energies E_a are estimated to be 40.2 and 48.9 kJ mol^{-1} s^{-1} for **3b** and **4b**, respectively. Introduction of the nitro group on the isopropoxybenzylidene results in an increase of the initial rate for both catalysts, for indeed, the presence of the electron withdrawing substituent *para* to the isopropoxy group should facilitate the ligand dissociation by decreasing the electron density on the coordinating oxygen, leading to the active species [15]. However, a closer examination at Table 1 indicates that the electronic effect is only minimal for catalyst **4a**, bearing the mesityl NHC ligand, conversely to what was observed in monocoupling reactions [8(f),16]. Indeed, catalysts **3a** and **4a** exhibit comparable initial rates regardless of the temperature (around 20 DP s^{-1} at 45 °C, and 42 DP s^{-1} at 60 °C). This observation emphasizes the fundamental difference between small molecule metathesis and ADMET, where the initial rate is not necessarily a direct correlation of the isopropoxystyrene dissociation rate, but also involves the stability of the 14e$^-$ complex. In this case, the propagating species Ru=CH$(CH_2)_6$CH=CH_2 is the same for catalysts **3a** and **4a**. The similarity of the initial rates obtained here, regardless of the dissociating ligand, seems to indicate that the propagation step is rate determining in ADMET, i.e. that dissociation is fast.

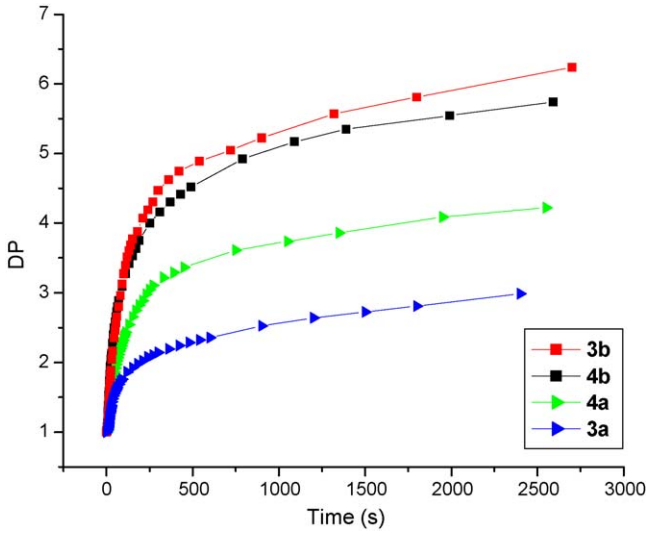

Fig. 3. Plots of DP vs. time for H_2IMes vs. H_2IPr ligated catalysts at 45 °C.

In the case of catalysts **3b** and **4b**, containing a bulkier NHC ligand, the nitro group seems to have a smaller effect on the initial rate, if any, at 30 and 45 °C than at 60 °C. For example, at 45 °C the nitro complex **4b** only exhibits a 3 DP s^{-1} rate increase (within the experimental error) compared to parent **3b**, while a 50 DP s^{-1} rate increase is reported at 60 °C for **4b**. The difference at 30 °C does not seem significant and will be further investigated by comparing other electronically modified catalysts **5b–7b**. The higher rates of complexes **3b** and **4b** versus **3a** and **4a** are due to the increase in steric bulk on the NHC ligand brought about by the isopropyl groups, which exert a stronger steric pressure on the benzylidene and therefore facilitate its dissociation [17]. As a consequence, at 60 °C complex **4b** exhibits one of the fastest initiation rates (117 DP s^{-1}) ever reported for the ADMET reaction of 1,9-decadiene.

This substituent effect is not as obvious when examining the overall activity of the catalysts **3a–4b** (Fig. 3). The 'tailing off' of each curve is due to the reaction mixture becoming more viscous as the DP increases until reaching a solid state (around a DP of 4–5) where the rate becomes diffusion controlled. Even so, the catalysts deviate from the initial trend discussed above before reaching the solid state and after dimerization. The catalysts bearing bulkier NHC ligands (**3b** and **4b**) seem to be unaffected by the presence of the nitro group, which is in striking contrast with analogs **3a** and **4a**. Indeed, complex **4a** shows almost a two-fold increase in its overall activity compared to the parent catalyst **3a** (at 30 min the DPs are 2.8 and 4.1 for **3a** and **4a**, respectively), while **3b** and **4b** show the same catalytic profile. The electronic effect on the isopropoxybenzilydene seems to be dominated by the steric hindrance of the NHC ligand. Following the model of ruthenium–phosphine complexes, if the presence of H_2IPr facilitates dissociation, then it also slows down catalyst deactivation by rebinding of free phosphine, or in this case, rebinding of the ether-tethered ligand (*i*PrO) [15(b)]. Thus, complexes **3b** and **4b** actually undergo more turnovers before being trapped by *i*PrO. The dissociation/rebinding rates ratio appears to approach an optimum with H_2IPr ligands, a ratio that is hardly disturbed by simply changing the electron density around the isopropoxystyrene. On the other hand, the rebinding of *i*PrO is rendered easier in the presence of the less hindered H_2IMes ligand. In this case, the electron density of the coordinating oxygen has a greater effect on both the dissociation

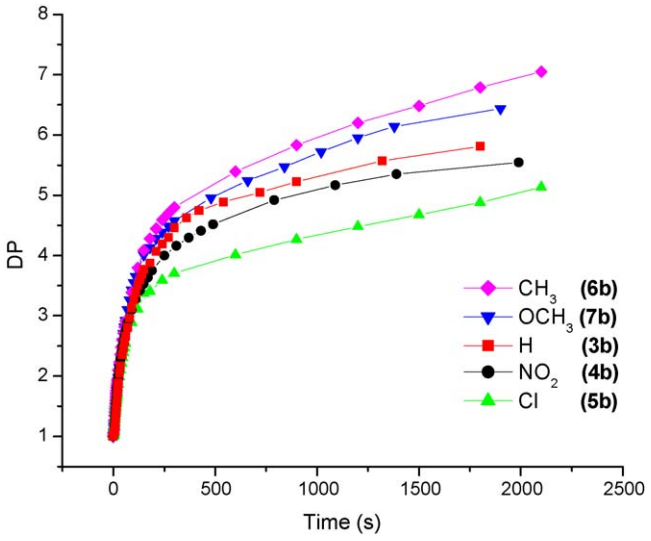

Fig. 4. Plots of DP vs. time for complexes **3b–7b** at 45 °C.

and rebinding rates, which explains the higher reactivity of **3b** whose nitro-substituted ligand will be less likely to recoordinate and therefore increases the amount of active species able to react. This electronic effect is not evident during the initial rate probably because ligand rebinding only becomes substantial after several turnovers.

2.2. Electronic effect on H_2IPr ligated complexes

The series of complexes **3b–7b** should allow us to better understand the importance of dissociation/rebinding of these ether-tethered ligands. All the synthesized complexes are efficient catalysts for the ADMET oligomerization of 1,9-decadiene reaching DPs of 4 and 5 under 5 min at 45 °C. As illustrated in Fig. 4, even at DP > 4 (where the viscosity becomes significant) the polymerization continues at a steady rate without any sign of extensive decomposition of the catalytic center, usually observable by a darkening of the solution, confirming the robust nature of these catalysts.

Table 2 gives an overview of the initial rates for complexes **3b–7b** at 30, 45 and 60 °C. As observed earlier, initial rates at 30 and 45 °C stay the same regardless of the isopropoxybenzylidene used (around 20 DP s^{-1} at 30 °C, and 45 DP s^{-1} at 45 °C within experimental error) except for parent catalyst **3b**, which exhibits a slightly lower initial rate at 30 °C. The difference noticed earlier (Table 1) could have been insignificant if the rates of the

Table 2
Initial rates in DP s^{-1} for catalysts **3b–7b**

	NO_2 (**4b**)	Cl (**5b**)	H (**3b**)	CH_3 (**6b**)	OCH_3 (**7b**)
$\sigma-$	0.71	0.37	0	−0.06	0.05
$\sigma+$	0.79	0.11	0	−0.31	−0.78
Temperature (°C)					
30	21 ± 4	21 ± 3	13 ± 2	22 ± 5	19 ± 4
45	48 ± 7	41 ± 8	45 ± 4	47 ± 2	40 ± 5
60	117 ± 8	118 ± 15	70 ± 10	136 ± 9	110 ± 7

Values for $\sigma-$ and $\sigma+$ were taken from Ref. [20].

electronically modified catalysts **4b–7b** had not been so reproducible. The singularity of the unsubstituted catalyst **3b** proves the existence of an electronic effect, albeit not qualitative. This lack of sensitivity to the electronic nature of the substituent is again in significant contrast to what was observed during CM and RCM reactions catalyzed by **3a** analogs; however, other reports have also referred to the unpredictability of other electronically modified Hoveyda-type catalysts [8(e,f),18]. Here, the steric hindrance present on the NHC ligand seems to overshadow the electronic nature of the dissociating ligand at low temperatures, canceling the effect predicted by sigma values [19]. This proposal finds credence in the X-ray structure of **3b**, **4b** and **7b**. The Ru–O bond length, usually indicative of the strength of the *i*PrO → Ru chelation, does not show significant variation. Conversely, nitro-substituted **4b** exhibits a slightly shorter Ru–O bond length (2.2462(3) Å) while methoxy-substituted **7b**'s is slightly longer (2.2486(18) Å).

At 45 °C all complexes follow about a similar catalytic profile, i.e. there is no major improvement brought about by the electronic substituents. However, there is a noticeable distinction between complexes (Fig. 4). Electron donating groups (EDG) appear to increase the catalytic activity while electron withdrawing groups (EWG) reduce the rate. Since the initial rates at 30 and 45 °C are the same for all catalysts, the dissociation rate of isopropoxybenzylidene cannot be the only determining factor. Theoretically, after dissociation the propagating species is the same for complexes **3b–7b**. Therefore, the lability of isopropoxystyrene must allow its rebinding to the ruthenium center so that it influences the overall catalytic activity.

The trend observed at 45 °C can be rationalized by considering the formation of the unstable $14e^-$ species, either the alkylidene or the methylidene complex. In an earlier report, we demonstrated the sensitivity of this type of catalyst to substrate polarity compared to their phosphine analogs [13(c)]. In the latter, the phosphine coordinates back to the $14e^-$ intermediate to stabilize it and forms a dormant state [17]. In Hoveyda-type complexes, this type of stabilization is lessened by the extreme lability of isopropoxy styrene. However, all substrates conventionally used to probe the metathesis activity of any catalyst contain some heteroatom that can serve as a stabilizer, along with the solvent used for the reaction. For example, during the ROMP reaction of diverse oxygen-containing monomers, Khosravi and co-workers showed that Hoveyda-type catalysts were stabilized through the chelation of an oxygen contained in the monomer unit [21]. In the case of substrates lacking any kind of electron donor or Lewis basic group, such as 1,9-decadiene, the $14e^-$ intermediate is not stabilized; therefore, the catalyst is more susceptible to decomposition, which results in slower rates. With this in mind, it is reasonable to assume that the catalysts with higher dissociation rates and/or slower rebinding rates should have a lower overall activity. According to sigma values, electron withdrawing substituents *para* to the isopropoxy group should facilitate the ligand dissociation by decreasing the electron density on the coordinating oxygen and increase its lability, while electron donating substituents should slow the dissociation step and facilitate its rebinding. Simply stated, donating groups should slow down catalyst decomposition. Consequently, com-

plexes **6** and **7** (EDG) show a slightly higher reactivity than complexes **4** and **5** (EWG), while neutral complex **3b** lies in between (Fig. 2).

2.3. Temperature effect

When the temperature is raised to 60 °C, the singularity of catalyst **3b** over the electronically modified **4b–7b** is accentuated. While initial rates for catalysts **4b–7b** are all around 120 DP s^{-1}, parent complex **3b** only affords a rate of 70 DP s^{-1}, broadly deriving from the predicted Arrhenius plot. Electronics now represent a determining factor on catalytic activity, which may be the result of a switch in the mechanism possibly due to a change in catalyst conformation. Similar temperature activation barriers have been witnessed with nitrogen-chelated complexes [22].

The same catalytic profile persists as the reaction continues, and the overall activity is now significantly higher for the modified catalysts **4b–7b** (Fig. 5). This suggests that the steric effect of the H_2IPr ligand is no longer dominant, even though the electronic factor cannot be qualified according to sigma values. This apparent lack of sensitivity towards the electronic nature of the substituents is more likely the result of several mechanistic processes operating simultaneously. While electron withdrawing groups could facilitate dissociation by weakening the *i*PrO → Ru chelation, electron donating groups could equally increase catalytic activity by reducing the Lewis acidity of the metal. The rate of decomposition of the methylidene intermediate, which is accelerated at elevated temperatures, is probably an important factor. Also, if we consider that the H_2IPr ligand does not hinder the rebinding of the *i*PrO moiety, the $14e^-$ species can be properly stabilized, but, since the dissociation is quite fast, the catalyst returns to the catalytic cycle affording higher DPs. The diminished steric effect may be due to a reorganization of the NHC ligand, possibly by ring rotation, often seen at high temperatures.

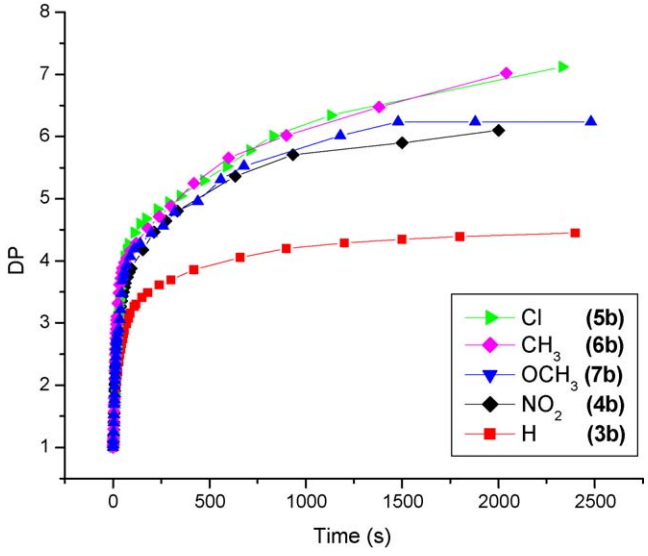

Fig. 5. Plots of DP vs. time for complexes **3b–7b** at 60 °C.

3. Conclusions

This report gives a different outlook on the influence of the ligand sphere's electronics/sterics on Hoveyda-type metathesis catalysts. Unlike most modification studies conducted on these complexes, the 'steric factor' is only located on the NHC ligand (isopropyl versus methyl groups) whereas the 'electronic factor' is on the isopropoxybenzilydene. All the complexes tested are efficient catalysts for the ADMET polymerization of 1,9-decadiene. However, in the polycondensation conditions of ADMET, the steric hindrance largely dominates any electronic effect at all temperatures. Interestingly, unsubstituted complex **3b** curiously stands out at 30 and 60 °C, suggesting some participation of electronics in the catalytic potential of these Hoveyda-type complexes. The overall activity of these complexes seems to depend only on the propensity of the isopropoxystyrene ligand to rebind to the ruthenium center and stabilize it in a similar way as their phosphine analogs, especially at low temperatures. As a result, complexes bearing EWGs result in lower DPs than complexes bearing EDGs, the more active catalyst being the better stabilized. In any case, complexes ligated to larger NHC ligands are better catalysts than any modified Hoveyda–Grubbs such as **4a**, again showing the prevalence of sterics over electronics.

At 60 °C, all electronically modified catalysts exhibit comparable initial rates and increased reactivities, while parent complex **3b** constitutes a significant exception. The catalytic profiles of **4b–7b** are similar and lay 2 DP over **3b**'s, implying that the different electronic groups are able to improve activity through different processes. A reorganization of the ligand sphere may occur at higher temperatures so that the steric bulk of the NHC ligand does not hinder the rebinding of isopropoxystyrene anymore. Consequently, catalysts **4b–7b** represent the fastest initiators ever tested for ADMET polymerization. Further experiments will be conducted to investigate the importance of ligand rebinding in these Hoveyda-type catalyts, which represent an interesting prospect for metathesis polycondensation.

4. Experimental

4.1. General

^{1}H NMR (300 MHz) and ^{13}C NMR (75 Hz) spectra of the organometallic complexes were recorded in $CDCl_3$ on either a Mercury series or Varian VXR-300 NMR superconducting spectrometer. Chemical shifts were referenced to residual $CHCl_3$ (7.27 for ^{1}H and 77.23 for ^{13}C) with 0.03% (v/v) TMS as an internal reference.

Complex **3a** was a gift from Materia Inc. and was used as received. Complexes **2a** [3], **2b** [4], **3b** [13(c)], and **4a** [16] were synthesized according to the literature procedure. All catalysts were stored in an argon-filled drybox prior to use in kinetic and polymerization experiments. 1,9-Decadiene (Aldrich) was distilled from Na/K alloy under reduced pressure into a Kontes flask equipped with a Teflon valve, degassed by three freeze–pump–thaw cycles, and stored in an argon-filled drybox. For the kinetic study, 1,9-decadiene was portioned into

small Teflon-capped vials in the drybox and were removed and stored in a dessicator until use.

All other starting material were distilled over Na/K alloy before use except chlorinated compounds which were distilled over CaH_2. After distillation, *d*-chloroform was degassed by three freeze–pump–thaw cycles, and stored in an argon-filled drybox.

4.2. General procedure for ligand synthesis

2-Isopropoxystyrene derivatives were synthesized by a standard Wittig reaction on the 2-isopropoxybenzylaldehyde parent using (methyl)triphenylphosphine iodide and potassium *t*-butoxide (Aldrich). All the 2-isopropoxybenzylaldehyde derivatives were synthesized via a Wilkinson-ether synthesis from the corresponding salicylaldehyde (Aldrich) and 2-bromopropane (Aldrich). Spectral data for 1-isopropoxy-2-vinyl-4-methylbenzene [8(e)], 1-isopropoxy-2-vinyl-4-nitrobenzene [16], and 1-isopropoxy-2-vinyl-4-methoxybenzene [18] match the literature.

4.3. General procedure for carbene exchange

In a glovebox complex **2a** (300 mg, 0.32 mmol) and CuCl (Aldrich) (32 mg, 0.32 mmol) were weighed into a 100 mL schlenk flask and dissolved in 15 mL of CH_2Cl_2. 2-Isopropoxy-5-nitrostyrene (133 mg, 0.64 mmol) was dissolved in 5 mL of CH_2Cl_2 and added to the solution of complex **2a** and CuCl at room temperature. The flask was equipped with a condenser and the solution was refluxed for 30 min or until the brown solution turns to a deep green. From this point forth, all manipulations were carried out in air with reagent-grade solvents. The reaction mixture was concentrated in vacuo to a green residue. The unpurified material was dissolved in a minimal volume of 5:2 cyclohexane/ethyl acetate and loaded onto a plug of silica gel. Insoluble copper–phosphine precipitates were removed prior to loading by passing the solution through a second Pasteur pipette containing a plug of glass wool. Elution with 5:2 cyclohexane/ethyl acetate removed a bright green band from the column. The solvent was evaporated and the residue washed with *n*-pentane.

4.3.1. Synthesis of complex **4b** (–NO_2)

The general procedure was followed to afford 200 mg (0.267 mmol, 83%) of a green powder. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 16.32 (s, 1H, Ru=C*H*Ph), 8.40 (d, 1H, *para* C*H*, $^2J_{H,H}$ = 8.4 Hz), 7.70 (s, 1H, *ortho* C*H*), 7.58 (t, 2H, *para* C*H*, $^3J_{H,H}$ = 7.2 Hz), 7.39 (d, 4H, *meta* C*H*), 6.90 (d, 1H, *meta* C*H*, $^2J_{H,H}$ = 8.4 Hz), 4.98 (sept, 1H, $(CH_3)_2CHOAr$, $^3J_{H,H}$ = 6.3 Hz), 4.20 (s, 4H, $N(CH_2)_2N$), 3.54 (sept, 4H, $CH(CH_3)_2$, $^3J_{H,H}$ = 6.6 Hz), 1.40 (d, 6H, $OCH(CH_3)_2$, $^2J_{H,H}$ = 6.3 Hz), 1.24 (d, 24H, $CH(CH_3)_2$, $^3J_{H,H}$ = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 284.4, 210.6, 156.9, 149.3, 143.9, 143.2, 136.4, 130.3, 124.7, 124.3, 117.0, 113.0, 77.9, 54.8, 29.1, 27.1, 26.8, 21.9. MS (HRMS/EI) calcd for $C_{37}H_{49}O_3N_3Cl_2Ru$ $[M]^+$ 755.2194, found 755.2161. Anal. Calcd for $C_{37}H_{49}O_3N_3Cl_2Ru$: C, 58.80; H, 6.53; N, 5.56. Found: C, 58.96; H, 6.83; N, 5.20.

4.3.2. Synthesis of complex **5b** (–Cl)

The general procedure was followed using 2-isopropoxy-5-chlorostyrene (125 mg, 0.64 mmol) to afford 202 mg (0.272 mmol, 85%) of a pale green powder. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 16.28 (s, 1H, Ru=C*H*Ph), 7.55 (t, 2H, *para* C*H*, $^3J_{H,H}$ = 7.2 Hz), 7.43 (s, 1H, *ortho* C*H*, $^2J_{H,H}$ = 8.8 Hz), 7.38 (d, 4H, *meta* C*H*, $^2J_{H,H}$ = 7.4 Hz), 6.80 (d, 1H, *para* C*H*, $^2J_{H,H}$ = 2.4 Hz), 6.72 (d, 1H, *meta* C*H*, $^2J_{H,H}$ = 8.8 Hz), 4.87 (sept, 1H, $(CH_3)_2CHOAr$, $^3J_{H,H}$ = 6.2 Hz), 4.19 (s, 4H, $N(CH_2)_2N$), 3.58 (sept, 1H, $CH(CH_3)_2$, $^3J_{H,H}$ = 6.6 Hz), 1.35 (d, 6H, $OCH(CH_3)_2$, $^2J_{H,H}$ = 6.3 Hz), 1.25 (d, 24H, $CH(CH_3)_2$, $^3J_{H,H}$ = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 286.3, 212.3, 150.9, 149.3, 145.0, 130.0, 128.1, 127.7, 124.6, 121.4, 114.1, 75.9, 54.7, 29.0, 26.7, 23.5, 21.8. MS (HRMS/EI) calcd for $C_{37}H_{49}ON_2Cl_3Ru$ $[M+Na]^+$ 767.1846, found 767.1941. Anal. Calcd for $C_{37}H_{49}ON_2Cl_3Ru$: C, 59.63; H, 6.63; N, 3.76. Found: C, 59.52; H, 7.03; N, 3.46.

4.3.3. Synthesis of complex **6b** (–CH_3)

The general procedure was followed using 2-isopropoxy-5-methylstyrene (113 mg, 0.64 mmol) to afford 209 mg (0.288 mmol, 90%) of a pale green powder. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 16.40 (s, 1H, Ru=C*H*Ph), 7.55 (t, 2H, *para* C*H*, $^3J_{H,H}$ = 7.6 Hz), 7.40 (d, 4H, *meta* C*H*, $^2J_{H,H}$ = 7.8 Hz), 7.24 (s, 1H, *ortho* C*H*), 6.68 (d, 1H, *para* C*H*, $^2J_{H,H}$ = 8.3 Hz), 6.58 (s, 1H, *meta* C*H*), 4.88 (sept, 1H, $(CH_3)_2CHOAr$, $^3J_{H,H}$ = 6.0 Hz), 4.18 (s, 4H, $N(CH_2)_2N$), 3.62 (sept, 1H, $CH(CH_3)_2$, $^3J_{H,H}$ = 6.5 Hz), 2.32 (s, 3H, CH_3), 1.36 (d, 6H, $OCH(CH_3)_2$, $^2J_{H,H}$ = 6.2 Hz), 1.27 (d, 24H, $CH(CH_3)_2$, $^3J_{H,H}$ = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 290.8, 214.4, 150.8, 149.5, 144.4, 137.1, 131.5, 129.9, 124.6, 122.6, 112.8, 74.9, 54.8, 29.0, 26.8, 23.6, 22.0, 20.2. MS (HRMS/EI) calcd for $C_{38}H_{52}O_2N_2Cl_2Ru$ $[M+Na]^+$ 747.2395, found 747.2427. Anal. Calcd for $C_{38}H_{52}O_2N_2Cl_2Ru$: C, 62.97; H, 7.23; N, 3.86. Found: C, 62.67; H, 7.31; N, 3.49.

4.3.4. Synthesis of complex **7b** (–OCH_3)

The general procedure was followed using 2-isopropoxy-5-methoxystyrene (123 mg, 0.64 mmol) to afford 229 mg (0.310 mmol, 97%) of a pale green powder. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 16.33 (s, 1H, Ru=C*H*Ph), 7.53 (t, 2H, *para* C*H*, $^3J_{H,H}$ = 7.2 Hz), 7.37 (d, 4H, *meta* C*H*), 7.02 (dd, 1H, *meta* C*H*, $^2J_{H,H}$ = 8.4 Hz), 6.69 (d, 1H, *para* C*H*, $^2J_{H,H}$ = 7.4 Hz), 6.37 (s, 1H, *ortho* C*H*), 4.83 (sept, 1H, $(CH_3)_2CHOAr$, $^3J_{H,H}$ = 6.3 Hz), 4.18 (s, 4H, $N(CH_2)_2N$), 3.72 (s, 3H, OCH_3), 3.60 (sept, 1H, $CH(CH_3)_2$, $^3J_{H,H}$ = 6.6 Hz), 1.35 (d, 6H, $OCH(CH_3)_2$, $^2J_{H,H}$ = 6.2 Hz), 1.24 (d, 24H, $CH(CH_3)_2$, $^3J_{H,H}$ = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 298.1, 208.9, 152.5, 149.4, 146.2, 131.9, 130.6, 129.9, 124.7, 117.7, 113.2, 111.4, 72.7, 55.8, 32.8, 29.0, 26.8, 23.6, 21.9. MS (HRMS/EI) calcd for $C_{38}H_{52}O_2N_2Cl_2Ru$ $[M+Na]^+$ 763.2344, found 763.2361. Anal. Calcd for $C_{38}H_{52}O_3N_2Cl_2Ru$: C, 61.61; H, 7.08; N, 3.78. Found: C, 61.86; H, 7.28; N, 3.63.

4.3.5. Kinetic study

The kinetic study was performed with the same apparatus and following the same procedure as previously described by Wagener [13(b,c)].

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