"Second Generation" Ruthenium Carbene Complexes with a *cis*-Dichloro Arrangement†

Christian Slugovc,*,‡ Bernhard Perner,‡ Franz Stelzer,‡ and Kurt Mereiter§

Institute for Chemistry and Technology of Organic Materials (ICTOS), Graz University of Technology, Stremayrgasse 16, A-8010 Graz, Austria, and Institute of Chemical Technologies and Analytics, Vienna University of Technology, Getreidemarkt 9/164, A-1060 Vienna, Austria

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The synthesis, characterization, and catalytic activity of a series of unprecedented ruthenium-based metathesis catalysts bearing a *cis*-dichloro arrangement, an N-heterocyclic carbene, and a chelating carbene ligand derived from 2-vinylbenzaldehyde or 2-vinylbenzoic acid ester are presented.

Introduction

Efficient, well defined, single-component homogeneous catalysts for olefin metathesis have provided powerful tools for C−C bond formation in polymer chemistry and organic synthesis.[1] In catalyst design, a breakthrough was the substitution of a phosphine ligand by an imidazol-2-ylidene ligand.[2] Thus, the catalyst generation trivially named "super-" or "second-generation", most prominently represented by the "Super-Grubbs" catalyst $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$[1] and the "Super-Hoveyda" catalyst (H_2IMes)(methylethoxybenzylidene-$\kappa^2(C,O)$)$(Cl)_2Ru$[3] (H_2IMes = 1,3-bis(mesityl)-4,5-dihydroimidazol-2-ylidene), exhibits a distinctly higher activity and higher functional group tolerance than the corresponding bisphosphine-based catalysts.[1,3,4]

Most of the defined catalysts of the first and second generation have in common a square-pyramidal coordination of Ru with trans stereochemistry of the two halide ligands. With regard to the first generation, chelating bisphosphine complexes introduced by Hofmann et al. constitute an exception.[5] In those complexes the chelating bisphosphine forces the P−Ru−Cl trans (i.e. Cl−Ru−Cl cis) arrangement. Until recently, only the common trans arrangement of the anionic coligands (halides, alkoxylates,[6] or trifluoroacetates[7]) in second-generation complexes has been observed, but very recently Fürstner et al. reported two complexes that rearranged from a *trans*-dichloro to a *cis*-dichloro disposition upon treating the starting materials with silica gel.[8]

In this contribution we describe recent results on the preparation of second-generation type complexes bearing a chelating carbene ligand combined with a *cis*-dichloro arrangement and the use of these compounds as initiators for ring-opening metathesis polymerization (ROMP) of norbornenes.

Results and Discussion

The preparation of the title compounds is straightforward, using recently established routes. The starting materials 2-bromobenzoic acid methyl (**2b**), ethyl (**2c**), or methylethyl ester (**2d**) were prepared by reacting 2-bromobenzoyl chloride with the corresponding alcohols using nucleophilic catalysis by DMAP (DMAP = 4-(dimethylamino)pyridine). The vinyl group was then introduced by a Suzuki−Miyaura cross-coupling reaction making use of 2,4,6-trivinylcyclotriboroxane−pyridine complex in the presence of catalytic amounts of $Pd(PPh_3)_4$ and K_2CO_3.[9] The corresponding vinyl derivatives **3a**−**d** were isolated in good yields (87−93%; Scheme 1).

As shown in Scheme 2, (H_2IMes)(2-formylbenzylidene-$\kappa^2(C,O)$)Cl_2Ru (**4a**), (H_2IMes)(2-methoxycarbonylbenzylidene-$\kappa^2(C,O)$)Cl_2Ru (**4b**), (H_2IMes)(2-ethoxycarbonylbenzylidene-$\kappa^2(C,O)$)Cl_2Ru (**4c**), and (H_2IMes)(2-isopropoxycarbonylbenzylidene-$\kappa^2(C,O)$)Cl_2Ru (**4d**) were prepared by a carbene exchange reaction of $(H_2IMes)(pyridine)_2(Cl)_2Ru{=}CHPh$ (**1a**) with the aforementioned vinyl derivatives. A mixture of 1 equiv of **1a** and 2 equiv of **3a** (or **3b**−**d**) was stirred in CH_2Cl_2 at room temperature according to a protocol similar to that used to obtain complexes of the type $(H_2IMes)(PR_3)(Cl)_2Ru{=}$

* To whom correspondence should be addressed. E-mail: slugi@ictos.tugraz.at. Fax: +43-316-873-8951. Tel: +43-316-873-8454.
† In memory of Prof. Dr. Roland Schmid (1945−2004).
‡ Graz University of Technology.
§ Vienna University of Technology.

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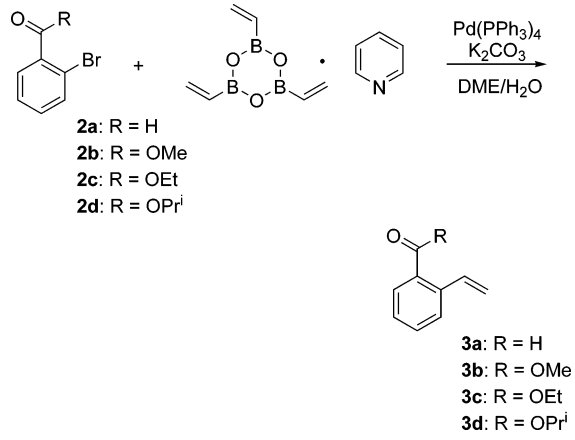
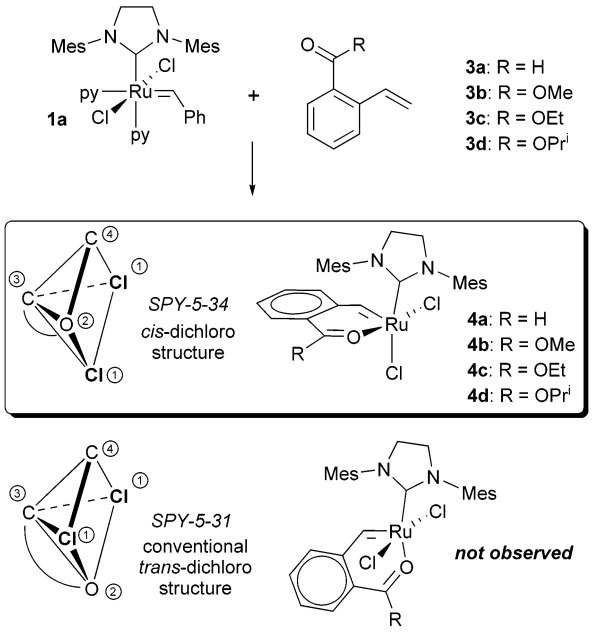
Scheme 1. Preparation of the Ligands



Scheme 2. Preparation of the Complexes



CHPh (e.g. R = Ph, *n*-Bu, *p*-$CF_3C_6H_4$).[10] **4a**−**d** were isolated as green microcrystals by precipitation upon addition of Et_2O in good yields (64−87%). Chromatographic workup as necessary when using the conventional $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$/CuCl protocol is thus avoided.[3] Compounds **4a**−**d** are perfectly stable in the solid state as well as in solution in the presence of air.

Elemental analysis fitted the calculated values in all cases. The spectroscopic data of **4a**−**d** were all similar and were in accordance with the proposed stoichiometry but did not agree with the initially assumed classical trans stereochemistry of the halide ligands (cf. Scheme 2, bottom). Therefore, crystals were grown from a saturated solution of **4a** in CH_2Cl_2 by layering with Et_2O and subjected to a X-ray structure analysis. As the most important result, the coordination geometry of Ru in **4a**·$2CH_2Cl_2$ is a distorted square pyramid with the two chloro ligands in a cis arrangement. The base of the square pyramid is formed by the two chloro ligands Cl(1) and Cl(2), the carbonyl oxygen O(49), and the C(11) atom of the H_2IMes ligand, while the apex is formed by

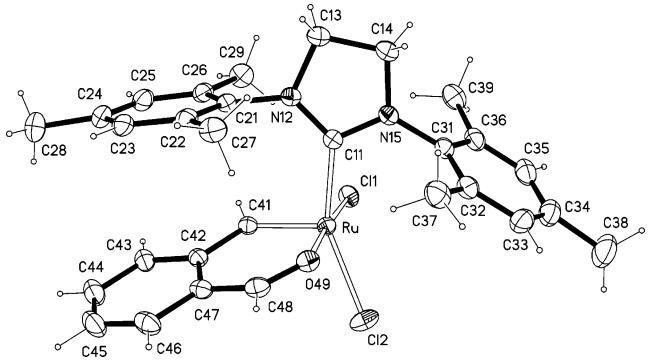


Figure 1. ORTEP plot of **4a**·$2CH_2Cl_2$ (displacement ellipsoids at the 20% probability level, CH_2Cl_2 molecules omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru−C(41) = 1.819(2), Ru−C(11) = 2.022(2), Ru−O(49) = 2.053(2), Ru−Cl(2) = 2.3642(7), Ru−Cl(1) = 2.3662(6), C(47)−C(48) = 1.434(4), C(48)−O(49) = 1.235(3); C(11)−Ru−Cl(2) = 154.5(1), O(49)−Ru−Cl(1) = 175.96(5), C(41)−Ru−C(11) = 97.6(1), C(41)−Ru−O(49) = 91.1(1), C(41)−Ru−Cl(1) = 90.4(1), C(41)−Ru−Cl(2) = 107.9(1).

the carbene carbon atom C(41). Important bond lengths and angles can be found in the caption of Figure 1. The phenyl ring of the 2-formylbenzylidene ligand and one of the *N*-mesityl substituents are approximately coplanar and are in close contact, pointing to a π-stacking interaction between these two moieties,[11] a feature that is common for second-generation carbene complexes.[8] Additionally, several intramolecular C−H- - -O/Cl/arene-π hydrogen bonds were observed, of which the one between O(49) and C(37) (C−O = 3.194(4) Å) is the most significant.

The spectral data of **4a** (and **4b**−**d**) confirmed that also in solution only *SPY*-5-34 diastereomers are present. Particularly diagnostic for the *SPY*-5-34 species is the loss of symmetry in their NMR spectra. Thus, all ^1H and ^{13}C NMR signals of the H_2IMes ligand are inequivalent in the ^1H and ^{13}C NMR spectra, which is not the case for e.g. the "Super-Hoveyda" catalyst[12] or (*SPY*-5-31)-(IMes)(2-isopropoxycarbonylbenzylidene-κ^2(*C*,*O*))-Cl_2Ru (IMes = 1,3-bis(mesityl)imidazol-2-ylidene), a related complex prepared by Fürstner et al.[13] This latter feature can be explained by the combination of a slow rotation around the Ru−C(11) bond (cf. Figure 1) and the *SPY*-5-34 structure. The aforementioned rotation is slowest in compound **4d** and becomes faster by decreasing the steric bulkiness of the substituent R. Unfortunately, the coalescence temperature for this process was to high to be reached with conventional NMR solvents and could not be determined, regardless of which complex was examined. The π−π interaction detected in the solid state might be the explanation for a pronounced high-field shift (5.81−5.92 ppm) of one of the hydrogens at the 3- (i.e. 5-) position of one of the mesityl substituents. This feature of the ^1H NMR spectra is indicative of all four complexes and might be used as a quick probe for the presence of *cis*-dichloro

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(11) The ring−ring angle C(21)−C(26)/C(42)−C(47) is 15.1(1)°, and the two rings are mutually partly slipped; π-stacking distances between three approximately superposed atom pairs are C(21)−C(41) = 2.99 Å, C(24)−C(43) = 3.43 Å, and C(22)−C(47) = 3.67 Å.

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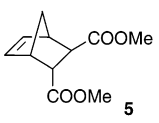
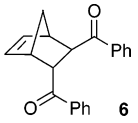
Table 1. ROMP of 5 and 6 Initiated by 4a−d[a]



5



6

entry	initiator/ monomer	temp (°C)	solvent	yield (%)	M_w	PDI
1	**4a**/**5**	45	CH_2Cl_2	96	1 820 000	1.7
2	**4b**/5	45	CH_2Cl_2	98	1 410 000	1.8
3	**4c**/**5**	45	CH_2Cl_2	98	1 610 000	1.8
4	**4d**/**5**	45	CH_2Cl_2	97	1 670 000	1.8
5	**4a**/**5**[b]	110		97	2 180 000	1.5
6	**4b**/**5**[b]	110		96	1 110 000	1.8
7	**4c**/**5**[b]	110		98	1 550 000	1.8
8	**4d**/**5**[b]	110		98	2 000 000	1.8
9	**4a**/**6**[c,d]	45	CH_2Cl_2	37	1 400 000	1.6
10	**4b**/**6**[c]	45	CH_2Cl_2	95	760 000	1.8
11	**4c**/**6**[c]	45	CH_2Cl_2	98	990 000	1.6
12	**4d**/**6**[c]	45	CH_2Cl_2	94	950 000	1.6

[a] General conditions: initiator:monomer = 1:600; reaction time 10 h; Yields are given for the isolated products; GPC against polystyrene. [b] No solvent used; reaction time 5 min. [c] Initiator: monomer = 1:300. [d] Reaction not complete.

derivatives in related compounds. The corresponding proton and carbon resonances of the carbene moiety are also pronounced signals. In the ^{1}H NMR the corresponding singlet was found at 18.86 (**4a**) and 18.95−18.94 ppm (**4b**−**d**), whereas in the $^{13}C\{^1H\}$ spectra signals at 285.8 (**4a**) and 283.9−283.8 ppm (**4b**−**d**) were present. Complexes **4a**−**d** can be kept in $CDCl_3$ solutions under ambient conditions for at least 2 months. Neither decomposition nor isomerization to e.g. the corresponding *SPY*-5-31 derivative occurred under these conditions.

To test the catalytic potential of complexes **4a**−**d**, ring-opening metathesis polymerizations (ROMP) of two functionalized norbornenes, **5** and **6**, were conducted. The results are summarized in Table 1.

All compounds were active ROMP initiators, although somewhat elevated temperatures were necessary to provide a reasonable initiation. Aldehyde derivative **4a** showed, when the weight average molecular weights of the polymers were taken into account, the lowest initiation (cf. Table 1) and is barely active at room temperature. For the ester series **4b**−**d** initiation efficiencies seem to increase with the decreasing steric bulk of the ester substituent. Nevertheless, initiation is in all cases low when comparing the M_w values listed in Table 1 to the corresponding values obtained with $(H_2IMes)(3\text{-bromo-pyridine})_2Cl_2Ru{=}CHPh$ (**1b**), an initiator providing complete initiation. **1b** afforded **poly5** with M_w = 255 000 (PDI 1.1) and **poly6** with M_w = 61 000 (PDI 1.06), respectively.[14] To gain more insight into the initiation behavior of **4a**−**d** the polymerizations of **5** by those compounds were monitored by NMR spectroscopy. Half-lives for the polymerization of 70 equiv of **5** at 60 °C were determined to be 30 min for **4a** and 2.5 min for **4b**−**d**, respectively (cf. Figure 2).[15]

Carbene peaks of the propagating species could not be detected; thus, it can be assumed that the initiation is lower than 10%. In general, the polymerization rate

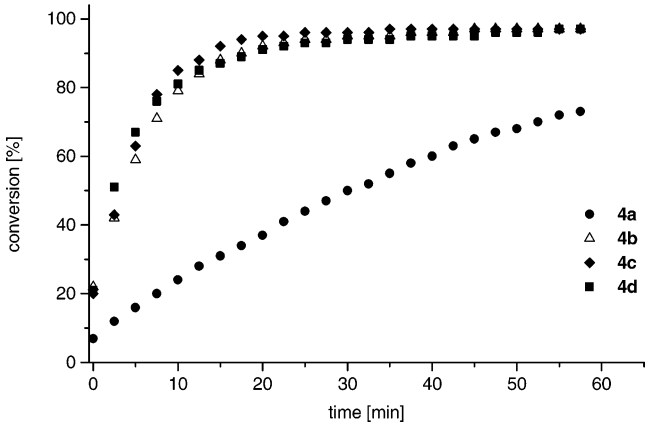


Figure 2. Plot of conversion versus time for the polymerization of **5** by **4a**−**d**, as determined by NMR spectroscopy. Conditions: 1 mg of **4a**−**d**; initiator:monomer = 1:70; 0.5 mL of $CDCl_3$; 60 °C.

is dependent on the rate of initiation and the rate of propagation. Taking into account that the latter is the same for all propagating species when using **4a**−**d**, it can be concluded that the slower polymerization of **5** with **4a** as the initiator is due to a distinctly lower initiation of this complex compared to that of the ester derivatives **4b**−**d**. The polymerization rates of **4b**−**d** are the same within the experimental error of this particular experimental setup, so that aforementioned initiation trend could not be proved. The drastic differences in the M_w values for the bulk polymerization (Table 1, entries 5−8) might also be connected to different solubilities of the initiators in the monomer.

Conclusion

In conclusion, we have described a new class of second-generation metathesis catalysts bearing a cis-dichloro arrangement and a chelating carbene ligand oriented parallel to a mesityl moiety of the H_2IMes coligand. These perfectly stable catalysts are easy to obtain in high-yield synthetic procedures. The same applies for the ligand precursors. The application of the compounds as initiators for ROM polymerization revealed that low initiation governs the chemistry of the introduced complexes.

Perfectly stable and thermally switchable initiators are of great interest in polymer chemistry. The aim is that monomers and initiator(s) can be mixed and stored without concomitant polymerization events. The presented initiators are a first step toward these needs. When the oxygen donor is exchanged for e.g. a nitrogen donor in the chelating carbene ligand, more inert initiators should be accessible. Research along these lines is currently ongoing in our laboratories.

Experimental Section

General Comments. $(H_2IMes)(pyridine)_2Cl_2Ru{=}CHPh$ (**1a**),[16] $(H_2IMes)(3\text{-bromopyridine})_2Cl_2Ru{=}CHPh$ (**1b**),[17] (±)-*endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl

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ester (**5**),[18] (±)-*endo,exo*-(3-benzoylbicyclo[2.2.1]hept-5-en-2-yl)-(phenyl)methanone (**6**),[19] and 2,4,6-trivinylcyclotriboroxane−pyridine complex were prepared according to the literature methods. 2-Bromobenzaldehyde, 2-bromobenzoyl chloride, 4-(dimethylamino)pyridine and $Pd(PPh_3)_4$ were purchased from Aldrich and were used as received. The weight-average molecular weights (M_w) and polydispersity indices (PDI) were determined by gel permeation chromatography using THF as the solvent in the following arrangement: Merck Hitachi L6000 pump, separation columns of Polymer Standards Service, 8 × 300 mm STV 5 μm grade size (10^6, 10^4, and 10^3 Å), refractive index detector from Wyatt Technology, model Optilab DSP interferometric refractometer. Polystyrene standards purchased from Polymer Standard Service were used for calibration. ^{1}H NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer operating at 499.803 MHz and were referenced to $SiMe_4$; the relaxation delay was set to 10 s. $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer operating at 125.687 MHz and were referenced to $SiMe_4$. IR spectra were recorded on a Perkin-Elmer Spectrum One spectrophotometer. Samples were measured as films on NaCl disks. Mass spectra (EI, 70 eV) were recorded on a KRATOS Profile HV-4 double-focusing magnetic sector instrument.

Synthesis of 2-Vinylbenzaldehyde (3a). A mixture of **2a** (418 mg, 2.26 mmol), 2,4,6-trivinylcyclotriboroxane−pyridine complex (528 mg, 2.26 mmol), K_2CO_3 (316 mg, 2.26 mmol), and $Pd(PPh_3)_4$ (128 mg, 0.113 mmol, 5 mol %) were placed under argon. A degassed mixture of DME and water was added, and the reaction mixture was heated at reflux temperature (the oil-bath temperature was set to 100 °C) for 15 h. The reaction mixture was extracted with CH_2Cl_2 and the organic fraction dried over Na_2SO_4. Insoluble materials were removed by filtration, and the solvent was removed under vacuum. The crude product was purified by column chromatography (50 g SiO_2, cyclohexane:ethyl acetate = 20:1). Yield: 278 mg (93%). ^{1}H NMR (δ, 20 °C, $CDCl_3$, 500 MHz): 10.31 (s, 1H, CHO), 7.85 (d, 1H, Ph^6), 7.59−7.43 (m, 4H, Ph^{3,4,5}, C*H*=CH$_2$), 5.72 (dd, 1H, $^3J_{HH}$(trans) = 17.0 Hz, $^2J_{HH}$ = 1.1 Hz, CH=C*H*$_2$); 5.53 (dd, 1H, $^3J_{HH}$(cis) = 11.2 Hz, $^2J_{HH}$ = 1.1 Hz, CH=C*H*$_2$). $^{13}C\{^1H\}$ NMR (δ, 20 °C, $CDCl_3$, 125 MHz): 192.7 (1C, C=O), 134.1, 133.6, 133.0, 131.5 (5C, Ph^{1,2,4,6}, *C*H=CH$_2$), 128.2 (1C, Ph^5), 127.7 (1C, Ph^3), 119.7 (1C, CH=*C*H$_2$). EI MS (*m*/*z*): [M$^+$] 132.056 94 (calcd 132.057 51).

Synthesis of 2-Vinylbenzoic Acid Methyl Ester (3b). 3b was prepared analogously to **3a** using **2b** (500 mg, 2.33 mmol), 2,4,6-trivinylcyclotriboroxane−pyridine complex (560 mg, 2.33 mmol), K_2CO_3 (321 mg, 2.33 mmol), and $Pd(PPh_3)_4$ (134.34 mg, 0.116 mmol, 5 mol %) as the starting materials. Yield: 342 mg (91%). ^{1}H NMR (δ, 20 °C, $CDCl_3$, 500 MHz): 7.88 (d, 1H, Ph^6), 7.58 (d, 1H, Ph^3), 7.47 (m, 2H, Ph^4, CH$_2$=C*H*−), 7.24 (dt, 1H, Ph^5), 5.65 (dd, 1H, $^3J_{HH}$(trans) = 17.9 Hz, $^2J_{HH}$ = 1.9 Hz, C*H*$_2$=CH), 5.36 (dd, 1H, $^3J_{HH}$(cis) = 10.8 Hz, $^2J_{HH}$ = 1.9 Hz, C*H*$_2$=CH), 3.90 (s, 3H, −OCH$_3$). $^{13}C\{^1H\}$ NMR (δ, 20 °C, $CDCl_3$, 125 MHz): 167.9 (1C, *C*OOCH$_3$), 139.7 (1C, C^2), 136.0 (1C, CH$_2$=*C*H), 132.2 (1C, C^4), 130.4 (1C, C^6), 128.7 (1C, C^1), 127.5, 127.3, 116.6 (1C, *C*H$_2$=CH), 52.2 (1C, O*C*H$_3$). EI MS (*m*/*z*): [M$^+$] 162.068 84 (calcd 162.068 08).

Synthesis of 2-Vinylbenzoic Acid Ethyl Ester (3c). 3c was prepared analogously to **3a** using **2c** (350 mg, 1.53 mmol), 2,4,6-trivinylcyclotriboroxane−pyridine complex (368 mg, 1.53 mmol), K_2CO_3 (211 mg, 1.53 mmol), and $Pd(PPh_3)_4$ (88.3 mg, 0.076 mmol, 5 mol %) as the starting materials. Yield: 237 mg (89%). ^{1}H NMR (δ, 20 °C, $CDCl_3$, 500 MHz): 7.86 (d, 1H, Ph^6), 7.58 (d, 1H, Ph^3), 7.46 (m, 2H, Ph^4, CH$_2$=C*H*), 7.32 (dt, 1H, Ph^5), 5.65 (dd, 1H, $^3J_{HH}$(trans) = 17.5 Hz, $^2J_{HH}$ = 1.8 Hz, C*H*$_2$=CH), 5.35 (dd, 1H, $^3J_{HH}$(cis) = 10.7 Hz, $^2J_{HH}$ = 1.8 Hz, C*H*$_2$=CH−), 4.38 (q, 2H, OC*H*$_2$CH$_3$), 1.40 (t, 3H, CH$_2$C*H*$_3$). $^{13}C\{^1H\}$ NMR (δ, 20 °C, $CDCl_3$, 125 MHz): 167.7 (1C, *C*OOEt), 139.7 (1C, C^2), 136.1 (1C, CH$_2$=*C*H), 132.2 (1C, C^4), 130.4 (1C, C^6), 129.2 (1C, C^1), 127.6, 127.4, 116.6 (1C, *C*H$_2$=CH), 61.3 (1C, O*C*H$_2$CH$_3$), 14.5 (1C, OCH$_2$*C*H$_3$). EI MS (*m*/*z*): [M$^+$] 176.083 83 (calcd 176.083 73).

Synthesis of 2-Vinylbenzoic Acid Isopropyl Ester (3d). 3d was prepared analogously to **3a** using **2d** (350 mg, 1.44 mmol), 2,4,6-trivinylcyclotriboroxane−pyridine complex (347 mg, 1.44 mmol), K_2CO_3 (199 mg, 1.44 mmol), and $Pd(PPh_3)_4$ (83 mg, 0.072 mmol, 5 mol %) as the starting materials. Yield: 241 mg (87%). ^{1}H NMR (δ, 20 °C, $CDCl_3$, 500 MHz): 7.85 (d, 1H, Ph^6), 7.58 (d, 1H, Ph^3), 7.44 (m, 2H, Ph^4, CH$_2$=C*H*), 7.33 (dt, 1H, Ph^5), 5.66−5.63 (dd, 1H, $^3J_{HH}$(trans) = 17.6 Hz, $^2J_{HH}$ = 1.5 Hz, C*H*$_2$=CH), 5.36−5.33 (dd, 1H, $^3J_{HH}$(cis) = 10.9 Hz, C*H*$_2$=CH−), 5.24 (hept, 1H, OC*H*(CH$_3$)$_2$), 1.38 (d, 6H, OCH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (δ, 20 °C, $CDCl_3$, 125 MHz): 167.3 (1C, *C*OOiPr), 139.5 (1C, C^2), 136.1 (1C, CH$_2$=*C*H), 132.1 (1C, C^4), 130.3 (1C, C^6), 129.7 (1C, C^1), 127.6, 127.4, 116.5 (1C, *C*H$_2$=CH), 68.8 (1C, O*C*H(CH$_3$)$_2$), 22.2 (1C, OCH(*C*H$_3$)$_2$). EI MS (*m*/*z*): [M$^+$] 190.100 68 (calcd 190.099 38).

Synthesis of (*SPY*-5-34)-Dichloro(2-formylbenzylidene-κ^2(*C*,*O*))(1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene)ruthenium (4a). A solution of **1a** (100 mg, 0.138 mmol) and **3a** (20 mg, 0.151 mmol) in CH_2Cl_2 (5 mL) was stirred at 25 °C for 4 h. During the reaction a green precipitate formed, which was collected on a glass frit washed with Et_2O (3 mL, 3 times) and dried under vacuum. Yield: 72 mg (87%). Anal. Calcd for $C_{29}H_{32}Cl_2N_2ORu$ (mol wt 596.55): C, 58.39; H, 5.41. Found: C, 58.12; H, 5.22. ^{1}H NMR (δ, 22 °C, $CDCl_3$, 500 MHz): 18.86 (s, 1H, Ru=C*H*), 10.03 (s, 1H, C*H*O), 7.91 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.0 Hz, Ph^4), 7.85 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.5 Hz, Ph^5), 7.74 (d, $^3J_{HH}$ = 7.5 Hz, 1H, Ph^6), 7.26 (d, $^3J_{HH}$ = 7.0 Hz, 1H, Ph^3), 7.22 (bs, 2H, Mes^{3,5}), 6.95 (bs, 1H, Mes^{3,5}), 5.85 (bs, 1H, Mes^{3,5}), 4.25, 3.96, 3.66 (bm, 4H, NC*H*$_2$C*H*$_2$N), 2.72, 2.49, 2.42, 2.12, 1.13 (bs, 18H, MesC*H*$_3$). ^{1}H NMR (δ, −35 °C, $CDCl_3$, 500 MHz): 18.77 (s, 1H, Ru=C*H*), 10.03 (s, 1H, C*H*O), 7.93 (bm, 1H, Ph^4), 7.87 (bm, 1H, Ph^5), 7.77 (bd, 1H, Ph^6), 7.30 (bs, 1H, Mes^{3,5}), 7.26 (bd, Ph^3), 7.21 (bs, 1H, Mes^{3,5}), 6.96 (bs, 1H, Mes^{3,5}), 5.81 (bs, 1H, Mes^{3,5}), 4.24, 3.96, 3.67 (bm, 4H, NC*H*$_2$C*H*$_2$N), 2.69, 2.48, 2.45, 2.40, 2.09, 1.14 (bs, 18H, MesC*H*$_3$). $^{13}C\{^1H\}$ NMR (δ, 20 °C, $CDCl_3$, 50 MHz): 285.8 (Ru=*C*H), 213.4 (Ru=*C*NN), 206.4 (*C*HO), 140.6, 140.0 (2C, C^q), 138.9 (1C, Ph^4), 138.6, 138.4, 137.4 (3C, C^q), 136.3 (1C, Ph^6), 135.6, 134.6 (2C, C^q), 133.7 (1C, Ph^2), 131.4 (1C, C^q), 131.1, 130.1, 129.8 (3C, Mes^{3,5}), 129.1 (1C, Ph^5), 128.6 (1C, Mes^{3,5}), 127.3 (1C, Ph^1), 126.1 (1C, Ph^3), 51.1 (2C, NCH$_2$*C*H$_2$N), 21.5, 21.1, 20.2, 18.5, 18.4, 16.9 (b, 6C, Mes*C*H$_3$).

Synthesis of (*SPY*-5-34)-Dichloro(2-methoxycarbonylbenzylidene-κ^2(*C*,*O*))(1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene)ruthenium (4b). A solution of **1a** (50 mg, 0.069 mmol) and **3b** (22.3 mg, 0.138 mmol) in CH_2Cl_2 (3 mL) was stirred at 25 °C for 4 h. The solution was evaporated to dryness, redissolved in 1 mL of CH_2Cl_2, and precipitated by slowly adding Et_2O (5 mL). The residue was separated and dried under vacuum. Yield: 32 mg (64%). Anal. Calcd for $C_{30}H_{34}Cl_2N_2O_2Ru$ (mol wt 626.58): C, 57.51; H, 5.47. Found: C, 57.32; H, 5.21. ^{1}H NMR (δ, 22 °C, $CDCl_3$, 500 MHz): 18.94 (s, 1H, Ru=C*H*), 8.05 (d, $^3J_{HH}$ = 7.5 Hz, 1H, Ph^6), 7.68 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.3 Hz, 1H, Ph^5), 7.65 (dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 7.3 Hz, 1H, Ph^4), 7.25 (d, $^3J_{HH}$ = 7.1 Hz, 1H, Ph^3), 7.20, 7.18, 6.93, 5.91 (bs, 4H, Mes^{3,5}), 4.08 (s, 3H, OC*H*$_3$), 4.26, 4.04, 3.76 (bm, 4H, NC*H*$_2$C*H*$_2$N), 2.68, 2.53, 2.47, 2.40, 2.08, 1.34 (bs, 18H, MesC*H*$_3$). $^{13}C\{^1H\}$ NMR (δ, 22 °C, $CDCl_3$, 125 MHz): 283.8 (1C, Ru=*C*H), 216.7 (1C, Ru=*C*NN), 177.3 (1C, COO), 142.3, 140.2, 139.8, 138.5, 138.0, 136.8 (6C, C^q), 136.0 (1C, Ph^4), 135.6, 134.8,132.2 (3C, C^q), 131.1, 131.0, 129.8, 129.7, 128.5, 128.2, 127.8 (7C, Ph^{3,5,6}, Mes^{3,5}), 120.0 (1C,

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C^q), 55.3 (1C, OCH_3), 51.2, 51.1 (2C, NCH_2CH_2N), 21.4, 21.0, 20.1, 18.4, 18.3, 16.3 (b, 6C, $MesCH_3$).

Synthesis of (*SPY*-5-34)-Dichloro(2-ethoxycarbonylbenzylidene-κ^2(*C*,*O*))(1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene)ruthenium (4c). 4c was prepared analogously to **4b** using **1a** (60 mg, 0.083 mmol) and **3c** (29 mg, 0.165 mmol) as the starting materials. Yield: 37 mg (70%). Anal. Calcd for $C_{31}H_{36}Cl_2N_2O_2Ru$ (mol wt 640.61): C, 58.12; H, 5.66. Found: C, 57.97; H, 5.32. ^{1}H NMR (δ, 22 °C, $CDCl_3$, 500 MHz): 18.95 (s, 1H, Ru=C*H*), 8.07 (d, $^3J_{HH}$ = 7.9 Hz, 1H, Ph^6), 7.69 (dd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.7 Hz, 1H, Ph^5), 7.63 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.7 Hz, 1H, Ph^4), 7.24 (d, $^3J_{HH}$ = 7.5 Hz, 1H, Ph^3), 7.20, 7.17, 6.93, 5.92 (bs, 4H, $Mes^{3,5}$), 4.64 (m, 1H, CH_2CH_3), 4.42 (m, 1H, OCH_2CH_3), 4.27, 4.02, 3.75 (bm, 4H, NCH_2CH_2N), 2.68, 2.52, 2.47, 2.41, 2.09, 1.34 (bs, 18H, $MesCH_3$), 1.47 (t, 3H, OCH_2CH_3). ^{13}C{^{1}H} NMR (δ, 22 °C, $CDCl_3$, 125 MHz): 283.8 (1C, Ru=*C*H), 217.2 (1C, Ru=*C*NN), 177.0 (1C, COO), 142.6, 140.2, 139.8, 138.5, 138.1, 137.0 (6C, C^q), 136.0 (1C, Ph^4), 135.6, 134.9,132.4 (3C, C^q), 131.1, 131.0, 129.8, 129.7, 128.6, 128.1, 127.9 (7C, $Ph^{3,5,6}$, $Mes^{3,5}$), 120.5 (1C, C^q), 64.8 (1C, OCH_2CH_3), 51.2, 51.1 (2C, NCH_2CH_2N), 21.5, 21.1, 20.2, 18.5, 18.4, 16.5 (6C, $MesCH_3$), 14.2 (1C, OCH_2CH_3).

Synthesis of (*SPY*-5-34)-Dichloro(2-isopropoxycarbonylbenzylidene-κ^2(*C*,*O*))(1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene)ruthenium (4d). 4d was prepared analogously to **4b** using **1a** (60 mg, 0.083 mmol) and **3d** (31 mg, 0.165 mmol) as the starting materials. Yield: 39 mg (71%). Anal. Calcd for $C_{32}H_{38}Cl_2N_2O_2Ru$ (mol wt 654.63): C, 58.71; H, 5.85. Found: C, 58.48; H, 5.49. ^{1}H NMR (δ, 22 °C, $CDCl_3$, 500 MHz): 18.94 (s, 1H, Ru=C*H*), 8.05 (d, $^3J_{HH}$ = 7.9 Hz, 1H, Ph^6), 7.67 (dd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.7 Hz, 1H, Ph^5), 7.62 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.7 Hz, 1H, Ph^4), 7.24 (d, $^3J_{HH}$ = 7.5 Hz, 1H, Ph^3), 7.20, 7.17, 6.92, 5.91 (bs, 4H, $Mes^{3,5}$), 5.13 (m, 1H, $OCH(CH_3)_2$), 4.27 (bm, 1H, NCH_2CH_2N), 4.04, 3.99, 3.75 (bm, 3H, NCH_2CH_2N), 2.67, 2.55, 2.46, 2.40, 2.07, 1.36 (bs, 18H, $MesCH_3$), 1.47 (d, 6H, $OCH(CH_3)_2$). ^{13}C{^{1}H} NMR (δ, 22 °C, $CDCl_3$, 125 MHz): 283.9 (1C, Ru=*C*H), 217.5 (1C, Ru=*C*NN), 176.3 (1C, COO), 142.6, 140.1, 139.8, 138.5, 138.1, 136.4 (6C, C^q), 136.0 (1C, Ph^4), 135.6, 134.9,132.6 (3C, C^q), 131.1, 131.0, 129.7, 129.7, 128.5, 128.1, 127.9 (7C, $Ph^{3,5,6}$, $Mes^{3,5}$), 120.9 (1C, C^q), 72.9 (1C, $OCH(CH_3)_2$), 51.3, 51.1 (2C, NCH_2CH_2N), 22.1, 21.9 (2C, $OCH(CH_3)_2$), 21.5, 21.1, 20.2, 18.5, 18.4, 16.5 (6C, $MesCH_3$).

Crystal Structure Determination. Crystal data for **4a**·$2CH_2Cl_2$: $C_{31}H_{36}Cl_6N_2ORu$, M_r = 766.39, monoclinic, $P2_1/c$, a = 12.1933(6) Å, b = 15.4520(7) Å, c = 19.3799(9) Å, β = 108.181(1)°, V = 3469.1(3) Å^3, Z = 4, T = 298 K, Bruker SMART APEX CCD three-circle diffractometer (sealed X-ray tube, Mo Kα radiation, graphite monochromator). Structure solution and refinement was carried out with Bruker SHELXTL software. Final R indices (7087 $I > 2\sigma(I)$, 410 parameters): R1 = 0.0369, wR2 = 0.0967.

Polymerization Procedures. Procedures were carried out under an inert atmosphere. To the monomer solutions of **5** and **6** (300 or 600 equiv) in CH_2Cl_2 (3 mL) were added initiators **4a**−**d** (1.00 mg, 1.0 equiv) dissolved in CH_2Cl_2 (1 mL). The reaction mixtures were stirred at 45 °C for variable times. The polymerizations were quenched by adding some drops of ethyl vinyl ether. After 30 min the solution was added slowly to stirred methanol (50 mL). The white precipitate was dried under vacuum.

The bulk polymerization was carried out by placing 600 equiv of **5** in a Schlenk tube and heating the monomer to 110 °C. The initiators **4a**−**d** (1.00 mg, 1.0 equiv) dissolved in CH_2Cl_2 (0.3 mL) were subsequently added to the stirred monomer at 110 °C. Immediate polymerization occurred. After 5 min at 110 °C, the reaction mixture was allowed to reach room temperature. Then ethyl vinyl ether (in 15 mL of CH_2Cl_2) was added. After 30 min the solution was added slowly to stirred methanol (50 mL). The white precipitate was dried under vacuum.

NMR and IR spectra of the polymers produced by the different initiators and different procedures are similar; therefore, only one set of data for each polymer is given. **Poly5**: ^{1}H NMR (δ, 20 °C, $CDCl_3$, 500 MHz) 5.6−5.1 (m, 2H, *H*C=C*H*), 3.7−3.6 (m, 6H, Me), 3.4−2.6 (m, 4H, cPen), 2.1−1.2 (m, 2H, cPen); ^{13}C{^{1}H} NMR (δ, 20 °C, $CDCl_3$, 125 MHz) 178−176 (2C, C=O), 134.0−129.7 (2C, H*C*=*C*H), 54.0−39.6 (7C, Me, cPen); FT-IR (NaCl, cm^{-1}) 3060−2844 (m, ν_{CH}), 1731 (s, $\nu_{C=O}$), 1437 (m), 1382 (w), 1336 (w), 1259 (m), 1198 (m), 1168 (m), 1001 (w), 971 (w), 730 (w). **Poly6**: ^{1}H NMR (δ, 20 °C, $CDCl_3$, 500 MHz) 7.8−7.1 (m, 10H, Ph), 5.3−4.7 (m, 2H, *H*C=C*H*), 4.3−2.3 (m, 4H, cPen), 1.9−1.1 (m, 2H, cPen); ^{13}C-{^{1}H} NMR (δ, 20 °C, $CDCl_3$, 125 MHz) 202.4, 200.7 (2C, C=O), 137.6 (2C, Ph^1), 133.4 (2C, Ph^4), 129.6−129.4 (2C, H*C*=*C*H), 129.0, 128.7 (8C, $Ph^{2,3}$), 53.3−39.9 (5C, cPen); FT-IR (NaCl, cm^{-1}) 3060−2864 (m, ν_{CH}), 1673 (s, $\nu_{C=O}$), 1596 (m), 1580 (w), 1447 (w), 1380 (w), 1330 (w), 1219 (m), 1180 (w), 1003 (m), 973 (m), 911 (w), 785 (w), 730 (m), 703 (m), 687 (m).

Polymerization Procedure in NMR tubes. Complexes **4a**−**d** (0.0017 mmol, 1.0 equiv) were weighed into a small vial containing $Si(SiMe_3)_4$ (0.0026 mmol, 0.25 equiv.) as the internal standard for integration. The solvent ($CDCl_3$, 0.3 mL) was used to transfer the contents into a NMR tube, which was fitted with a screw cap containing a rubber septum and taped caps. Monomer **5** (70 equiv) was dissolved in 0.2 mL of solvent and injected into the NMR tube. The desired temperature (60 °C) was reached after 4 min. A ^{1}H NMR timing sequence was started when the temperature reached 59 °C. The propagation was followed by integration of the olefinic proton resonances of the monomer and the polymer in dependence of time.

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Supporting Information Available: X-ray crystallographic file in CIF format for the structure of compound **4a**·$2CH_2Cl_2$ and text giving details of the preparations for compounds **2b**−**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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