Synthesis of Ruthenium Olefin Metathesis Catalysts with Linear Alkyl Carbene Complexes

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Second-generation ruthenium olefin metathesis catalysts with linear alkyl carbenes were needed to install a linear alkyl end group on ROMP polymers. The ethylidene complexes $RuCl_2(PCy_3)(SIMes)CHMe$ (PCy_3 = tricyclohexylphosphine; SIMes = 1,3-bis(mesityl)-imidazolidin-2-ylidene) and $RuCl_2(3BP)_2(SIMes)CHMe$ (3BP = 3-bromopyridine) were readily accessible by reaction of $RuCl_2(PCy_3)(SIMes)CHPh$ with 2-butene. Synthesis of higher alkyl analogues, such as propylidene and heptylidene, are complicated by the intervention of olefin isomerization. Although slightly less reactive than the parent complex, these complexes are suitable catalysts for both ADMET and ROMP.

Introduction

Acyclic diene metathesis (ADMET) polymerization[2] results in polymers with well-defined vinyl end groups.[1] On the other hand, ring-opening metathesis polymerization[3] (ROMP) results in incorporation of the carbene fragment of the initiator complex as a polymer end group (Figure 1)—the other end group can be provided by chemical reaction on the polymeric carbene such as reaction with a vinyl ether to form a vinyl end group and a relatively inert Fisher carbene complex.[4] Our study of functionalized polyethylene via the ROMP−hydrogenation route[5] called for a linear alkyl carbene initiator in order to install a primary alkyl end group.

Grubbs et al. have synthesized bis(phosphine) linear alkyl carbene complexes by reaction of $RuCl_2(PCy_3)_2$-CHPh with acyclic olefins such as propene and 3-hexene.[6] However, linear carbene versions of the more recently developed N-heterocyclic carbene[7] (NHC) and bis(pyridine)[9] analogues of $RuCl_2(PCy_3)_2CHPh$ are more desirable than the parent bis(phosphine) complexes for a number of reasons and, to our knowledge, have not been described in the literature. Thus, a study of linear alkyl carbene second-generation ruthenium olefin metathesis catalysts was undertaken and resulted in discovery of a facile synthetic route to $RuCl_2(PCy_3)$-$(SIMes)CHMe$ (PCy_3 = tricyclohexylphosphine; SIMes = 1,3-bis(mesityl)imidazolidin-2-ylidene) and $RuCl_2$-$(3BP)_2(SIMes)CHMe$ (3BP = 3-bromopyridine). The synthesis, structure, and spectroscopy of these complexes and some comparisons of polymerization behavior are given in this paper.

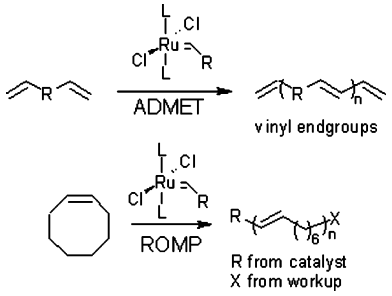

Figure 1. Comparison of polymer end groups produced by ADMET and ROMP.

Results and Discussion

Synthesis. Synthesis of $RuCl_2(PCy_3)(SIMes)CHMe$ was accomplished in 94% yield by reaction of $RuCl_2$-$(PCy_3)(SIMes)CHPh$ with 2-butene gas (mixture of cis and trans isomers) in degassed benzene solution at 60 °C for 15 min (Figure 2). Procedures employing lower temperatures required longer reaction times and resulted in lower yields. The ethylidene complex may be separated from the benzylidene complex by very careful

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(9) Steric repulsion between the carbene unit and the phosphine ligand is expected to weaken the Ru−P bond, leading to more rapid dissociation—the larger the carbene, the more it is expected to weaken the Ru−P bond.

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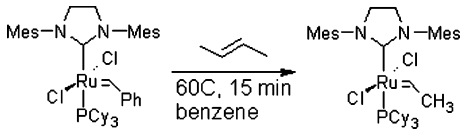

Figure 2. Synthesis of $RuCl_2(PCy_3)(SIMes)CHMe$.

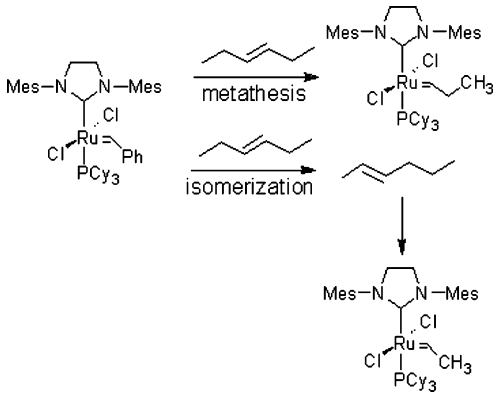

Figure 3. Attempted synthesis of $RuCl_2(PCy_3)(SIMes)$-CHEt from $RuCl_2(PCy_3)(SIMes)CHPh$ and *trans*-3-hexene.

chromatography (the benzylidene elutes first), but the reaction conditions given above require no chromatography and result in complete conversion to the desired ethylidene complex. The preferred method of isolation is freeze−drying the reaction mixture.

The synthesis of higher alkyl homologues of the complex $RuCl_2(PCy_3)(SIMes)CHMe$ was explored, since larger alkyl groups might be expected to increase the rate of phosphine dissociation,[9] but the intervention of olefin isomerization[10] complicated their syntheses. For example, reaction of $RuCl_2(PCy_3)(SIMes)CHPh$ with *trans*-3-hexene was studied by NMR spectroscopy. This reaction results in the formation of the expected propylidene complex $RuCl_2(PCy_3)(SIMes)CHEt$ as well as the ethylidene complex $RuCl_2(PCy_3)(SIMes)CHMe$ by isomerization of 3-hexene to 2-hexene followed by metathesis to form $RuCl_2(PCy_3)(SIMes)CHMe$ (Figures 3 and 4). Note that the ethylidene complex $RuCl_2(PCy_3)$-$(SIMes)CHMe$ is the major product, which speaks to the greater stability of this complex compared to the higher alkyl homologue. Reaction of $RuCl_2(PCy_3)(SIMes)CHPh$ with internal or external olefins higher than 2-butene, therefore, is not a viable route to well-defined ruthenium alkylidene NHC−phosphine complexes. The reaction of $RuCl_2(PCy_3)(SIMes)CHPh$ with 2-butene depicted in Figure 2 results in a single product, presumably because the rate of isomerization of the double bond to an external position is much slower than the rate of metathesis of 2-butene with $RuCl_2(PCy_3)(SIMes)CHPh$.

Reaction of the bis(phosphine) complex $RuCl_2(PCy_3)_2$-$CHPh$ with an internal olefin[6] followed by attachment of the NHC ligand[11] is another route to higher homologues of $RuCl_2(PCy_3)(SIMes)CHMe$ and was used to synthesize the propylidene $RuCl_2(PCy_3)(SIMes)CHEt$ and heptylidene $RuCl_2(PCy_3)(SIMes)CHHex$ without the intervention of olefin isomerization. Unfortunately, the attachment of the NHC ligand was plagued by low

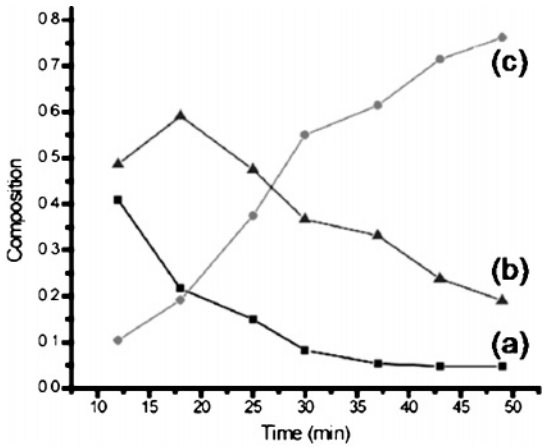

Figure 4. Progress of reaction of $RuCl_2(PCy_3)(SIMes)$-$CHPh$ with *trans*-3-hexene tracked by ^1H NMR spectroscopy: (a) $RuCl_2(PCy_3)(SIMes)CHPh$; (b) $RuCl_2(PCy_3)(SIMes)$-$CHEt$; (c) $RuCl_2(PCy_3)(SIMes)CHMe$. The formation of $RuCl_2(PCy_3)(SIMes)CHMe$ occurs via olefin migration of 3-hexene followed by metathesis.

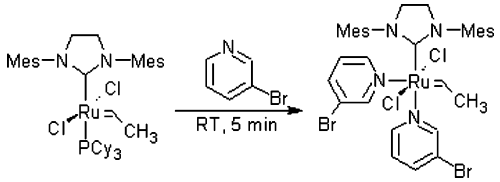

Figure 5. Synthesis of $RuCl_2(3BP)_2(SIMes)CHMe$.

yields, due to decomposition of the products and formation of two additional carbene species (by ^1H NMR) that remain undefined, although one appears to be the methylidene complex (singlet at 18.4 ppm, C_6D_6). These byproducts could not be separated from the desired complexes by chromatography, thus preventing rigorous characterization of the compounds, although the ^1H NMR spectra were consistent with the expected structures. On the basis of the integration of the carbene ^1H NMR peaks, the impurities likely constitute 5−10% of the material.

The synthesis of $RuCl_2(3BP)_2(SIMes)CHMe$ from $RuCl_2(PCy_3)(SIMes)CHMe$ proceeds in 95% yield without the need for any chromatography by stirring $RuCl_2$-$(PCy_3)(SIMes)CHMe$ with excess (∼10 equiv) 3-bromopyridine in an open vial in air for 5 min (Figure 5).[12]

Spectroscopy and Structure of Linear Alkyl Carbene Complexes. The structure of $RuCl_2(PCy_3)$-$(SIMes)CHMe$ was confirmed by X-ray crystallography and reveals that the complex adopts the expected distorted-square-pyramidal geometry (Figure 6). The torsional angle about the Cl_{cis}−Ru−C−C atoms is only 7°, which is less than that of $RuCl_2(PCy_3)(SIMes)$-$CHPh$[13] (12°) (Table 1). This was somewhat surprising, given that the ^1H NMR spectrum of $RuCl_2(PCy_3)$-$(SIMes)CHMe$ in deuterated benzene reveals a 0.7 Hz coupling of the carbene proton to phosphorus, forming a doublet of quartets.[14−16] The methyl protons of the carbene fragment (doublet of doublets) are coupled to the phosphorus (over four bonds) to a greater extent

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(13) In the course of this work, an X-ray structure for $RuCl_2(PCy_3)$-$(SIMes)CHPh$ was collected. The data are reported in the Supporting Information.

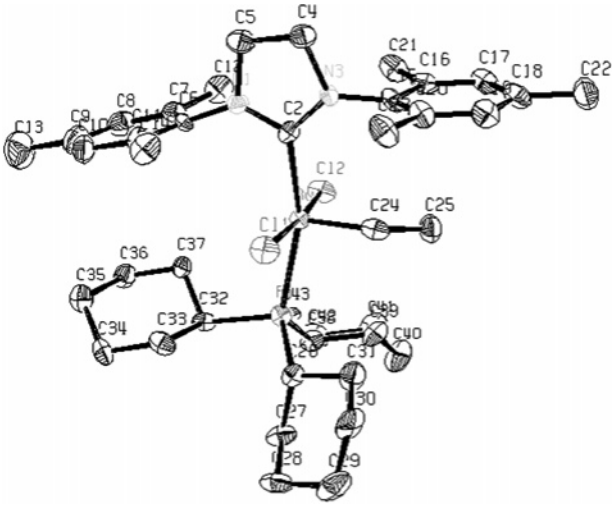

Figure 6. X-ray crystal structure of $RuCl_2(PCy_3)(SIMes)$-CHMe.

Table 1. Relevant Bond Lengths (Å) and Angles (deg)

	$RuCl_2(PCy_3)$-(SIMes)CHPh	$RuCl_2(PCy_3)$-(SIMes)CHMe	$RuCl_2(3BP)_2$-(SIMes)CHMe
$Ru-C_{carbene}$	1.836(2)	1.809(11)	1.847(3)
$Ru-C_{NHC}$	2.088(2)	2.101(10)	2.048(3)
Ru−P	2.4268(6)	2.432(3)	
Ru−N1			2.207(2)
Ru−N2			2.366(3)
$C_{carbene}-C$	1.464(3)	1.455(15)	1.485(5)
Cl−Ru−Cl	167.66(2)	174.05(11)	175.71(3)
$C_{NHC}-Ru-C_{carbene}$	99.90(9)	99.1(4)	94.58(12)
$Cl1-Ru-C_{carbene}$	104.53(8)	91.1(3)	88.18(11)
$Cl2-Ru-C_{carbene}$	87.78(8)	94.8(3)	95.12(11)
$Cl_{cis}-Ru-C-C$	11.58	7.04	25.63

than the carbene proton, presumably due to the accessibility of planar H−C−C−Ru−P configurations (J_{HP} = 1.2 Hz). In all other regards, the spectra and structure of $RuCl_2(PCy_3)$(SIMes)CHMe are similar to those of $RuCl_2(PCy_3)$(SIMes)CHPh.

The structures of complexes $RuCl_2(PCy_3)$(SIMes)-CHEt and $RuCl_2(PCy_3)$(SIMes)CHHex can be inferred from the ^{1}H NMR spectra, which are similar to the spectrum for $RuCl_2(PCy_3)$(SIMes)CHMe. The carbene protons form a doublet of triplets due to coupling to the CH_2 protons (J_{HH} = 4.2, both complexes, C_6D_6) and the phosphorus atom (J_{HP} = 1.1 Hz, $RuCl_2(PCy_3)$(SIMes)-CHEt; J_{HP} = 1.2 Hz, $RuCl_2(PCy_3)$(SIMes)CHHex). These H−P couplings are of greater magnitude than that for $RuCl_2(PCy_3)$(SIMes)CHMe, indicating that the higher alkyl fragments are distorted further from the mesityl group than the methyl group. The protons of the methylene bonded to the carbene carbon are very broad for both of these complexes, the remaining methylenes of the carbene group are coincidental with the tricyclohexylphosphine protons, and the terminal methyl group forms a triplet.

(14) The H−P coupling for the first-generation ruthenium catalysts is known to obey a Karplus-like relationship. This coupling was not seen in deuterated chloroform solution at 300 MHz, and thus the coupling witnessed in benzene could be due to some property of the solvent that has the effect of distorting the methyl group from coplanarity with the Cl−Ru−Cl unit.

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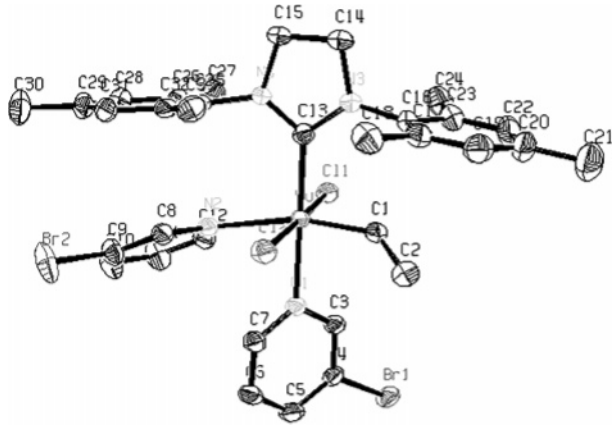

Figure 7. X-ray crystal structure for $RuCl_2(3BP)_2$-(SIMes)CHMe.

The structure of $RuCl_2(3BP)_2$(SIMes)CHMe was revealed by X-ray crystallography and shows a pseudo-octahedral geometry with cis pyridines and trans chlorines with a Cl−Ru−Cl bond angle of 175.71°. (Figure 7) In contrast to $RuCl_2(PCy_3)$(SIMes)CHMe, the methyl group of the carbene fragment of $RuCl_2(3BP)_2$(SIMes)-CHMe is significantly distorted from planarity with the Cl−Ru−Cl fragment by about 26° (toward the pyridine ligand). The pyridine ligand trans to the carbene ligand resides 0.16 Å closer to the ruthenium atom than the cis pyridine ligand.

Thermolytic Decomposition. The higher alkyl complexes decompose more rapidly in air than the ethylidene complex, as witnessed visually by conversion of solutions of the higher alkyl carbene complexes to brown insolubles in 5 min compared to about 20 min for the ethylidene complex. Thermolytic decomposition rates were also investigated by monitoring the intensity of the carbene proton NMR signal in 0.23 M solutions of the complexes in deuterated benzene at 55 °C over several hours.[17] The decomposition behavior of $RuCl_2$-(PCy_3)(SIMes)CHMe was vastly different if the solution was prepared on the benchtop rather than in the glovebox. The solution prepared on the benchtop decomposed semimonotonically with a half-life of 2.8 h. Decomposition of the same solution prepared in the absence of oxygen and moisture in a glovebox, however, showed entirely different behavior; the decomposition was much slower with more complicated kinetics. There was an initial period of relatively rapid decomposition followed by a much slower decomposition that could not be carried out to the half-life in a reasonable time. Extrapolation of the data to 50% decomposition gives an approximate half-life of 100 h (Figure 8).

Thermolytic decomposition of $RuCl_2(PCy_3)$(SIMes)-CHHex displayed kinetics similar to that of $RuCl_2$-(PCy_3)(SIMes)CHMe, but the rate of the slow portion of the decomposition was somewhat faster than that with $RuCl_2(PCy_3)$(SIMes)CHMe (Figure 9). Extrapolation of the data gave a thermolytic half-life of 12 h. These data indicate that $RuCl_2(PCy_3)$(SIMes)CHHex is less stable than $RuCl_2(PCy_3)$(SIMes)CHMe, which would be expected on the basis of greater phosphine dissociation with larger alkyl size. The kinetics of decomposition

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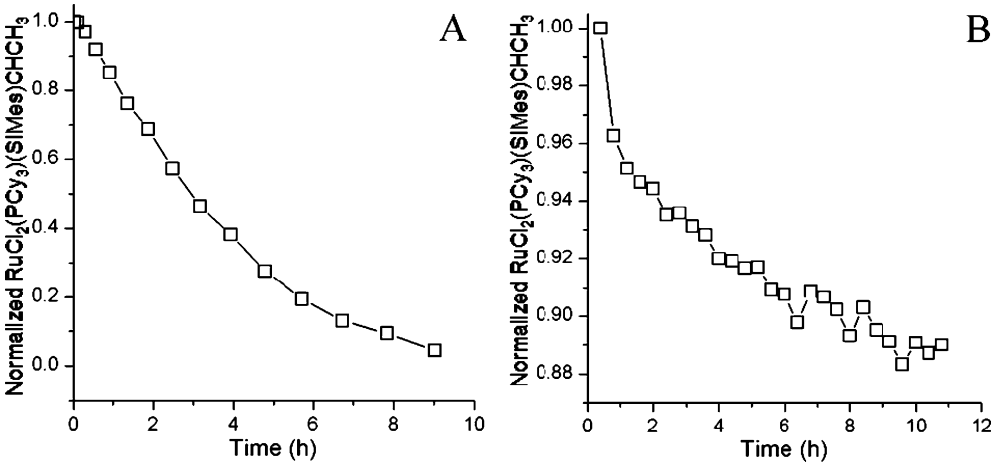

Figure 8. Thermolytic decomposition of $RuCl_2(PCy_3)(SIMes)CHMe$ solution in benzene-d_6 at 55 °C: (A) solution prepared on bench; (B) solution prepared in the absence of air.

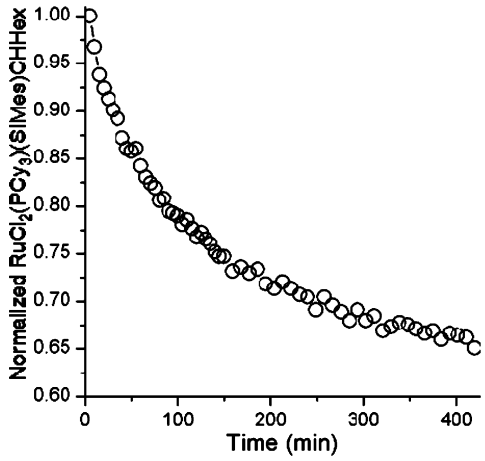

Figure 9. Thermolytic decomposition of $RuCl_2(PCy_3)$-(SIMes)CHHex solutions in benzene-d_6 at 55 °C.

are similar to those observed by Grubbs and co-workers for the first-generation ruthenium olefin metathesis catalysts.[17] The rapid initial decomposition forms free phosphine, which retards further decomposition by reducing the amount of the phosphine-dissociated complex in solution. The decomposition pathway in the presence of air is not known and was not investigated in this work but may be similar to the conversion of $RuCl_2(PCy_3)_2CHPh$ and $RuCl_2(PCy_3)(SIMes)CHPh$ to give $Ru(PCy_3)_2Cl(CO)Ph$ and $Ru(SIMes)(PCy_3)Cl(CO)$-Ph (and other products), respectively, in the presence of oxygen as described by Grubbs et al.[11] and Dinger and Mol.[18]

ADMET of 1,9-Decadiene. The complex $RuCl_2$-$(PCy_3)(SIMes)CHEt$ was used to polymerize 1,9-decadiene at 70 °C under vacuum in order to compare the results to those obtained with $RuCl_2(PCy_3)(SIMes)$-CHPh. The properties of this polyoctenamer were quite similar to those of polyoctenamer produced with $RuCl_2$-$(PCy_3)(SIMes)CHPh$. The cis contents and peak melting temperatures were 19 and 18% and 38.4 and 42.5 °C for $RuCl_2(PCy_3)(SIMes)CHEt$ and $RuCl_2(PCy_3)(SIMes)$-CHPh, respectively. The low melting temperatures are due in part to olefin isomerization occurring during the polymerization.[10] On the other hand, the molecular weight of the polyoctenamer produced with $RuCl_2$-$(PCy_3)(SIMes)CHEt$ was significantly lower than that produced with $RuCl_2(PCy_3)(SIMes)CHPh$—$M_n = 17\,055$ (PDI 2.0) and 43 930 (PDI 1.8), respectively. The discrepancy between these complexes is not easily explained, since after the first turnover, the species involved in the polymerization are expected to be identical. Further experimentation on this subject will be the topic of a future publication.

ROMP of Cyclooctene. The ROMP of cyclooctene was performed with these complexes at room temperature using 2000 equiv of cyclooctene per ruthenium complex in bulk monomer. The higher activity of $RuCl_2$-$(3BP)_2(SIMes)CHMe$ compared to that of $RuCl_2(PCy_3)$-$(SIMes)CHMe$ for ROMP of cyclooctene in bulk monomer was apparent by the almost immediate formation of a solid polymer with $RuCl_2(3BP)_2(SIMes)CHMe$, whereas the same polymerization with $RuCl_2(PCy_3)$-$(SIMes)CHMe$ gave a viscous liquid polymer that solidified after several hours. The polymerizations with $RuCl_2(PCy_3)(SIMes)CHEt$ and $RuCl_2(PCy_3)(SIMes)$-CHHex were also noticably more rapid than that with $RuCl_2(PCy_3)(SIMes)CHMe$. The results are given in Table 2. Note that the melting points for the polymer as formed are much higher than those after melting and recrystallization. Also note that the cis to trans ratio varies with the carbene identity, which is not easily reconcilable with the dissociative mechanism of metathesis.

Conclusions

A series of linear alkyl carbene complexes were synthesized, although the ethylidenes were the only members of the series that could be synthesized in high yield in a pure form. The higher alkyl carbene complexes were found to decompose during synthesis and in general to be less stable than the ethylidenes. These complexes were found to be active for ROMP of cyclooctene and for ADMET of 1,9-decadiene.

Experimental Section

General Considerations. $RuCl_2(PCy_3)_2CHPh$ was purchased from Strem and used as received. The complex $RuCl_2$-$(PCy_3)(SIMes)CHPh$ was synthesized from $RuCl_2(PCy_3)_2CHPh$ by generating the NHC carbene ligand in situ by two methods: deprotonation of the tetrafluoroborate salt of the corre-

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Table 2. Results for Cyclooctene Polymerization

catalyst[a]	yield (%)[b]	M_n/PDI UC[c]	M_n/PDI LS[d]	T_m (°C)[e]	ΔH_f (J/g)[e]	cis:trans[f]
$RuCl_2(PCy_3)$(SIMes)CHPh	100	143 965/1.5				20:80
$RuCl_2(3BP)_2$(SIMes)CHPh	100	55 044/4.2				22:78
$RuCl_2(PCy_3)$(SIMes)CHMe	100	95 420/2.9	114 300/1.6	73.7	90.6	17:83
				52.4	36.8	
$RuCl_2(PCy_3)$(SIMes)CHEt	100	74 360/1.5	55 200/1.5	73.5	124.8	10:90
				53.2	46.2	
$RuCl_2(PCy_3)$(SIMes)CHHex	100	66 840/1.5	60 730/1.5	73.3	125.0	13:87
				53.4	46.0	
$RuCl_2(3BP)_2$(SIMes)CHMe	100	79 940/3.2	74 830/1.6	62.5	70.8	22:78
				56.7	53.7	

[a] Conditions: 2000:1 monomer to catalyst ratio, bulk monomer, room temperature, overnight. [b] Without precipitation. [c] Conditions: universal calibration constructed with PS standards, THF, 40 °C. [d] Two-angle laser light scattering. [e] Top row for the polymer as formed in bulk polymerization, second row after cooling from the melt at 10 °C/min. [f] Determined from ^{13}C NMR.

sponding imidazolium cation[19] or by α-elimination of chloroform from the chloroform adduct of the carbene.[11] The latter method is preferred. Complexes $RuCl_2(PCy_3)_2$CHEt and $RuCl_2(PCy_3)_2$CHHex[6] were synthesized by the methods of Grubbs et al. Ethyl vinyl ether (EVE; Aldrich), butylated hydroxytoluene (BHT; Aldrich), 2-butene (Aldrich), and 3-bromopyridine (Aldrich) were used as received. *trans*-3-Hexene (Aldrich) was degassed by three freeze−pump−thaw cycles. Cyclooctene (Aldrich) was distilled from CaH_2. 1,9-Decadiene (Aldrich) was distilled from CaH_2, degassed by three freeze−pump−thaw cycles, and stored in a glovebox. ACS grade solvents were used unless otherwise noted.

NMR spectroscopy was conducted on a Varian Gemini 300, VXR 300, or Mercury 300 spectrometer operating at 300.071 MHz for proton and 75.460 MHz for carbon nuclei or an Inova 500 spectrometer operating at 499.497 MHz for proton and 125.610 MHz for carbon. $CDCl_3$, toluene-d_8, CD_2Cl_2, and C_6D_6 were either used as received or distilled, degassed by three freeze−pump−thaw cycles, and stored in a glovebox, and reported chemical shifts were referenced to residual protio solvent or TMS. Whatman aluminum-backed silica plates were used for TLC. Chromatography was performed on neutral silica gel 60 from TSI Scientific (Cambridge, MA). IR spectroscopy was performed on a Bruker 200 instrument. The University of Florida Spectroscopic Services Group conducted HRMS-FAB on a Finnigan MAT95 Q instrument. Elemental analysis was conducted by Atlantic Microlab (Norcross, GA). GPC analysis was conducted on a Waters Associates GPCV2000 liquid chromatography system equipped with two Waters Styragel HR-5E columns (10 μm PD, 7.8 mm i.d., 300 mm length), an internal differential refractive index detector (DRI), an internal differential viscosity detector (DP), and a Precision two-angle light scattering detector (LS) using HPLC grade tetrahydrofuran as a mobile phase at 45 °C (1.0 mL/min flow rate; 0.05−0.07% w/v sample concentration using a 322.5 μL injection volume). The columns were calibrated with polystyrene standards (Polymer Laboratories, Amherst, MA, or American Polymer Standards Corporation, Mentor, OH), employing differential refractive index and differential viscosity detectors. The molecular weight was quantified by universal calibration using 10 polystyrene standards. Molecular weights were measured by two-angle light scattering (GPC-LS) collected at a 15° angle, and the three in-line detectors were operated in series in the order LS-DRI-DP. DSC was conducted on a Perkin-Elmer DSC 7 instrument, and all samples were analyzed at a scan rate of 10 °C/min.

Synthesis of $RuCl_2(PCy_3)$(SIMes)CHMe. The complex $RuCl_2(PCy_3)$(SIMes)CHPh (127 mg, 0.150 mmol) was placed in a 25 mL flask with 10 mL of benzene and degassed by bubbling argon through the solution for 25 min. The flask was then immersed in a 60 °C oil bath, and 2-butene (mixture of cis and trans) was then bubbled rapidly through the solution for 15 min, resulting in a color change from purple to dark orange. The solution was then frozen and freeze−dried overnight under high vacuum at room temperature to give 110 mg of product (93% yield).

^1H NMR (299.631 MHz, $CDCl_3$): δ (ppm) 18.54 (d, Ru=C*H*, J_{HH} = 7 Hz, 1H), 6.98, 6.93 (s, aryl *H*, 1H, 1H), 3.90 (m, NCH_2CH_2N, 4H), 2.62, 2.44, 2.31, 2.30 (s, mesityl CH_3, 6H, 6H, 3H, 3H), 2.1−2.3 (br, PCy_3, 3H) 1.4−1.7 (br, PCy3 and $RuCHCH_3$, 33H). ^{13}C NMR (75.357 MHz, $CDCl_3$): δ (ppm) 315.15, 219.90 (J_{CP} = 74.9 Hz), 138.82, 138.37, 138.02, 137.99, 137.37, 129.77, 129.33, 51.85 (J_{CP} = 2.8 Hz), 51.53 (J_{CP} = 2.3 Hz), 46.43, 31.49 (J_{CP} = 16.6 Hz), 29.09, 27.58 (J_{CP} = 10.2 Hz), 26.18, 21.05, 20.97, 19.63, 18.54. HRMS-FAB: calcd, 786.3143; found, 751.3400 $[M - Cl]^+$. Anal. Calcd for $C_{44}H_{49}Cl_2N_2PRu$: C, 62.58; H, 8.07; N; 3.56. Found: C, 62.61; H, 7.89; N; 3.34.

Synthesis of $RuCl_2(PCy_3)$(SIMes)CHEt. $RuCl_2(PCy_3)_2$CHEt (183 mg, 0.236 mmol) and SIMes·$CHCl_3$ (205 mg, 0.481 mmol, 2.1 equiv) were combined in a dry round-bottom flask in a glovebox, covered with 2 mL of toluene (distilled from sodium metal, degassed by three freeze−pump−thaw cycles), and stoppered with a septum. The flask was removed from the glovebox and submerged in a 60 °C oil bath for 1.5 h. Solvent was then evaporated, and the mixture was chromatographed on neutral silica (4:1 hexanes−ether) to give 129 mg of product (68% yield). Fractions containing the desired complex should be evaporated as quickly as possible to minimize decomposition.

^1H NMR (499.462 MHz, C_6D_6): δ (ppm) 19.06 (dt, Ru=C*H*Et, J_{HH} = 4.2 Hz, J_{HP} = 1.2 Hz, 1H), 6.91, 6.79 (s, aryl *H*, 1H, 1H), 3.24 (m, NCH_2CH_2N, 4H), 2.79, 2.55, 2.17, 2.13 (s, mesityl CH_3, 6H, 6H, 3H, 3H), 2.35−2.44 (br, PCy_3, 3H), 2.00 (br, $RuCHCH_2CH_3$, 2H), 1.5−1.8 (br, PCy_3, 15H), 1.12−1.28 (br, PCy_3, 15H), 1.07 (t, $RuCHCH_2CH_3$, 3H). HRMS−FAB: calcd, 765.3611 $[M - Cl]^+$; found, 765.3612 $[M - Cl]^+$.

Synthesis of $RuCl_2(PCy_3)$(SIMes)CHHex. $RuCl_2(PCy_3)_2$CHHex (66 mg, 0.0794 mmol) and SIMes·$CHCl_3$ (79 mg, 0.186 mmol, 2.3 equiv) were combined in a dry round-bottom flask in a glovebox, covered with 1 mL of toluene (distilled from sodium metal, degassed by three freeze−pump−thaw cycles), and stoppered with a septum. The flask was removed from the glovebox and submerged in a 60 °C oil bath for 1.5 h. Solvent was then evaporated, and the mixture was chromatographed on neutral silica (4:1 hexanes−ether) to give 39 mg (57% yield). Fractions containing the desired complex should be evaporated as quickly as possible to minimize decomposition.

^1H NMR (499.462 MHz, C_6D_6): δ (ppm) 19.08 (dt, Ru=C*H*Hex, J_{HH} = 4.5 Hz, J_{HP} = 1.3 Hz, 1H), 6.91, 6.79 (s, aryl *H*, 1H, 1H), 3.30 (m, NCH_2CH_2N, 4H), 2.79, 2.56, 1.91 (s, mesityl CH_3, 6H, 6H, 6H), 2.32−2.2.52 (br, PCy_3, 3H), 2.00 (br, $RuCHCH_2Pen$, 2H), 1.4−1.7 (br, PCy_3 and CH_2, 19H), 1.0−1.4 (br, PCy_3 and CH_2, 19H), 0.95 (t, $RuCHCH_2CH_3$, 3H). HRMS-FAB: calcd, 821.4237 $[M - Cl]^+$, found, 821.4291 $[M - Cl]^+$.

(19) Scholl, M.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953−956.

Synthesis of $RuCl_2(3BP)_2(SIMes)CHMe$. The complex $RuCl_2(PCy_3)(SIMes)CHMe$ (110 mg, 0.140 mmol) was placed in a vial with 0.5 mL of 3-bromopyridine (excess) and the mixture stirred in air for 5 min. ACS pentane was carefully layered over the solution, and the vial was then capped and cooled in a freezer overnight. The supernatant was decanted, and the red solid was washed with four 1 mL portions of ACS pentane and dried under high vacuum at room temperature overnight to give 108 mg of product (93% yield).

^{1}H NMR (299.631 MHz, $CDCl_3$): δ (ppm) 19.07 (q, Ru=C*H*, J_{HH} = 6 Hz, 1H), 7.75 (br, 4H), 7.11 (br, 4H), 7.01 (s, 2H), 6.95 (s, 2H), 4.08 (m, 4H), 2.59 (s, 6H), 2.38 (s, 6H), 2.33 (s, 6H), 1.82 (d, J_{HH} = 6 Hz, 3H). ^{13}C NMR (75.357 MHz, $CDCl_3$): δ (ppm) 281.16, 218.93, 151.24, 148.30, 139.11, 138.54, 137.93, 134.87, 129.23, 129.14, 124.42, 120.32, 51.13, 50.82, 46.84, 20.99, 19.75, 18.43. Anal. Calcd: C, 48.19; H, 4.66; N, 6.81, Found: C, 47.41; H, 4.43; N, 6.93.

Attempted Synthesis of $RuCl_2(PCy_3)(SIMes)CHEt$ from $RuCl_2(PCy_3)(SIMes)CHPh$. $RuCl_2(PCy_3)(SIMes)CHPh$ (50 mg), C_6D_6 (0.6 mL), and *trans*-3-hexene (0.1 mL) were combined in an NMR tube in the glovebox. The sample was warmed to 45 °C in the NMR probe, and spectra were collected at intervals. Integration of the carbene protons was used to calculate the relative amounts of the complexes in solution.

ADMET of 1,9-Decadiene. 1,9-Decadiene (1.0 g, 7.2 mmol) was placed in a 50 mL round-bottom flask with a stirbar, and 0.1 mol % of catalyst was added. A vacuum adapter was fitted to the flask, and the flask was then removed from the box and attached to a vacuum line. The pressure was gradually stepped down while the mixture was heated with a 70 °C oil bath. Ethylene generation and viscosity buildup were apparent within minutes to 1 h, depending on the catalyst used. After 4 days the polymerization was treated with trace amounts of EVE and BHT in 5−10 mL of toluene with heating until the polymer completely dissolved. Yields after precipitation into room-temperature methanol were typically 90%.

^{1}H NMR (299.631 MHz, $CDCl_3$): δ (ppm) 1.32 (br, 8H), 1.98 (br, 4H), 5.38 (br, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 130.31 (trans), 129.85 (cis), 32.61, 29.76, 29.65, 29.19, 29.09, 29.05.

ROMP of Cyclooctene. Cyclooctene (550 mg) was placed in a vial with a magnetic stirbar. A trace of BHT was added, 2−2.3 mg of ruthenium carbene complex (2000:1 cyclooctene−catalyst) was added as a solution in a minimal amount of dichloromethane, and the solution was stirred. The onset of polymerization was witnessed by a rapid increase in viscosity and generation of heat. The polymer rapidly solidified. The vial was then capped and allowed to stand at room temperature overnight. The vial was then broken to remove the solid polymer, which was cut up with scissors and dried under high vacuum overnight at room temperature. Yields were quantitative and NMR spectra identical with that of polyoctenamer produced by ADMET.

Thermolytic Decomposition. A 0.023 M solution of the carbene complex with a drop of pentafluorobenzene (internal standard) was prepared in C_6D_6 in the glovebox and the cap wrapped well with Teflon tape. The solution was then heated to 55 °C in the NMR probe, and spectra were acquired at specific intervals. The integral of the carbene proton was compared to the integral of pentafluorobenzene or protio solvent to obtain the rate of disappearance of the carbene.

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Supporting Information Available: Figures and tables giving NMR spectra and X-ray crystallographic data for the complexes in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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