Synthesis of Polymerizable Carbene and Alkenyl Ruthenium Complexes and of a Ruthenium Containing Copolymer

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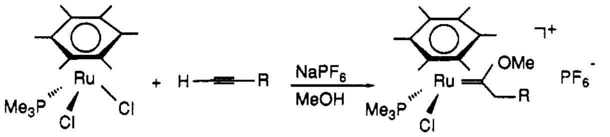
Summary: The complex $RuCl_2(PMe_3)(C_6Me_6)$ *(**1**) reacts with homopropargylic alcohol derivatives* $HC{\equiv}CCH_2CH_2OY$ *(**2a–d**)* ($Y = COC(Me){=}CH_2$, $COCH{=}CH_2$, $CH_2C(Me){=}CH_2$, $CO(CH_2)_8CH{=}CH_2$) *and* $NaPF_6$ *in methanol to give a variety of cationic ruthenium carbene complexes containing a polymerizable chain end* $[Ru\{{=}C(OMe)(CH_2)_3OY\}Cl(PMe_3)(C_6Me_6)]^+PF_6^-$ *(**5a–d**). These salts are easily deprotonated by tBuOK to produce the corresponding neutral ruthenium alkenyl monomers* $Ru\{C(OMe){=}CHCH_2CH_2OY\}Cl(PMe_3)(C_6Me_6)$ *(**6a,b**). Radical copolymerization of methyl methacrylate with the monomer* $HC{\equiv}CCH_2CH_2OCOC(Me){=}CH_2$ *(**2a**) or the monomer* $Ru\{C(OMe){=}CHCH_2CH_2OCOC(Me){=}CH_2\}Cl(PMe_3)(C_6Me_6)$ *(**6a**) leads to the formation of free alkyne containing copolymer 4 or of a ruthenium containing polymer 7.*

Introduction

Transition metal containing polymers are currently receiving considerable attention due to their numerous properties.[1] They display a variety of useful applications as catalysts,[2] precursors to ceramics[3] and conductors,[4] liquid crystal materials,[5] or solutions of small metal particles.[6] These applications motivate the search for general methods to *build* specific polymers. Metal containing polymers are usually obtained via chemical modification of functionalized preformed polymers by organometallic complexes. However, this technique has some limitations. For example the reaction between organic polymers and organometallic complexes is rarely complete and some remaining free functional groups of preformed polymers can significantly affect properties of metal containing polymers. Another limitation is the difficulty of controlling the concentration and the distribution of metal fragments on polymers.[7] Copolymerization of organometallic monomers with organic compounds is another way to produce metal containing polymers. This strategy has some key advantages such as the ability to control the concentration and the distribution at the microstructural level in metal fragments or to modify the nature of the organic monomer, providing hydrophobic, hydrophilic, or polar properties to the polymer matrix. We have investigated such an approach to produce ruthenium containing polymers. We report here the synthesis and the characterization of new ruthenium carbene complexes containing a polymerizable moiety, alkenylruthenium monomers, and a novel ruthenium–alkenyl group containing methyl methacrylate copolymer.

Results and Discussion

A possible method to insert a ruthenium(II) complex into a polymer is to react $RuCl_2(L)(arene)$ derivative 1 with a polymer containing terminal alkyne side chains, under conditions similar to those allowing the carbene formation reaction already performed with molecular alkynes (eq 1),[8] and then to deprotonate the carbene moieties in order to produce a neutral compound.



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However, these types of organic polymers containing free $C{\equiv}CH$ groups are scarce. Some of them have already been obtained by esterification of a polycarboxylic acid with homopropargylic alcohol derivatives,[9] but the reaction could not be completed, as free acid groups were found in the resulting polymers. We have thus considered the possibility of producing copolymers of type 4.

The new copolymer 4 was prepared by AIBN initiated radical copolymerization of homopropargylic alcohol methacrylate (**2a**) and 6 equiv of methyl methacrylate (**3**) in THF (eq 2). Derivative **2a** was obtained by transes-

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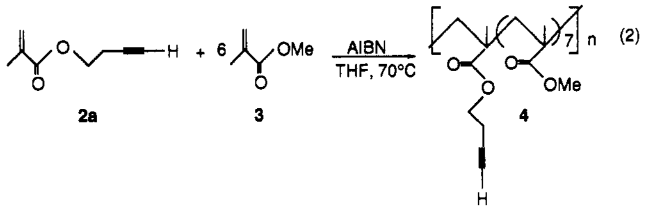


terification of 2-hexenyl methacrylate resulting from the ruthenium catalyzed addition of methacrylic acid to hexyne.[10] The ratio of monomers **3**/**2a** = 7 was established by ^{1}H NMR spectroscopy on the basis of relative intensities of the OCH_3 (δ = 3.5 ppm)/OCH_2 (δ = 4.0 ppm) group signals and was found to be consistent with elemental analysis. However the ^{1}H NMR spectra did not give any information about the spatial distribution of the two monomers in **4**.

Reaction of copolymer **4** with ruthenium complex **1** in methanol and in the presence of $NaPF_6$ did not allow access to the expected cationic ruthenium carbene complex containing polymer, via activation of the C≡CH group by the $[RuCl(L)(arene)]^+$ moiety, similarly to reaction 1. This failure led us to study a second strategy based on polymerization of ruthenium containing monomers.

The homopropargylic alcohol derivatives **2a–d**, containing methyl methacrylate, acrylate, and vinyl polymerizable groups with short or long chains, have been chosen with the aim of using different polymerization methods. They were allowed to react in methanol with complex **1** and $NaPF_6$ under conditions adapted from reaction 1.[8]

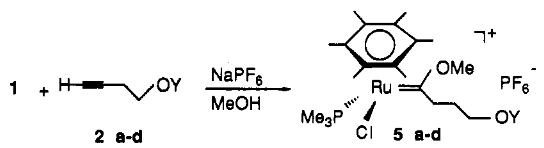
New cationic, functional carbene–ruthenium complexes **5a** (63%), **5b** (82%), **5c** (55%), and **5d** (30%) were obtained (Scheme 1). The $^{13}C\{^1H\}$ NMR spectra of complex **5a** showed a low field doublet resonance for the Ru=C carbon nucleus coupled with the PMe_3 phosphorus nucleus [**5a**: δ = 327.7 ppm; $^2J_{PC}$ = 20.7 Hz] which is consistent with that of the $Ru{=}(C(OMe)CH_2Ph)Cl(PMe_3)(C_6Me_6)^+PF_6^-$ complex already described.[11] The α-methylene protons Ru=C—*CH*$_2$ are magnetically nonequivalent since the ruthenium moiety is chiral.

The cationic carbene complexes **5a** and **5b** were easily deprotonated by treatment with 1 equivalent of potassium *tert*-butoxide in THF at 0 °C (Scheme 2) to give the orange neutral functional alkenyl–ruthenium monomers **6a** (63%) and **6b** (50%). Their ^{1}H NMR spectra indicate the presence of only one isomer.

Copolymerization of monomer **6a** was attempted with 6 equiv of methyl methacrylate (**3**) in THF in the presence of AIBN at 70 °C (Scheme 3). The novel ruthenium complex linked to a polymer by an alkenyl chain **7** was isolated in 50% yield as an orange powder.

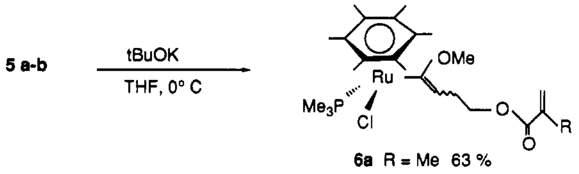
The ^{1}H NMR spectrum of **7** indicates the presence of the $(C_6Me_6)(Me_3P)Ru—C(OMe){=}CH$–unit. It allows the determination of the monomer ratio **3**/**6a** = 6 on the basis of relative intensities of the OMe groups of methyl methacrylate and of the Ru—C(OMe) group. This ratio is also consistent with elemental analysis. The number average molar mass M_n has been measured by osmometry in methylene chloride M_n: 60 000 g/mol. The number average degree of polymerization was 52 (molar mass of repeat unit: 1144 g/mol). No signal was detected by GPC measurements for molecular weight determination. The peak for the poly(methyl methacrylate) polymer was absent; this means that the polymer **7** was a real copolymer and not a mixture of two homopolymers obtained by independent polymerization of the two monomers.

Scheme 1



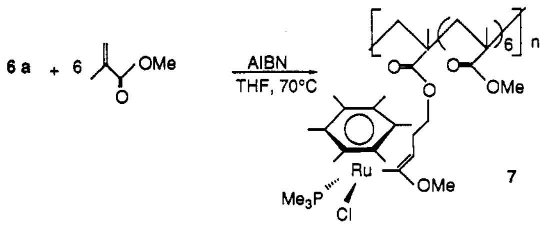
5 a	Y: $COC(Me){=}CH_2$	83%
b	Y: $COCH{=}CH_2$	82%
c	Y: $CH_2C(Me){=}CH_2$	55%
d	Y: $CO(CH_2)_8CH{=}CH_2$	30%

Scheme 2



6a R = Me 63 %
6b R = H 50 %

Scheme 3



Conclusion

Our results show that molecules containing at one end a polymerizable group and a terminal alkyne group at the other end can be used to produce ruthenium containing organometallic monomers. Polymerization of a ruthenium complex monomer seems to be the best way to obtain a ruthenium containing polymer. A novel polymer with ruthenium–alkenyl fragments linked to a poly(methyl methacrylate) has been obtained and characterized. The easy synthesis of ruthenium monomers in two steps from homopropargylic derivatives and $RuCl_2(PR_3)(arene)$ complexes represents an attractive way to produce several monomers. It opens the route to a variety of ruthenium containing polymers by changing the nature of the polymerizable group of organometallic monomers and organic monomers. A ruthenium containing polymer offers potential as a catalyst or as a precursor of solid solutions of small ruthenium particles diluted in a polymer matrix.

Experimental Section

General Data. Solvents were dried by standard methods, and all reactions involving ruthenium complexes were conducted under nitrogen by standard Schlenck techniques. Elemental analyses were performed by the CNRS analysis laboratory, Villeurbanne, France. NMR spectra were recorded on a Bruker AMWB 300 operating at 300.134 MHz for ^{1}H, 75.469 MHz for ^{13}C, and 121.496 MHz for ^{31}P nuclei; ^{31}P chemical shifts are relative to external H_3PO_4 (85%). Mass spectra were obtained on an

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AutoSpecEQ spectrometer (FAB positive mode). Glycerol was used as the matrix for the FAB spectra. The copolymers were characterized by size exclusion chromatography (SEC) and osmometry. SEC measurements were carried out on a Waters GPC system, equipped with a differential refractometer (Waters 401) as detector. They were run in CH_2Cl_2, at a flow rate of 1 mL/min. The molecular weights were evaluated, using polystyrene standards. The osmometer used was a 503 high speed membrane osmometer (Hewlett-Packard). The osmotic pressure was measured at 37 °C in toluene. $RuCl_2(PR_3)$(arene) complexes were prepared by previously described procedures.[12]

Synthesis of Cationic Complexes 5. General Procedure. An equimolar mixture of 1 and $NaPF_6$ was added to a large excess of 2 in methanol. After stirring at room temperature for 17 h the solvent was removed in vacuo. The crude product was washed twice with diethyl ether (2 × 10 mL) and dissolved in methylene dichloride (40 mL). After filtration on a glass frit a large volume of diethyl ether (100 mL) was carefully added in order to obtain a biphasic system. Upon standing for 24 h a brown oil was decanted, washed twice by diethyl ether (2 × 10 mL), and dried in vacuo to give a powder.

[Ru{=C(OMe)(CH$_2$)$_3$OCOC(Me)=CH$_2$}Cl(PMe$_3$)(C$_6$Me$_6$)]$^+$PF$_6$$^-$ (5a). **5a** was obtained from 2 g (4.9 mmol) of complex **1**, 0.82 g (4.9 mmol) of $NaPF_6$, and 1.34 g (9.7 mmol) of **2a** in 80 mL of methanol, as a yellow powder in 83% yield (2.8 g). IR (cm^{-1}, KBr): 1715 (s, ν_{COO}), 1632 (m, $\nu_{C=C}$), 840 (s, ν_{P-F}). ^1H NMR (300.134 MHz, CD_2Cl_2, 297 K), δ (ppm): 6.08 (m, 1 H, =CH_2), 5.58 (m, 1 H, =CH_2), 4.53 (s, 3 H, OMe), 4.14 (t, 2 H, CH_2O, $^3J_{HH}$ = 6 Hz), 3.52 (t, 2 H, =C(OMe)CH_2, $^3J_{HH}$ = 8 Hz), 2.08 (s, 18 H, C_6Me_6), 1.86 (s, 3 H, CH_3), 1.70 (m, 2 H, CH_2), 1.37 (d, 9 H, PMe_3, $^2J_{PH}$ = 10 Hz). $^{31}P\{^1H\}$ NMR (121.496 MHz, CD_2Cl_2, 297 K), δ (ppm): 9.02 (s, PMe_3), −143.9 (sept, PF_6, $^1J_{PF}$ = 6 Hz). $^{13}C\{^1H\}$ NMR (75.469 MHz, CD_2Cl_2, 297 K), δ (ppm): 327.72 (d, Ru=C, $^2J_{PC}$ = 20.7 Hz), 167.44 (s, C=O), 136.65 (s, *C*=CH_2), 126.06 (s, C=*C*H_2), 107.76 (s, *C*$_6$Me$_6$), 66.57 (s, OCH_3), 63.6 (s, OCH_2), 49.25 (s, =C—*C*H_2), 23.56 (s, –CH_2–), 18.53 (s, CH_3), 16.62 (s, C$_6$*Me*$_6$), 16.02 (d, PMe_3, $^1J_{PC}$ = 35 Hz).

[Ru{=C(OMe)(CH$_2$)$_3$OCO(CH$_b$=CH$_a$H$_c$)}Cl(PMe$_3$)(C$_6$Me$_6$)]$^+$PF$_6$– (5b). **5b** was obtained from 2.48 g (6 mmol) of complex **1**, 1.02 g (6 mmol) of $NaPF_6$, and 1.51 g (12.1 mmol) of **2b** in 80 mL of methanol, as a yellow powder in 82% yield (3.33 g). Anal. Calcd for $C_{23}H_{39}RuClP_2F_6O_3$: C, 40.86; H, 5.81; Cl, 5.24. Found: C, 40.85; H, 5.78; Cl, 6.42. IR (cm^{-1}, KBr): 1719 (s, ν_{COO}), 1636, 1618 (m, $\nu_{C=C}$), 841 (s, ν_{P-F}). ^1H NMR (300.134 MHz, CD_2Cl_2, 297 K), δ (ppm): 6.39 (dd, 1 H, H_a, $^3J_{H_aH_b}$ = 15 Hz, $^2J_{H_aH_c}$ = 2 Hz), 6.10 (m, 1 H, H_b, $^3J_{H_aH_b}$ = 15 Hz, $^3J_{H_cH_b}$ = 10 Hz), 5.84 (dd, 1 H, H_c, $^3J_{H_cH_b}$ = 10 Hz, $^2J_{H_aH_c}$ = 2 Hz), 4.53 (s, 3 H, OMe), 4.18 (m, 2 H, CH_2O), 3.55 (t, 2 H, =C(OMe)CH_2, $^3J_{HH}$ = 7 Hz), 2.08 (s, 18 H, C_6Me_6), 1.85–1.50 (m, 2 H, CH_2), 1.35 (d, 9 H, PMe_3, $^2J_{PH}$ = 10 Hz). $^{31}P\{^1H\}$ NMR (121.496 MHz, CD_2Cl_2, 297 K), δ (ppm): 9.18 (s, PMe_3), −143.9 (sept, PF_6, $^1J_{PF}$ = 6 Hz). $^{13}C\{^1H\}$ NMR (75.469 MHz, $CDCl_3$, 297 K), δ (ppm): 326.98 (d, Ru=C, $^2J_{PC}$ = 20.4 Hz), 166.08 (s, C=O), 131.32 (s, CH=*C*H_2), 128.19 (s, *C*H=CH_2), 107.28 (d, *C*$_6$Me$_6$, $^2J_{CP}$ = 1.6 Hz), 66.55 (s, OCH_3), 63.22 (s, OCH_2), 48.68 (s, =C—*C*H_2), 23.07 (s, –CH_2–), 16.14 (s, C$_6$*Me*$_6$), 15.75 (d, PMe_3, $^1J_{PC}$ = 34.81 Hz).

[Ru{=C(OMe)(CH$_2$)$_3$OCH$_2$C(Me)=CH$_2$}Cl(PMe$_3$)(C$_6$Me$_6$)]$^+$PF$_6$– (5c). **5c** was obtained from 1 g (2.4 mmol) of complex **1**, 0.405 g (2.4 mmol) of $NaPF_6$, and 0.6 g (4.8 mmol) of **2c** in 25 mL of methanol as an orange sticky solid in 55% yield (0.9 g). Anal. Calcd for $C_{24}H_{43}RuClP_2F_6O_2$: C, 42.64; H, 6.41; Cl, 5.24. Found: C, 42.56; H, 6.43; Cl, 5.08. IR (cm^{-1}, KBr): 1665 (m, $\nu_{C=C}$), 841 (s, ν_{P-F}). ^1H NMR (300.134 MHz, CD_2Cl_2, 297 K) δ (ppm): 4.89 (m, 1 H, =CH_2), 4.85 (m, 1 H, =CH_2), 4.53 (s, 3 H, OMe), 3.84 (s, 2 H, OCH_2—C=), 3.52 (m, 2 H, =C(OMe)CH_2), 3.42 (t, 2 H, CH_2O, $^3J_{HH}$ = 6 Hz), 2.08 (s, 18 H, C_6Me_6), 1.85–1.48 (m, 2 H, CH_2), 1.68 (s, 3 H, CH_3), 1.35 (d, 9 H, PMe_3, $^2J_{PH}$ = 10 Hz). $^{31}P\{^1H\}$ NMR (121.496 MHz, CD_2Cl_2, 297 K), δ (ppm): 9.44 (s, PMe_3), −143.9 (sept, PF_6, $^1J_{PF}$ = 6 Hz).

[Ru{=C(OMe)(CH$_2$)$_3$OCO(CH$_2$)$_8$(CH=CH$_2$)}Cl(PMe$_3$)(C$_6$Me$_6$)]$^+$PF$_6$– (5d). **5d** was obtained from 1 g (2.4 mmol) of complex **1**, 0.405 g (2.4 mmol) of $NaPF_6$, and 0.95 g (3.8 mmol) of **2d** in 30 mL of methanol as an orange oil in 30% yield (0.583 g). This oily product tenaciously retains fractional amounts of solvent. IR (cm^{-1}, KBr): 1729 (s, ν_{COO}), 1637 (m, $\nu_{C=C}$), 841 (s, ν_{P-F}). ^1H NMR (300.134 MHz, CD_2Cl_2, 297 K), δ (ppm): 5.80, 5.40, and 4.90 (m, 3 H, *H*C=C*H*$_2$), 4.52 (s, 3 H, OMe), 4.07 (m, 2 H, CH_2O), 3.45 (m, 2 H, =C(OMe)CH_2), 2.28 (t, 2 H, $COCH_2$, $^3J_{HH}$ = 8 Hz), 2.07 (s, 18 H, C_6Me_6), 1.98–1.26 (m, $(CH_2)_n$), 1.37 (d, 9 H, PMe_3, $^2J_{HP}$ = 10 Hz). $^{31}P\{^1H\}$ NMR (121.496 MHz, CD_2Cl_2, 297 K), δ (ppm): 9.15 (s, PMe_3), −143.9 (sept, PF_6, $^1J_{PF}$ = 6 Hz).

Synthesis of Monomers 6. General Procedure. To a solution of 4 mmol of complex **5a,b** in 80 mL of THF at −80 °C was added 4 mmol of tBuOK. The mixture was stirred at 0 °C for 4 h and filtered on an alumina column with THF as eluent. Solvent was removed in vacuo and the orange crude product was washed with a small volume of diethyl ether to give a yellow powder.

Ru{C(OMe)=CH(CH$_2$)$_2$OCOC(Me)=CH$_2$}Cl(PMe$_3$)(C$_6$Me$_6$) (6a). **6a** was obtained from 2.8 g (4 mmol) of complex **5a** and 0.46 g (4 mmol) of tBuOK in 63% yield (1.36 g). Anal. Calcd for $C_{24}H_{40}RuClPO_3$: C, 52.98; H, 7.41; P, 5.69; Cl, 6.52. Found: C, 52.87; H, 7.05; P, 5.41; Cl, 7.26. IR (cm^{-1}, KBr): 1708 (s, ν_{COO}), 1635 (m, $\nu_{C=C}$), 1575 (m, $\nu_{Ru-C=C}$). ^1H NMR (300.134 MHz, CD_2Cl_2, 297 K), δ (ppm): 6.02 (m, 1 H, C=CH_2), 5.47 (m, 1 H, C=CH_2), 4.80 (m, 1 H, CH=), 3.95 (m, 2 H, CH_2O), 3.35 (s, 3 H, OMe), 2.60 and 2.25 (m, 2 H, CH_2), 1.92 (s, 18 H, C_6Me_6), 1.89 (s, 3 H, CH_3), 1.26 (d, 9 H, PMe_3, $^2J_{HP}$ = 10 Hz). $^{31}P\{^1H\}$ NMR (121.496 MHz, CD_2Cl_2, 297 K), δ (ppm): 7.40 (s, PMe_3). $^{13}C\{^1H\}$ NMR (75.469 MHz, CD_2Cl_2, 297 K), δ (ppm): 186.94 (d, Ru—C=, $^2J_{PC}$ = 24 Hz), 167.96 (s, C=O), 137.72 (s, *C*=CH_2), 124.402 (s, C=*C*H_2), 98.04 (d, CH=, $^3J_{PC}$ = 1.8 Hz), 97.98 (d, *C*$_6$Me$_6$, $^2J_{CP}$ = 3.4 Hz), 68.85 (s, OCH_2), 55.70 (s, OCH_3), 30.00 (s, CH_2), 18.66 (s, CH_3), 16.07 (d, PMe_3, $^1J_{PC}$ = 32 Hz), 16.04 (s, C$_6$*Me*$_6$).

Ru{C(OMe)=CH(CH$_2$)$_2$OCOCH=CH$_2$}Cl(PMe$_3$)(C$_6$Me$_6$) (6b). **6b** was obtained from 3.33 g (4.9 mmol) of complex **5b** and 0.8 g (4.9 mmol) of tBuOK in 50% yield (1.29 g). IR (cm^{-1}, KBr): 1724 (s, ν_{COO}), 1637, 1620 (m, $\nu_{C=C}$), 1575 (m, $\nu_{Ru-C=C}$). ^1H NMR (300.134 MHz, CD_2Cl_2, 297 K), δ (ppm): 6.40 (m, 1 H, CH=C*H*$_2$), 6.10 (m, 1 H, C*H*=CH_2), 5.22 (m, 1 H, CH=C*H*$_2$), 5.05 (m, 1 H, =CH), 3.27 (s, 3 H, OMe), 4.60 (m, 2 H, CH_2O), 3.15 and 2.70 (m, 2 H, CH_2), 1.69 (s, 18 H, C_6Me_6), 1.35 (d, 9 H, PMe_3, $^2J_{PH}$ = 10 Hz). $^{31}P\{^1H\}$ NMR (121.496 MHz, CD_2Cl_2, 297 K), δ (ppm): 7.24 (s, PMe_3). $^{13}C\{^1H\}$ NMR (75.469 MHz, CD_2Cl_2, 297 K), δ (ppm): 187.09 (d, Ru—C=, $^2J_{PC}$ = 24 Hz), 166.78 (s, C=O), 129.74 (s, *C*H=CH_2), 129.72 (s, CH=*C*H_2), 97.98 (d, *C*$_6$Me$_6$, $^2J_{CP}$ = 3.0 Hz), 97.81 (d, CH=, $^3J_{PC}$ = 1.7 Hz), 68.6 (s, OCH_2), 55.75 (s, OCH_3), 30.02 (s, CH_2), 16.04 (d, PMe_3, $^1J_{PC}$ = 32 Hz), 16.03 (s, C$_6$*Me*$_6$). HRMS (FAB$^+$): *m/z* (I) 531.2 (MH$^+$, 43%), 375.1 (RuCl(PMe$_3$)(C$_6$Me$_6$)$^+$, 61%), 339.1 (RuCl(PMe$_3$)(C$_6$Me$_6$)$^+$ − HCl, 100%). For the ruthenium atom and other elements the observed isotopic amount corresponds to that calculated.

Synthesis of Polymers 4 and 7. Copolymer 4. A 0.54-g (4-mmol) amount of **2a**, 2.31 g (24 mmol) of methyl methacrylate, and 44 mg (0.03 mmol) of AIBN in 34 mL of THF were heated under nitrogen at 70 °C for 20 h. The polymer was isolated as a white powder by pouring the solution into 20 mL of cold methanol and then filtering the precipitate. The polymer was dried in vacuo for 12 h (1.3 g, yield 46%). Anal. Calcd for $C_{43}H_{66}O_{16}$: C, 61.56; H, 7.93. Found: C, 61.69; H, 8.11. IR (cm^{-1}, KBr): 1730 (s, ν_{COO}), 3290 (m, $\nu_{\equiv CH}$). ^1H NMR (300.134 MHz, CD_2Cl_2, 297 K), δ (ppm): 4.00 (broad s, 2 H, CH_2O), 3.54 (broad s, 21 H, OMe), 2.51 (broad s, 2 H, $CH_2C{\equiv}C$), 2.15 and 2.12 (broad s, 1 H, $HC{\equiv}C$), 1.84 and 1.77 (broad s, 16 H, CH_2), 0.95 and 0.78 (broad s, 24 H, CH_3). $^{13}C\{^1H\}$ NMR (75.469 MHz, CD_2Cl_2, 297 K), δ (ppm): 178.44, 178.17, 177.66, and 177.30 (s, CO), 80.74 (s, *C*≡CH), 70.61 and 70.47 (s, C≡*C*H), 63.14 (s, CH_2O), 54.80 (broad s, *C*H$_2$—C≡C), 45.23 and 44.88 (s, C), 19.22, 18.99, 18.90, and 18.85 (s, CH_2), 16.79 (broad s, CH_3). M_w (SEC): 40 000 g/mol.

Ruthenium Containing Polymer 7. A 0.533-g (0.98-mmol) amount of **6a**, 0.58 g (6 mmol) of methyl methacrylate, and 11.3

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[12] (a) Zelonga, R. A.; Baird, M. C. *Can. J. Chem.* **1972**, *50*, 3063. (b) Bennett, M. A.; Smith, K. A. *J. Chem. Soc., Dalton Trans.* **1974**, 233.

mg (0.07 mmol) of AIBN in 9 mL of THF were heated under nitrogen at 70 °C for 20 h. The polymer was isolated as an orange powder by pouring the solution dropwise into 100 mL of cold methanol and then filtering the precipitate. The polymer was dried in vacuo for 12 h (0.6 g, yield 66%). Anal. Calcd for $C_{54}H_{88}O_{15}RuClP$: C, 56.65; H, 7.75; Ru, 8.82. Found: C, 56.09; H, 7.65; Ru, 7.89. IR (cm^{-1}, KBr): 1732 (s, ν_{COO}). ^1H NMR (300.134 MHz, CD_2Cl_2, 297 K), δ (ppm): 4.83 (broad s, 1 H, CH=C), 3.19 (broad m, 2 H, CH_2O), 3.54 (s, 18 H, OMe), 3.39 (s, 3 H, C=C(OMe)), 2.55 and 2.20 (m, 2 H, CH_2—C=), 1.94 (s, 18 H, C_6Me_6), 1.89 and 1.77 (broad s, 14 H, CH_2), 1.26 (d, 9 H, PMe_3, $^2J_{HP} = 10$ Hz), 0.95 and 0.79 (broad s, 21 H, CH_3). $^{31}P\{^1H\}$ NMR (121.496 MHz, CD_2Cl_2, 297 K), δ (ppm): 7.49 (s, PMe_3). M_n (osmometry): 60 000 g/mol.

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