ORGANOMETALLICS
Article

Organometallics **2010,** *29,* 6675–6686 6675
DOI: 10.1021/om1006177

Homobimetallic Ruthenium−Arene Complexes Bearing Vinylidene Ligands: Synthesis, Characterization, and Catalytic Application in Olefin Metathesis

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Received June 27, 2010

Five new arylvinylidene complexes with substituents ranging from electron-donating to strongly withdrawing (*p*-OMe, *p*-Me, *p*-Cl, *p*-CF_3, and *m*-$(CF_3)_2$) were isolated in high yields by reacting [(*p*-cymene)Ru(μ-Cl)$_3$RuCl(η^2-C_2H_4)(PCy_3)] (**3**) with the corresponding phenylacetylene derivatives. The known phenylvinylidene complex [(*p*-cymene)Ru(μ-Cl)$_3$RuCl(=C=CHPh)(PCy_3)] (**5**) was also obtained from [$RuCl_2$(*p*-cymene)]$_2$, tricyclohexylphosphine, and phenylacetylene under microwave irradiation. The influence of the remote aryl substituents on structural features was investigated by IR, NMR, and XRD spectroscopies. A very good linear relationship was observed between the chemical shift of the vinylidene α-carbon atom and the Hammett σ-constants of the aryl group substituents. The catalytic activity of the six homobimetallic complexes was probed in various types of olefin metathesis reactions. Unsubstituted phenylvinylidene compound **5** served as a lead structure for these experiments. Its reaction with norbornene afforded high molecular weight polymers with a broad polydispersity index and mostly *trans* double bonds. Aluminum chloride was a suitable cocatalyst for the ring-opening metathesis polymerization of cyclooctene and led to the formation of high molecular weight polyoctenamer with a rather narrow polydispersity index ($M_w/M_n = 1.25$) and an almost equimolar proportion of *cis* and *trans* double bonds. No major changes were observed in the polymer yields and microstructures when complexes bearing donor groups on their aryl rings were employed as catalyst precursors. On the other hand, compounds bearing strongly electron-withdrawing substituents were significantly less active. Model vinylidene compound **5** and its ruthenium−ethylene parent (**3**) both required the addition of phenylacetylene to achieve the ring-closing metathesis of diethyl 2,2-diallylmalonate. Thus, the role of this terminal alkyne cocatalyst goes beyond the facile replacement of the η^2-alkene ligand with a vinylidene fragment.

Introduction

Thanks to the development of the well-defined ruthenium−benzylidene catalyst [$RuCl_2$(=CHPh)(PCy_3)$_2$] (PCy_3 is tricyclohexylphosphine) initiated by Grubbs in the late 1990s,[1] olefin metathesis has become a key methodology in organic synthesis and in polymer chemistry.[2] Countless subsequent studies have been aimed at improving the catalytic efficiency of this archetypal compound. The most significant advances were achieved by replacing one of its phosphine ligands with an N-heterocyclic carbene (NHC), and tireless research efforts from several groups have led to improved second- and third-generation ruthenium−alkylidene complexes, which display extremely high catalytic activities and excellent tolerance toward polar functional groups.[3]

From a practical point of view, the introduction of an alkylidene fragment onto a group 8 transition metal usually requires the use of either cyclopropenes[4] or diazoalkanes.[5] Because these two types of reagents are rather difficult to prepare and to handle, especially on a large scale, the straightforward access to ruthenium−benzylidene complexes remains

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(1) (a) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446–452. (b) Grubbs, R. H. *Tetrahedron* **2004**, *60*, 7117–7140. (c) Grubbs, R. H. *Adv. Synth. Catal.* **2007**, *349*, 34–40.

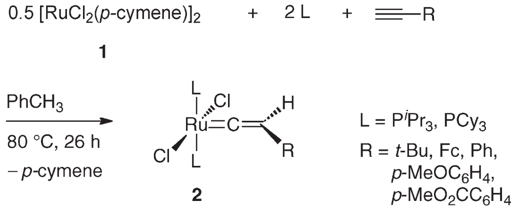
(2) For monographs, see: (a) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: San Diego, 1997. (b) *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, 2003. (c) *Green Metathesis Chemistry*; Dragutan, V.; Demonceau, A.; Dragutan, I.; Finkelshtein, E. S., Eds.; NATO Science for Peace and Security Series-A: Chemistry and Biology, Springer: Dordrecht, 2010.

(3) (a) Beligny, S.; Blechert, S. In *N-Heterocyclic Carbenes in Synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, 2006; pp 1−25. (b) Despagnet-Ayoub, E.; Ritter, T. In *N-Heterocyclic Carbenes in Transition Metal Catalysis*; Glorius, F., Ed.; Topics in Organometallic Chemistry, Vol. *21*; Springer: Berlin, 2007; pp 193−218. (c) Colacino, E.; Martinez, J.; Lamaty, F. *Coord. Chem. Rev.* **2007**, *251*, 726–764. (d) Samojłowicz, C.; Bieniek, M.; Grela, K. *Chem. Rev.* **2009**, *109*, 3708–3742. (e) Vougioukalakis, G. C.; Grubbs, R. H. *Chem. Rev.* **2010**, *110*, 1746–1787.

(4) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974–3975.

(5) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **1995**, *34*, 2039–2041.

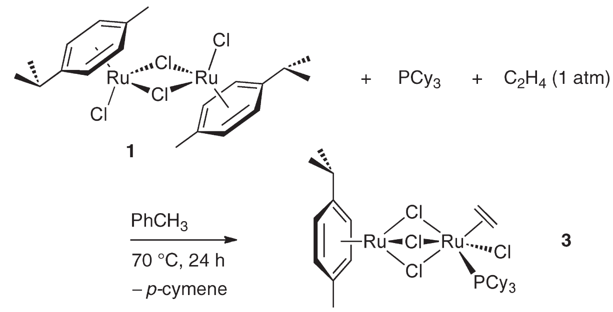
Scheme 1. Synthesis of Monometallic Ruthenium−Vinylidene Complexes



a major issue, and a great deal of attention has been paid to other catalyst precursors bearing a metal−carbon multiple bond that are more convenient to synthesize. Among them, ruthenium−vinylidene,[6−8] −allenylidene,[7−9] and −indenylidene[8,10] species have generated much interest, because they are readily obtained from commercially available alkyne derivatives using safe and efficient experimental procedures.

In particular, monometallic ruthenium−vinylidene complexes are easily isolated from the reaction of [RuCl$_2$(*p*-cymene)]$_2$ (**1**) with an excess of phosphine and terminal alkyne (Scheme 1). This simple and efficient methodology was devised by Ozawa and co-workers in 1998.[11] The Japanese team successfully applied it to prepare a range of complexes with the generic formula [RuCl$_2$(=C=CHR)L$_2$] (L = PPr$^i_3$ or PCy$_3$) (**2**), which were probed as catalysts for the ring-opening metathesis polymerization (ROMP) of norbornene derivatives and the ring-closing metathesis (RCM) of α,*ω*-dienes.[12] Subsequent reports from other groups further demonstrated the validity of this approach,[13] although the first-generation vinylidene complexes turned out to be less efficient metathesis initiators than their benzylidene counterparts. Recourse to [RuCl$_2$(=C=CHR)(PCy$_3$)(NHC)] complexes with mixed phosphine/NHC ligands helped reduce this gap. Such second-generation ruthenium−vinylidene catalysts were first reported by Louie and Grubbs in 2001[14] and further investigated by Opstal and Verpoort in 2003.[15] It should be pointed out that the catalytic activity of the nonsubstituted vinylidene complex [RuCl$_2$(=C=CH$_2$)(PCy$_3$)$_2$] in the ROMP of norbornene and cyclooctene was already evidenced by Grubbs et al. in 1996.[16] At that time, installation of the vinylidene fragment was achieved via stoichiometric metathesis between [RuCl$_2$(=CHPh)(PCy$_3$)$_2$] and 1,2-propadiene (allene).

Scheme 2. Synthesis of Homobimetallic Ruthenium−Ethylene Complex 3



In 2005, Severin and co-workers investigated the reaction of [RuCl$_2$(*p*-cymene)]$_2$ (**1**) with 1 equiv of PCy$_3$ under an ethylene atmosphere. Under these conditions, the ruthenium dimer afforded a new type of molecular scaffold (**3**), in which a RuCl(η^2-C$_2$H$_4$)(PCy$_3$) fragment was connected via three *μ*-chloro bridges to a ruthenium−(*p*-cymene) moiety (Scheme 2).[17] In view of the enhancements brought by the replacement of phosphines with NHCs in monometallic ruthenium−arene catalyst precursors for olefin metathesis[18,19] and atom transfer radical reactions,[19,20] we have adopted the same strategy to synthesize two homobimetallic complexes of type **3** bearing NHC instead of phosphine ligands, which were found suitable for promoting olefin metathesis.[21] Results from this study indicated that the ethylene ligand was highly labile and that adding a small amount of phenylacetylene to the reaction media had a beneficial influence on the metathetical activity. We attributed this catalytic enhancement to the in situ formation of a vinylidene complex.

While work was in progress in our laboratory to validate this hypothesis, Severin et al. independently reported the synthesis of two homobimetallic ruthenium−vinylidene complexes by displacing the ethylene ligand in **3** with *tert*-butylacetylene or phenylacetylene (Scheme 3).[22] Complexes **4** and **5** were fully characterized by NMR and single-crystal X-ray diffraction (XRD) analyses, but their catalytic activity was not assessed. Hence, we decided to study their behavior in various ruthenium-promoted organic transformations. We also chose to prepare additional complexes bearing electron-donating or -withdrawing substituents on the phenylvinylidene ligand and to investigate their catalytic activity. In this contribution, we disclose the synthesis and characterization of five new homobimetallic ruthenium−vinylidene complexes bearing a tricyclohexylphosphine ligand (**6**−**10**), and we probe the influence of their remote aryl substituents on structural

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(6) (a) Dragutan, V.; Dragutan, I. *Platinum Met. Rev.* **2004**, *48*, 148–153. (b) Katayama, H.; Ozawa, F. *Coord. Chem. Rev.* **2004**, *248*, 1703–1715. (c) Trost, B. M.; McClory, A. *Chem. Asian J.* **2008**, *3*, 164–194.

(7) (a) Bruneau, C.; Dixneuf, P. H. *Angew. Chem., Int. Ed.* **2006**, *45*, 2176–2203. (b) *Metal Vinylidenes and Allenylidenes in Catalysis*; Bruneau, C.; Dixneuf, P. H., Eds.; Wiley-VCH: Weinheim, 2008.

(8) Lozano-Vila, A.; Monsaert, S.; Bajek, A.; Verpoort, F. *Chem. Rev.* **2010**, *110*, 4865–4909.

(9) Dragutan, I.; Dragutan, V. *Platinum Met. Rev.* **2006**, *50*, 81–97.

(10) (a) Dragutan, V.; Dragutan, I.; Verpoort, F. *Platinum Met. Rev.* **2005**, *49*, 33–40. (b) Boeda, F.; Clavier, H.; Nolan, S. P. *Chem. Commun.* **2008**, 2726–2740.

(11) Katayama, H.; Ozawa, F. *Organometallics* **1998**, *17*, 5190–5196.

(12) (a) Katayama, H.; Ozawa, F. *Chem. Lett.* **1998**, 67–68. (b) Katayama, H.; Urushima, H.; Ozawa, F. *Chem. Lett.* **1999**, 369–370. (c) Katayama, H.; Urushima, H.; Ozawa, F. *J. Organomet. Chem.* **2000**, *606*, 16–25. (d) Katayama, H.; Yonezawa, F.; Nagao, M.; Ozawa, F. *Macromolecules* **2002**, *35*, 1133–1136.

(13) (a) del Río, I.; van Koten, G. *Tetrahedron Lett.* **1999**, *40*, 1401–1404. (b) Saoud, M.; Romerosa, A.; Peruzzini, M. *Organometallics* **2000**, *19*, 4005–4007. (c) Maya, V. G.; Contreras, A. P.; Canseco, M.-A.; Tlenkopatchev, M. A. *React. Funct. Polym.* **2001**, *49*, 145–150. (d) Contreras, A. P.; Cerda, A. M.; Tlenkopatchev, M. A. *Macromol. Chem. Phys.* **2002**, *203*, 1811–1818.

(14) Louie, J.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2001**, *40*, 247–249.

(15) Opstal, T.; Verpoort, F. *J. Mol. Catal. A: Chem.* **2003**, *200*, 49–61.

(16) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100–110.

(17) Quebatte, L.; Solari, E.; Scopelliti, R.; Severin, K. *Organometallics* **2005**, *24*, 1404–1406.

(18) (a) Delaude, L.; Demonceau, A.; Noels, A. F. *Chem. Commun.* **2001**, 986–987. (b) Delaude, L.; Szypa, M.; Demonceau, A.; Noels, A. F. *Adv. Synth. Catal.* **2002**, *344*, 749–756.

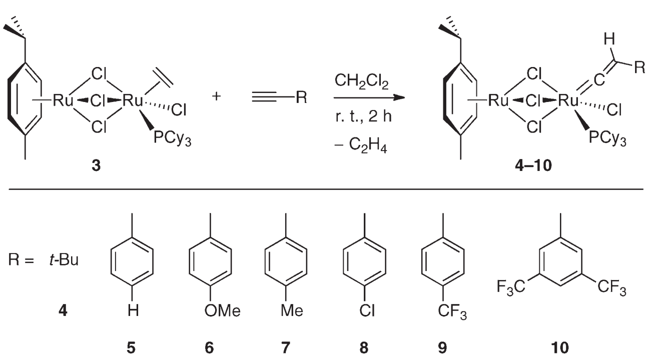
(19) Delaude, L.; Demonceau, A.; Noels, A. F. *Curr. Org. Chem.* **2006**, *10*, 203–215.

(20) (a) Delaude, L.; Delfosse, S.; Richel, A.; Demonceau, A.; Noels, A. F. *Chem. Commun.* **2003**, 1526–1527. (b) Richel, A.; Delfosse, S.; Cremasco, C.; Delaude, L.; Demonceau, A.; Noels, A. F. *Tetrahedron Lett.* **2003**, *44*, 6011–6015.

(21) Sauvage, X.; Borguet, Y.; Noels, A. F.; Delaude, L.; Demonceau, A. *Adv. Synth. Catal.* **2007**, *349*, 255–265.

(22) Solari, E.; Antonijevic, S.; Gauthier, S.; Scopelliti, R.; Severin, K. *Eur. J. Inorg. Chem.* **2007**, 367–371.

Scheme 3. Synthesis of Homobimetallic Ruthenium−Vinylidene Complexes 4−10



features determined by NMR and XRD spectroscopies. We also present the results of our investigations on the ROMP of norbornene and cyclooctene using these catalyst precursors. A few CM and RCM reactions were also carried out on model substrates to help us better evaluate the potentials of [(p-cymene)Ru(μ-Cl)$_3$RuCl(=C=CHR)(PCy$_3$)] species for olefin metathesis and to gain insight into their mode of action.

Results and Discussion

Synthesis and Characterization of Complexes 6−10. The reaction of homobimetallic ruthenium−ethylene complex **3** with a 2-fold excess of various phenylacetylene derivatives was carried out in dichloromethane at room temperature (Scheme 3). The course of the transformation was monitored by ^{31}P NMR analysis of samples spiked with CD$_2$Cl$_2$. Within 2 h, the resonance of the starting material located at 44.3 ppm vanished, while a single new line at ca. 55 ppm indicated the clean formation of the desired products. A simple workup involving solvent removal and washing of the alkyne in excess with *n*-pentane afforded new arylvinylidene complexes **6−10**, with substituents ranging from electron-donating (like the *para*-methoxy group in **6**) to strongly electron-withdrawing (such as the bis-*meta*-trifluoromethyl groups in **10**). Our procedure closely matched the one reported by Severin et al. for the preparation of compounds **4** and **5**, starting from *tert*-butylacetylene and phenylacetylene, respectively.[22] High yields (>80%) were obtained in all cases. The mechanism most likely involves the displacement of the labile ethylene ligand, followed by an alkyne-to-vinylidene tautomerization.[23] A similar reaction with a face-bridged Ru dimer was also reported by Fogg et al., who found that the addition of *tert*-butylacetylene to [(dcypb)ClRu(μ-Cl)$_3$Ru(dcypb)(N$_2$)] (dcypb is 1,4-bis(dicyclohexylphosphino)butane) afforded the vinylidene complex [(dcypb)ClRu(μ-Cl)$_3$Ru(=C=CH-*t*-Bu)(dcypb)] with evolution of dinitrogen gas.[24]

In order to streamline the preparation of homobimetallic ruthenium−vinylidene complexes, we investigated the possibility of starting directly from dimer **1** instead of intermediate **3**, bearing a sacrificial ethylene ligand. Unsubstituted phenylvinylidene derivative **5** was chosen as a representative target for these experiments. Preliminary tests were carried out by heating a mixture of [RuCl$_2$(p-cymene)]$_2$, 1 equiv of tricyclohexylphosphine, and a small excess of phenylacetylene (1.2 equiv) in dichloromethane at 40 °C under argon. After 16 h, ^{31}P NMR analysis revealed the formation of [(p-cymene)Ru(μ-Cl)$_3$RuCl(=C=CHPh)(PCy$_3$)] (**5**) together with [RuCl$_2$(p-cymene)(PCy$_3$)] in a ca. 1:3 molar ratio. Performing the synthesis in toluene at 70 °C and extending the reaction time increased the selectivity toward the desired bimetallic product, but the monometallic intermediate was still present. We reasoned that recourse to microwave irradiation would prove a more convenient way to speed up the displacement of the arene π-ligand.[25] Indeed, a rapid optimization of the microwave heating conditions allowed us to isolate complex **5** in almost quantitative yield starting from the widely available ruthenium dimer **1** (Scheme 4). Thus, heating a dichloromethane solution of the reagents for 15 min at 105 °C in a pressure vial led to the pure homobimetallic vinylidene compound in 93% yield, with no trace of monometallic [RuCl$_2$(p-cymene)(PCy$_3$)] byproduct detectable by ^{31}P NMR spectroscopy.

Scheme 4. Microwave-Assisted Synthesis of Homobimetallic Ruthenium−Vinylidene Complex 5

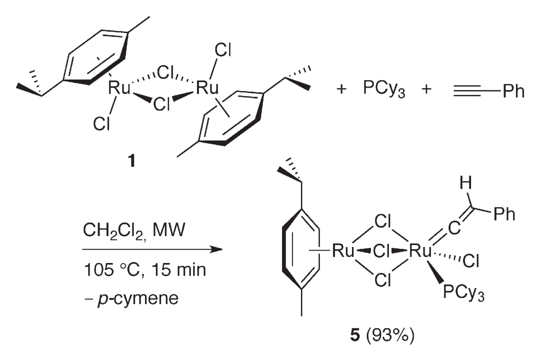


Table 1. Selected Wavenumbers (cm^{-1}), Chemical Shifts (ppm), and Coupling Constants (Hz) Recorded on IR Spectroscopy (KBr) or NMR Spectroscopy (CD$_2$Cl$_2$, 25 °C) for Complexes 5−10

complex	$\bar{\nu}$ C=C	δ H$_\beta$ (d)	$^4J_{PH}$ H$_\beta$	δ C$_\alpha$ (d)	$^2J_{PC}$ C$_\alpha$	δC$_\beta$ (s)	δ PCy$_3$ (s)
5	1621	4.87	3.2	355.0	19.4	114.2	54.2
6	1631	4.85	3.5	357.6	19.4	113.7	55.0
7	1630	4.85	3.3	356.4	19.4	114.0	55.0
8	1619	4.86	3.0	353.6	19.4	113.5	54.9
9	1600	4.91	3.3	351.2	19.4	113.6	54.9
10	1598	5.01	3.3	348.5	18.6	113.2	55.4

Complexes **5−10** were isolated as stable microcrystalline solids that could be stored in open-air vials for more than a year. They readily dissolved in dichloromethane and chloroform, but were only sparingly soluble in THF, benzene, or toluene, and quickly decomposed in acetonitrile. They were fully characterized by various analytical techniques, viz., ^{1}H, ^{13}C, and ^{31}P NMR, IR, XRD, and elemental analyses. Their most salient spectroscopic features are summarized in Table 1. In addition to strong aliphatic C−H stretching vibration bands at 2928 and 2849 cm^{-1}, a sharp absorption due to the vinylidene C=C bond stretching was visible on IR spectroscopy at wavenumbers ranging from 1598 to 1631 cm^{-1}. ^{1}H NMR analysis confirmed that the vinylidene and the arene ligands were coordinated to ruthenium in a 1:1 ratio. This stoichiometry was most easily established by comparing the integrals of the signals arising from the vinylidene proton,

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(23) Wakatsuki, Y. *J. Organomet. Chem.* **2004**, *689*, 4092–4109.

(24) Amoroso, D.; Yap, G. P. A.; Fogg, D. E. *Organometallics* **2002**, *21*, 3335–3343.

(25) (a) Borguet, Y.; Richel, A.; Delfosse, S.; Leclerc, A.; Delaude, L.; Demonceau, A. *Tetrahedron Lett.* **2007**, *48*, 6334–6338. (b) Delfosse, S.; Borguet, Y.; Delaude, L.; Demonceau, A. *Macromol. Rapid Commun.* **2007**, *28*, 492–503. (c) Nicks, F.; Libert, L.; Delaude, L.; Demonceau, A. *Aust. J. Chem.* **2009**, *62*, 227–231. (d) Albrecht, C.; Gauthier, S.; Wolf, J.; Scopelliti, R.; Severin, K. *Eur. J. Inorg. Chem.* **2009**, 1003–1010.

which resonated as a doublet at about 4.9 ppm due to its small, albeit visible ${}^4J_{PH}$ coupling with the phosphorus atom, together with the methine proton of the *p*-cymene isopropyl group that appeared as a septet at 2.95 ppm.

In ${}^{13}C\{{}^1H\}$ NMR spectroscopy, the most interesting signals were observed in the downfield region of the spectra. A noticeable feature was the highly deshielded doublet due to the Ru=*C*=C α-carbon atom located at about 350 ppm (Table 1). The fine structure of this signal was ascribed once again to the occurrence of a strong coupling with the phosphorus nucleus, in this case a ${}^2J_{PC}$ coupling through the metal center. The corresponding vinylidene C_β remote end resonated as a singlet at ca. 114 ppm. It is noteworthy that the six aromatic carbons of the η^6-arene ligand gave rise to six distinct absorptions. Further evidence for the asymmetric nature of complexes **6**−**10** came from the observation of two separate doublets for the methyl groups of the *p*-cymene isopropyl units in ${}^1H$ NMR spectroscopy, although these signals often collapsed into a pseudotriplet, due to their proximity. Last but not least, the ${}^{31}P\{{}^1H\}$ NMR spectra displayed only one sharp absorption at ca. 55 ppm (Table 1). The chemical shift of this signal remained roughly unaffected (less than 1 ppm variation) when the substituents on the vinylidene ligand were modified.

Hammett Correlation. Although the Hammett equation (eq 1) was originally formulated to quantify the effect of structure on reactivity,[26] it was also applied to correlate physical measurements, such as NMR chemical shifts (eq 2),[27] IR absorptions,[28] or redox potentials,[28,29] with the electron-donating or -withdrawing properties of substituents attached to a phenyl ring. Attempts to correlate the chemical shifts of side-chain protons with Hammett σ-constants have met with success in some instances, but in the majority of cases, the ρ values are rather small and obtaining data of sufficient precision for meaningful analyses remains difficult.[30] Correlations based on ${}^{13}C$ NMR spectroscopy usually give much better results, and the terminal carbon atom of a vinyl group attached to a *meta*- or *para*-substituted aromatic ring is particularly sensitive to substituent effects.[31]

$$\log \frac{k}{k_0} = \sigma\rho \qquad (1)$$

$$\delta - \delta_0 = \sigma\rho \qquad (2)$$

This prompted us to examine the possible correlation between the chemical shift of the Ru-bonded vinylidene carbon atom in complexes **6**−**10** (labeled C_α in Table 1) and the Hammett σ-constants for *p*-OMe, *p*-Me, *p*-Cl, *p*-CF$_3$, and *m*-(CF$_3$)$_2$ groups,[32] using unsubstituted phenylvinylidene compound **5** as a reference. Gratifyingly, a very good linear relationship between the two sets of data was observed (Figure 1). This means that the electron density at C_α is directly related to the polar and resonance effects of the aryl ring substituents. None of the other ${}^1H$, ${}^{13}C$, or ${}^{31}P$ nuclei within the $P-Ru=C_\alpha=CH_\beta-C_6H_4X$ sequence afforded a satisfactory correlation, and the IR $\bar{\nu}$ C=C wavenumber was also of no use for that matter. Yet, the fact that the electronic properties of the vinylidene carbon atom coordinated to the metal center could be fine-tuned simply by changing the substituent on a distant *meta* or *para* position was deemed a good omen for potential catalytic applications.

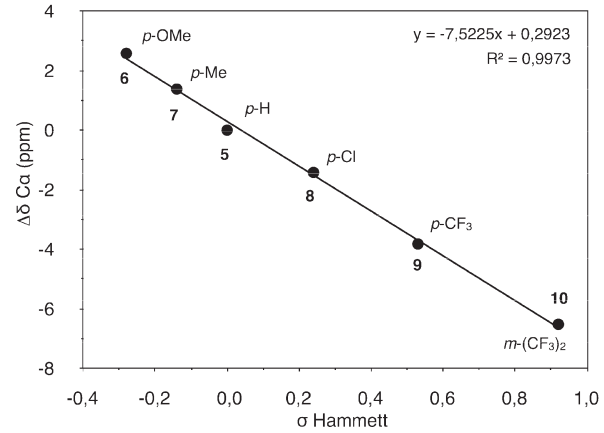

Figure 1. Plot of $\Delta\delta$ C_α vs Hammett σ-constants for complexes **5**−**10**.

Crystal Structures. The solid-state structures of homobimetallic Ru−vinylidene complexes **6**−**10** were determined by X-ray diffraction analysis (XRD). Single crystals of all five compounds were obtained by slow diffusion of cyclohexane into a dichloromethane solution. In several cases, these solvents cocrystallized with the organometallic products in variable proportions (see Supporting Information for details). Before discussing the results of this crystallographic study, it should be pointed out that compounds **6**−**10** are chiral due to the presence of two stereogenic centers located on the ruthenium atoms and that these asymmetric units are not independent, because of geometric constraints imposed by the three μ-chloro bridges. Hence, our syntheses always afforded racemic mixtures of two enantiomers. Moreover, ${}^1H$ and ${}^{13}C$ NMR analyses had shown that the products were configurationally stable in solution and that the *p*-cymene ligand did not rotate freely on the NMR time scale (vide supra). Further evidence of this asymmetry was obtained by XRD. Thus, the unit cells of complexes **7**, **8**, and **9** contained two nonequivalent molecules, which differed primarily in the relative orientation of their *p*-cymene and vinylidene ligands (Figure 2). Of course, the mirror images of these two molecules were also present. This is in sharp contrast with the crystals obtained previously for complexes **4** and **5**, which contained only molecules having the isopropyl group of their *p*-cymene ligand oriented in the same direction as the vinylidene ligand (designated as configuration **A** in Figure 2).[22] Complex **6** provided an additional example of this spatial arrangement, while the reverse situation occurred with complex **10**. Indeed, the solid-state structure of this compound revealed only the presence of molecules with a roughly antiparallel orientation between the isopropyl group of their *p*-cymene ligand and the vinylidene fragment (designated as

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(26) (a) Hammett, L. P. *J. Am. Chem. Soc.* **1937**, *59*, 96–103. (b) Jaffé, H. H. *Chem. Rev.* **1953**, *53*, 191–261.

(27) Ewing, D. F. In *Correlation Analysis in Chemistry: Recent Advances*; Chapman, N. B.; Shorter, J., Eds.; Plenum: New York, 1978; p 357.

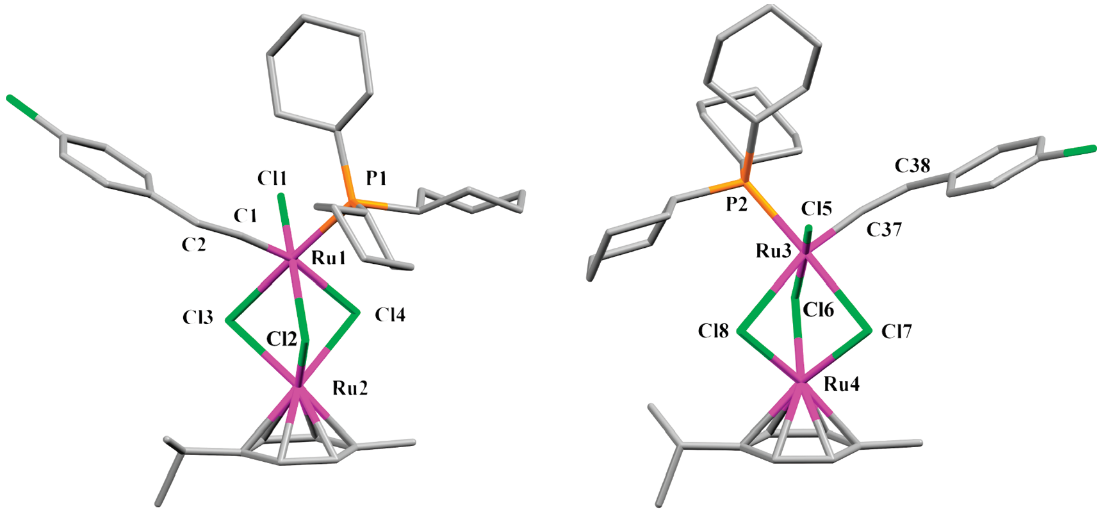
(28) Paul, F.; Ellis, B. G.; Bruce, M. I.; Toupet, L.; Roisnel, T.; Costuas, K.; Halet, J.-M.; Lapinte, C. *Organometallics* **2006**, *25*, 649–665.

(29) (a) Halbach, D. P.; Hamaker, C. G. *J. Organomet. Chem.* **2006**, *691*, 3349–3361. (b) Hamaker, C. G.; Halbach, D. P. *Polyhedron* **2009**, *28*, 2228–2232.

(30) Happer, D. A. R. *Aust. J. Chem.* **1976**, *29*, 2607–2614.

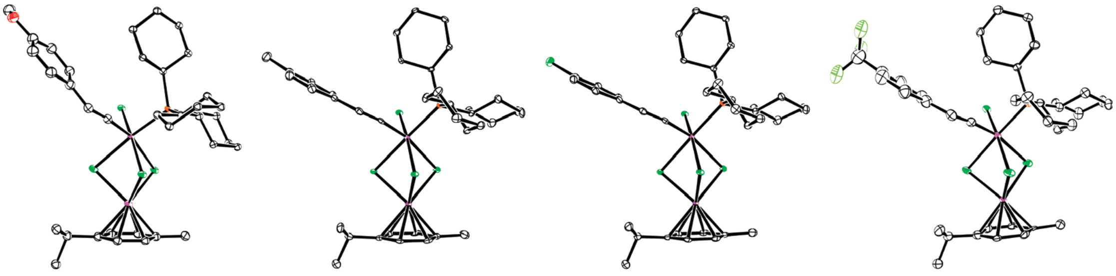
(31) See, for example: (a) Nagy, A. G. *J. Organomet. Chem.* **1985**, *291*, 335–340. (b) Aun, C. E.; Clarkson, T. J.; Happer, D. A. R. *J. Chem. Soc., Perkin Trans. 2* **1990**, 645–649. (c) Jovanović, B. Ž.; Mišić-Vuković, M.; Marinković, A. D.; Csanádi, J. *J. Mol. Struct.* **1999**, *482–483*, 371–374.

(32) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165–195.



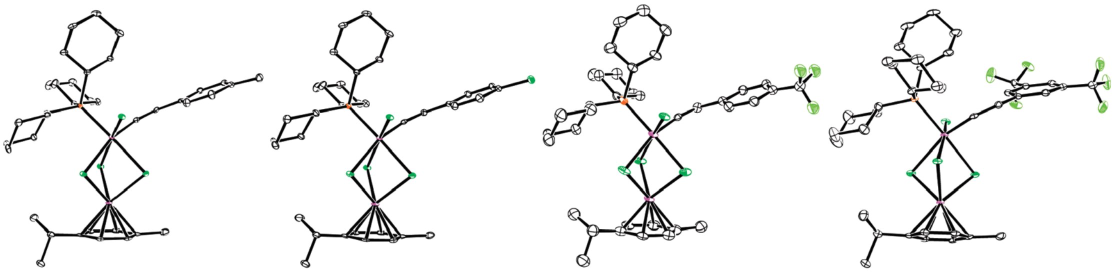
Configuration **A** Configuration **B**

Figure 2. Atom-numbering system and molecular structures of homobimetallic ruthenium–vinylidene complex **7** showing two nonequivalent configurations of the *p*-cymene ligand relative to the vinylidene fragment.



6 **7** **8** **9**

Figure 3. ORTEP diagrams of complexes **6**–**9** showing their molecular structure in configuration **A**. Thermal ellipsoids were drawn at the 50% probability level. For the sake of clarity, hydrogen atoms and the solvent molecules that cocrystallized with complexes **7**, **8**, and **9** were omitted. See Tables 2 and 3 for selected bond lengths and angles.



7 **8** **9** **10**

Figure 4. ORTEP diagrams of complexes **7**–**10** showing their molecular structure in configuration **B**. Thermal ellipsoids were drawn at the 50% probability level. For the sake of clarity, hydrogen atoms and the cocrystallized solvent molecules were omitted. See Tables 4 and 5 for selected bond lengths and angles.

configuration **B** in Figure 2). ORTEP plots of individual molecules displaying configurations **A** and **B** are represented in Figures 3 and 4, respectively, while relevant bond lengths and angles are listed in Tables 2–5. For the sake of comparison, data pertaining to complex **5** are also included.

Except for the orientation of the *p*-cymene ligand, the molecular structures of complexes **6**–**10** were very similar to those already reported for compounds **4** and **5**.[22] They consisted of a (*p*-cymene)Ru unit connected to the RuCl(=C=CHAr)(PCy$_3$) fragment via three μ-chloro bridges. A typical piano stool geometry was observed for the (arene)RuCl$_3$ moiety, with three Ru–Cl bonds of similar lengths (2.39–2.46 Å). The other ruthenium atom lay in a highly distorted octahedral environment with Ru–Cl bond lengths varying between 2.34 and 2.63 Å. In all the complexes under scrutiny, the shortest distances corresponded to the terminal halogen (Cl1 or Cl5). The bridging chloro substituent *trans* to it (Cl2 or Cl6) was slightly more distant from the metal center. A further elongation was recorded for Cl3 (or Cl7) facing the tricyclohexylphosphine ligand. The vinylidene unit displayed the strongest *trans* effect within the coordination sphere of the octahedral ruthenium center and was responsible for the

Table 2. Selected Bond Lengths (Å) Derived from the Crystal Structures of Complexes 5–9 (Configuration A)[a]

	5[b]	6	7	8	9
Ru1–Cl1	2.362(2)	2.360(3)	2.3614(11)	2.3609(8)	2.358(3)
Ru1–Cl2	2.403(2)	2.389(3)	2.4132(16)	2.4137(8)	2.408(4)
Ru1–Cl3	2.541(2)	2.531(3)	2.5059(12)	2.5103(8)	2.499(5)
Ru1–Cl4	2.630(2)	2.617(3)	2.6012(12)	2.6081(8)	2.592(4)
Ru1–P1	2.325(2)	2.303(3)	2.3107(12)	2.3150(8)	2.313(4)
Ru1–C1	1.778(8)	1.786(13)	1.785(5)	1.780(3)	1.799(15)
C1–C2	1.329(11)	1.329(17)	1.314(6)	1.311(5)	1.243(19)
Ru2–Cl2	2.428(2)	2.440(3)	2.4379(12)	2.4349(8)	2.429(4)
Ru2–Cl3	2.437(2)	2.429(4)	2.3923(13)	2.3977(8)	2.386(6)
Ru2–Cl4	2.427(2)	2.422(3)	2.4568(13)	2.4565(9)	2.449(5)

[a] See Figure 2 for the atom-numbering system. [b] Data from ref 22.

Table 3. Selected Bond Angles (deg) Derived from the Crystal Structures of Complexes 5–9 (Configuration A)[a]

	5[b]	6	7	8	9
Ru1–Cl2–Ru2	87.61(7)	86.58(10)	85.58(4)	85.75(3)	85.53(12)
Ru1–Cl3–Ru2	84.39(7)	83.73(11)	84.53(4)	84.43(3)	84.46(13)
Ru1–Cl4–Ru2	82.69(7)	82.07(10)	81.26(4)	81.23(3)	81.27(15)
P1–Ru1–Cl3	176.17(8)	174.18(12)	177.45(4)	178.04(3)	177.48(14)
Cl1–Ru1–Cl2	164.32(8)	166.58(11)	164.74(4)	163.97(3)	165.19(13)
C1–Ru1–Cl4	167.0(3)	165.1(4)	167.72(14)	167.35(10)	167.2(5)
Cl4–Ru1–Cl2	77.17(7)	77.76(11)	78.10(4)	78.85(3)	78.06(13)
Cl1–Ru1–Cl4	88.85(7)	89.69(11)	89.52(4)	88.93(3)	89.69(12)
Cl2–Ru1–C1	96.0(3)	95.1(4)	93.76(14)	94.08(10)	94.2(5)
Cl1–Ru1–C1	96.3(3)	96.0(4)	96.90(14)	97.27(10)	96.2(5)

[a] See Figure 2 for the atom-numbering system. [b] Data from ref 22.

Table 4. Selected Bond Lengths (Å) Derived from the Crystal Structures of Complexes 7–10 (Configuration B)[a]

	7	8	9	10
Ru3–Cl5	2.3627(11)	2.3585(8)	2.357(4)	2.3416(13)
Ru3–Cl6	2.4015(11)	2.4020(7)	2.398(4)	2.4043(13)
Ru3–Cl7	2.5171(10)	2.5167(8)	2.523(4)	2.5127(14)
Ru3–Cl8	2.6004(11)	2.5991(8)	2.601(4)	2.6176(14)
Ru3–P2	2.3139(12)	2.3173(8)	2.319(4)	2.3270(14)
Ru3–C37	1.779(4)	1.776(3)	1.774(14)	1.777(6)
C37–C38	1.313(6)	1.325(4)	1.296(18)	1.313(8)
Ru4–Cl6	2.4574(11)	2.4578(7)	2.456(4)	2.4484(13)
Ru4–Cl7	2.4204(11)	2.4209(8)	2.408(4)	2.4197(14)
Ru4–Cl8	2.4104(12)	2.4117(8)	2.434(4)	2.4166(14)

[a] See Figure 2 for the atom-numbering system.

Table 5. Selected Bond Angles (deg) Derived from the Crystal Structures of Complexes 7–10 (Configuration B)[a]

	7	8	9	10
Ru3–Cl6–Ru4	85.65(3)	85.66(2)	85.90(13)	85.97(4)
Ru3–Cl7–Ru4	83.95(3)	83.99(2)	84.22(14)	84.24(4)
Ru3–Cl8–Ru4	82.38(3)	82.42(2)	82.04(13)	82.08(4)
P2–Ru3–Cl7	177.55(4)	177.61(3)	177.82(14)	177.03(5)
Cl5–Ru3–Cl6	165.73(4)	165.76(3)	165.16(13)	164.64(5)
Cl8–Ru3–C37	165.66(15)	165.75(10)	165.6(4)	164.86(17)
Cl6–Ru3–Cl8	77.71(3)	77.70(2)	77.73(13)	77.11(4)
Cl5–Ru3–Cl8	88.96(4)	89.04(3)	88.34(12)	88.04(5)
Cl6–Ru3–C37	96.21(14)	96.21(10)	96.8(5)	97.70(17)
Cl5–Ru3–C37	95.58(14)	95.50(10)	95.5(5)	95.69(17)

[a] See Figure 2 for the atom-numbering system.

Scheme 5. ROMP of Norbornene

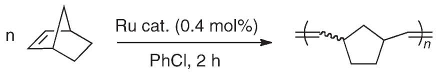


Table 6. ROMP of Norbornene Catalyzed by Complex 5 at Various Temperatures[a]

temperature (°C)	conversion (%)[b]	yield (%)	$10^{-3}M_n$[c]	M_w/M_n[c]	σ_{cis}[d]
30	95	76	77	2.2	0.15
40	97	81	39	2.9	0.14
60	>99	80	22	4.3	0.16

[a] Experimental conditions: Ru cat. (0.015 mmol), norbornene (3.75 mmol), PhCl (12.5 mL), 2 h under Ar. [b] Determined by GC using norbornane as internal standard. [c] Determined by SEC in THF with polystyrene calibration. [d] Fraction of *cis* double bonds in the polymer, determined by ^{13}C NMR spectroscopy.

significantly longer distances measured for Ru1–Cl4 (or Ru3–Cl8) in comparison with other Ru–Cl bonds. Thus, the bond lengths always increased in the order Ru1–Cl1 < Ru1–Cl2 < Ru1–Cl3 < Ru1–Cl4 (or Ru3–Cl5 < Ru3–Cl6 < Ru3–Cl7 < Ru3–Cl8). Moreover, the *trans* effect of the vinylidene unit in homobimetallic complexes **4–10** may be ranked slightly inferior to that of an indenylidene group[33] and considerably stronger than the one exerted by the ethylene ligand in complex **3**.[22]

The Ru=C and C=C bond lengths within the polyunsaturated fragments of complexes **5–10** were similar to those recorded for complex **4**[22] and other monometallic, hexacoordinated ruthenium–vinylidene complexes, such as $[RuCl(=C=CHPh)(\kappa^2P,O\text{-}Pr^i{}_2PCH_2CH_2OMe)_2](OTf)$[34] or [TpRuCl(=C=CHPh)(PPh_3)] (Tp is tris(pyrazolyl)borate).[35] Furthermore, they remained seemingly independent from the exact nature of the aryl group attached to them. At ca. 1.78 Å, the vinylidene Ru=C bonds in complexes **4–10** are, however, slightly longer than in unsaturated, pentacoordinated complexes of type **2** having a square-pyramidal structure with the vinylidene ligand in the apical position, like $[RuCl_2(=C=CHPh)(PPr^i{}_3)_2]$ (1.750(4) Å) and $[RuCl_2(=C=CHPh)(PCy_3)_2]$ (1.761(2) Å) (cf. Scheme 1).[11] Conversely, they are significantly shorter than the Ru=C distances measured in pincer complexes $[RuCl_2(=C=CHPh)(\kappa^3P,N,P\text{-dcpmp})]$ (1.816(6) Å) and $[RuCl_2\{=C=C(SiMe_3)Ph\}(\kappa^3P,N,P\text{-dcpmp})]$ (1.845(4) Å) (dcpmp is 2,6-bis{(dicyclohexylphosphino)methyl}pyridine), in which the vinylidene fragment is facing a nitrogen donor.[36] Thus, the Ru=C$_\alpha$ distance between a ruthenium center and the carbon atom of the vinylidene ligand attached to it is mainly determined by the presence or the absence of a coaxial ligand and its donor strength, while the substituents on C$_\beta$ are considerably less influential.

ROMP of Norbornene and Cyclooctene. In order to assess the catalytic activity of homobimetallic ruthenium–vinylidene complexes in olefin metathesis, we first investigated the ROMP of norbornene in chlorobenzene using a monomer-to-catalyst ratio of 250 (Scheme 5). Due to its high strain, ring-opening metathesis of this bicyclic monomer is particularly easy to carry out and occurs under almost any circumstances, provided that enough time is allowed for the reaction.[37] It was therefore not surprising to observe the full conversion of norbornene into polynorbornene using unsubstituted phenylvinylidene

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(33) Sauvage, X.; Borguet, Y.; Zaragoza, G.; Demonceau, A.; Delaude, L. *Adv. Synth. Catal.* **2009**, *351*, 441–455.

(34) Martín, M.; Gevert, O.; Werner, H. *J. Chem. Soc., Dalton Trans.* **1996**, 2275–2283.

(35) Slugovc, C.; Mereiter, K.; Zobetz, E.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 5275–5277.

(36) Katayama, H.; Wada, C.; Taniguchi, K.; Ozawa, F. *Organometallics* **2002**, *21*, 3285–3291.

(37) Lebedev, B.; Smirnova, N.; Kiparisova, Y.; Makovetsky, K. *Makromol. Chem.* **1992**, *193*, 1399–1411.

Scheme 6. ROMP of Cyclooctene

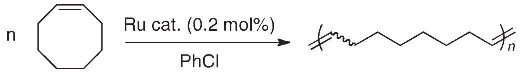

Table 7. Influence of the Temperature on the ROMP of Cyclooctene Catalyzed by Complex 5[a]

temperature (°C)	conversion (%)[b]	yield (%)	$10^{-3}M_n$[c]	M_w/M_n[c]	σ_{cis}[d]
100	2	<1			
120	20	15	85	1.9	0.47
140	33	26	115	1.8	0.46
160	24	19	71	1.7	0.47
140[e]	50	40	202	1.7	0.52

[a] Experimental conditions: Ru cat. (0.0075 mmol), cyclooctene (3.75 mmol), PhCl (2.5 mL), 2 h under Ar. [b] Determined by GC using cyclooctane as internal standard. [c] Determined by SEC in THF with polystyrene calibration. [d] Fraction of *cis* double bonds in the polymer, determined by ^{13}C NMR spectroscopy. [e] Reaction in a sealed tube heated in an oil bath instead of a monomodal microwave reactor.

Table 8. Influence of the Reaction Time on the ROMP of Cyclooctene Catalyzed by Complex 5 at 140 °C[a]

time (h)	conversion (%)[b]	yield (%)	$10^{-3}M_n$[c]	M_w/M_n[c]	σ_{cis}[d]
0.5	31	19	100	1.5	0.58
2	33	26	115	1.8	0.46
6	34	25	122	1.6	0.41
8.5	34	26	119	2.0	0.54

[a] Experimental conditions: Ru cat. (0.0075 mmol), cyclooctene (3.75 mmol), PhCl (2.5 mL), 140 °C under Ar. [b–d] See footnotes in Table 7 for details.

Table 9. Influence of the Lewis Acid Cocatalyst on the ROMP of Cyclooctene Catalyzed by Complex 5 at 60 °C[a]

Lewis acid	conversion (%)[b]	yield (%)	$10^{-3}M_n$[c]	M_w/M_n[c]	σ_{cis}[d]
$AlCl_3$	>99	84	453	1.26	0.48
AgOTf	>99	82	427	1.90	0.46
$BF_3 \cdot OEt_2$	48	37	544	1.24	0.51
$FeCl_3$	83	64	439	1.29	0.39
$Sc(OTf)_3$	93	80	523	1.31	0.43
$TiCl_4$	50	37	322	1.38	0.45
WCl_6	90	80	125	1.63	0.44
$ZnCl_2$	93	81	270	1.52	0.42

[a] Experimental conditions: Ru cat. (0.0075 mmol), Lewis acid (0.0075 mmol), cyclooctene (3.75 mmol), PhCl (2.5 mL), 2 h at 60 °C under Ar. [b–d] See footnotes in Table 7 for details.

compound **5** as a model initiator at 60 °C (Table 6). Even when the temperature was decreased to 30 or 40 °C, high molecular weight polymers with a broad polydispersity index and mostly *trans* double bonds were isolated in high yields. Similar results were already obtained when homobimetallic ruthenium–ethylene complex **3** served as catalyst precursor.[21] Thus, the presence of a vinylidene fragment is of little added value for this reaction. Activation of the monomer via ill-defined mechanisms is sufficient to generate metathetically active species from the bulk of the ruthenium precursor.[38] The consequence is a poor control over the initiation and the formation of polymers with a broad molecular weight distribution. It should be pointed out, however, that narrow polydispersities are not essential in many polymer applications and can even hamper processing in some cases.[39]

Compared to norbornene, cyclooctene is significantly less strained and more difficult to ring-open.[40] Hence, formation of polyoctenamer occurs only at a reasonable rate with highly active catalytic systems. In order to determine whether or not homobimetallic Ru–vinylidene complexes fall into this category, polymerization tests were performed in chlorobenzene using a monomer-to-catalyst ratio of 500 (Scheme 6). A monomodal microwave reactor served as a convenient heating device for these experiments. Under these conditions, only traces of polymer were isolated when complex **5** served as catalyst precursor for 2 h at 60 or 100 °C (Table 7). When the reaction was carried out at higher temperatures (120 and 140 °C), conversion increased and high molecular weight polymers with an almost equimolar proportion of *cis* and *trans* double bonds were isolated in modest yields. A further experiment performed at 160 °C eventually led to a drop in activity, most likely due to a thermal decomposition of the catalyst. Switching from microwave irradiation to conventional heating in an oil bath at 140 °C slightly increased the monomer conversion and the polymer yield, but did not affect the microstructure of the macromolecular chains.

Next, we examined the influence of the reaction time on the ROMP of cyclooctene carried out in a microwave reactor at 140 °C using complex **5** as initiator (Table 8). These experiments showed that conversion stopped increasing already after ca. 30 min and that extending the reaction time beyond this period did not significantly improve the outcome of the polymerization. Thus, the need for a long induction time before the active species are generated from the catalyst precursor may be ruled out under these conditions.

Because the two ruthenium centers in complex **5** are coordinatively saturated, dissociation of a ligand is required prior to any interaction between the catalyst and the monomer. For the ROMP of cyclooctene, results gathered in Tables 7 and 8 clearly indicated that a thermal activation was not sufficient to promote this mandatory step. Alternatively, we reasoned that adding a Lewis acid to the reaction media might help generate active species. Indeed, a 1998 report by Ozawa and co-workers had shown that the catalytic activity of the 18-electron monometallic complex [TpRuCl(=C=CHPh)(PPh_3)] (Tp is tris(pyrazolyl)borate) in the ROMP of norbornene was considerably enhanced by the addition of boron trifluoride diethyl etherate.[41] This additive was assumed to facilitate the decoordination of a phosphine ligand. Accordingly, we have probed the influence of various Lewis acids on the ROMP of cyclooctene catalyzed by complex **5** (Table 9). A mixture of the two catalyst components in 1:1 molar proportion was suspended in chlorobenzene under argon and stirred for a few minutes in an oil bath at 60 °C before the monomer was added. Under these conditions, $BF_3 \cdot OEt_2$ displayed a moderate, albeit encouraging, activating effect. Addition of 1 equiv of this cocatalyst to the ruthenium–phenylvinylidene precursor afforded a high molecular weight polyoctenamer in 37% yield after 2 h, whereas the use of complex **5** alone did not lead to any conversion of the cycloolefin within the same

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(38) (a) Bencze, L.; Kraut–Vass, A.; Prókai, L. *Chem. Commun.* **1985**, 911–912. (b) Mühlebach, A.; Bernhard, P.; Bühler, N.; Karlen, T.; Ludi, A. *J. Mol. Catal.* **1994**, *90*, 143–156. (c) Al Samak, B.; Amir-Ebrahimi, V.; Corry, D. G.; Hamilton, J. G.; Rigby, S.; Rooney, J. J.; Thompson, J. M. *J. Mol. Catal. A: Chem.* **2000**, *160*, 13–21. (d) Alvarez, P.; Gimeno, J.; Lastra, P. *Organometallics* **2002**, *21*, 5678–5680.

(39) Böhm, L. L.; Enderle, H. F.; Fleissner, M. In *Catalyst Design for Tailor-Made Polyolefins*; Soga, K.; Terano, M., Eds.; *Stud. Surf. Sci. Catal.*, Vol. *89*; Elsevier Science: Amsterdam, 1994; pp 351–363.

(40) Lebedev, B.; Smirnova, N. *Macromol. Chem. Phys.* **1994**, *195*, 35–63.

(41) Katayama, H.; Yoshida, T.; Ozawa, F. *J. Organomet. Chem.* **1998**, *562*, 203–206.

period of time. Another liquid catalyst modifier, $TiCl_4$, behaved in pretty much the same way as the boron trifluoride adduct. Recourse to other strong Lewis acids based on transition metals, such as $FeCl_3$, $Sc(OTf)_3$, WCl_6, or $ZnCl_2$ further boosted the catalytic activity and led to almost quantitative conversions of cyclooctene. Although it is a weak Lewis acid, the halide-abstracting AgOTf salt was another serious contender. Yet, the best results were obtained with aluminum chloride, which allowed a total consumption of the monomer within 2 h and the formation of high molecular weight polyoctenamer with a rather narrow polydispersity index ($M_w/M_n = 1.25$) and an almost equimolar proportion of *cis* and *trans* double bonds ($\sigma_{cis} = 0.48$). Similar yields and macromolecular parameters were obtained when the molar proportion of $AlCl_3$ relative to complex **5** was doubled and when a 1 or 2 h delay was introduced prior to the addition of the monomer. These experiments confirmed that the Lewis acid acted as a fast and efficient activator. Conversely, neither $SnCl_2$, $CuCl_2$, $CuCl_2 \cdot xH_2O$, nor CuCl afforded any polymer. This last result has important mechanistic implications (vide infra), because copper(I) salts are well-known phosphine scavengers, which have been frequently employed to displace PCy_3 from metathetically active ruthenium−alkylidene or −indenylidene complexes.[42] Therefore, the absence of ROMP when complex **5** was treated with CuCl suggests that the formation of active species does not involve a dissociation of the tricyclohexylphosphine ligand.

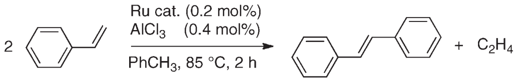
Having identified aluminum chloride as the most suitable cocatalyst to activate ruthenium−phenylvinylidene complex **5**, we launched a final series of ROMP experiments to probe how the introduction of electron-donating or -withdrawing groups on the vinylidene moiety affected the metathetical process. Thus, complexes **6**−**10** were tested as catalyst precursors for the polymerization of cyclooctene in the presence of $AlCl_3$ (1 equiv) at 60 °C (Table 10). After 2 h of reaction, high yields of polyoctenamer were isolated with complexes **6** and **7** bearing *para*-methoxy and *para*-methyl donor groups. No major differences were observed in the polymer microstructures compared to those obtained with unsubstituted compound **5**. In all three cases, the molecular weights remained very high, which indicates that only small amounts of active species were generated, regardless of the actual substituent present on the arylvinylidene unit. Indeed, the initiation efficiencies $f = M_{n,\mathrm{theor}}/M_{n,\mathrm{exp}}$ (calculated with $M_{n,\mathrm{theor}} = ([\mathrm{monomer}]/[\mathrm{Ru\ cat.}])_o \times \mathrm{MW}_{\mathrm{monomer}} \times \mathrm{conversion}$) never exceeded 15%. Introduction of a *para*-chloro electron-withdrawing group in catalyst precursor **8** did not have any adverse influence on the polymer yield, but slightly increased the polydispersity index and altered the *cis*/*trans* ratio of the double bonds. These changes became more obvious with complexes **9** and **10**, bearing *para*-trifluoromethyl and bis-*meta*-trifluoromethyl substituents, which gradually lost any activity. When a 1:1 mixture of *tert*-butylvinylidene−ruthenium complex **4** and $AlCl_3$ was tested under the same experimental conditions, no sign of reaction was detected after 2 h at 60 °C. This was an unexpected result, because related monometallic complexes of the type $[\mathrm{RuCl_2({=}C{=}CHBu^{\it t})(PR_3)_2}]$ (PR_3 = PPr^i_3 or PCy_3) were found to catalyze various ROMP and RCM reactions.[12] Therefore, an aryl group on the β-position of the vinylidene unit seems essential to the catalytic activity of homobimetallic species **4**−**10**, but except for strongly electron-withdrawing groups, the exact nature of the substituents on the aromatic ring has little influence on the polymerization outcome.

Table 10. ROMP of Cyclooctene Catalyzed by Complexes 5−10 in the Presence of $AlCl_3$ at 60 °C[a]

complex	conversion (%)[b]	yield (%)	$10^{-3}M_n$[c]	M_w/M_n[c]	σ_{cis}[d]
5	>99	86	453	1.25	0.48
6	>99	82	392	1.29	0.50
7	95	86	341	1.37	0.43
8	>99	84	355	1.79	0.37
9	33	24	149	1.96	0.35
10	<5	0			

[a] Experimental conditions: Ru cat. (0.0075 mmol), $AlCl_3$ (0.0075 mmol), cyclooctene (3.75 mmol), PhCl (2.5 mL), 2 h at 60 °C under Ar. [b−d] See footnotes in Table 7 for details.

Scheme 7. Self-Metathesis of Styrene



Other Metathesis Reactions. In order to further evaluate the scope of homobimetallic ruthenium−vinylidene catalysts for olefin metathesis, we have carried out the homodimerization of styrene using complexes **5** and **6** (Scheme 7). In the absence of any cocatalyst, no reaction took place after 2 h at 85 °C under low catalyst loading conditions (0.2 mol %). Addition of $AlCl_3$ (2 equiv) led to the formation of *trans*-stilbene, as evidenced by GC analysis of the reaction mixture, but conversion remained very limited (<5%). Previous work from our group had already shown that first-generation ruthenium catalysts were not suitable for styrene homocoupling, whether they were mono-[43] or bimetallic.[21] Second-generation NHC-based species were required to achieve satisfactory reaction rates, in good agreement with the general ranking of olefin reactivity proposed by Grubbs and co-workers for predicting the selectivity of cross-metatheses.[44] Therefore, we did not further investigate this transformation.

Instead, we focused on the RCM of diethyl 2,2-diallylmalonate (DEDAM). Preliminary tests were carried out in toluene at 85 °C using 2 mol % of complex **5**. Under these conditions, conversion of the α,ω-diene stagnated below 10% even when the reaction time was extended to more than 5 h (Figure 5). These results were only slightly superior to those obtained with the ruthenium−ethylene complex **3**. When phenylacetylene (6 mol %) was added to the reaction media, consumption of the substrate occurred much faster, and diethyl cyclopent-3-ene-1,1-dicarboxylate was the sole product formed (Scheme 8). It is noteworthy that complexes **3** and **5** displayed the same reaction profile in the presence of the terminal alkyne cocatalyst. Thus, the role of this additive goes beyond the replacement of the ethylene ligand with a vinylidene fragment, as we

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[42] (a) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887–3897. (b) Wakamatsu, H.; Blechert, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 794–796. (c) Connon, S. J.; Rivard, M.; Zaja, M.; Blechert, S. *Adv. Synth. Catal.* **2003**, *345*, 572–575. (d) Buschmann, N.; Wakamatsu, H.; Blechert, S. *Synlett* **2004**, 667–670. (e) Vehlow, K.; Maechling, S.; Blechert, S. *Organometallics* **2006**, *25*, 25–28. (f) Grela, K.; Harutyunyan, S.; Michrowska, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 4038–4040. (g) Michrowska, A.; Harutyunyan, S.; Sashuk, V.; Dolgonos, G.; Grela, K. *J. Am. Chem. Soc.* **2004**, *126*, 9318–9325. (h) Bieniek, M.; Michrowska, A.; Gułajski, Ł.; Grela, K. *Organometallics* **2007**, *26*, 1096–1099. (i) Rix, D.; Caijo, F.; Laurent, I.; Boeda, F.; Clavier, H.; Nolan, S. P.; Mauduit, M. *J. Org. Chem.* **2008**, *73*, 4225–4228.

[43] Ferré-Filmon, K.; Delaude, L.; Demonceau, A.; Noels, A. F. *Eur. J. Org. Chem.* **2005**, 3319–3325.

[44] Chatterjee, A. K.; Choi, T.-L.; Sanders, D. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 11360–11370.

initially assumed. Its possible implication to the catalytic process will be further discussed in the next section.

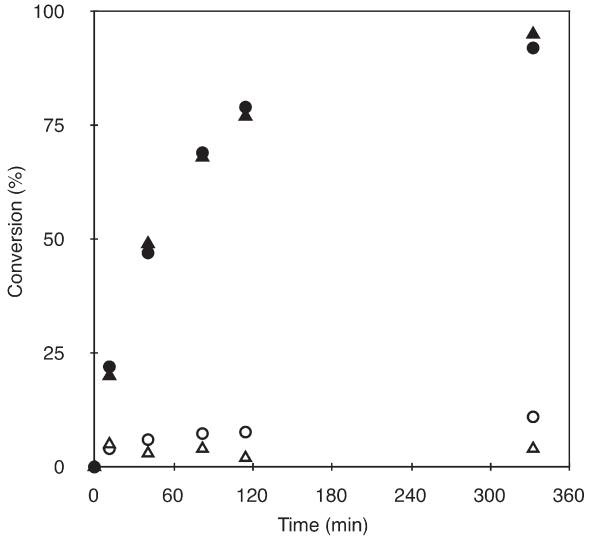
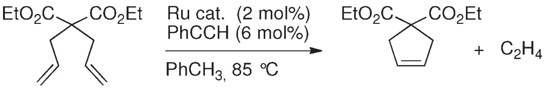
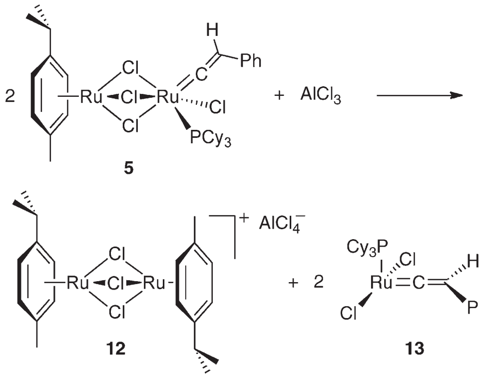


Figure 5. Time course of the RCM of DEDAM catalyzed by complexes **3** (▲,△) and **5** (●,○) at 85 °C in the presence (▲,●) or in the absence (△,○) of phenylacetylene.

Scheme 8. RCM of DEDAM



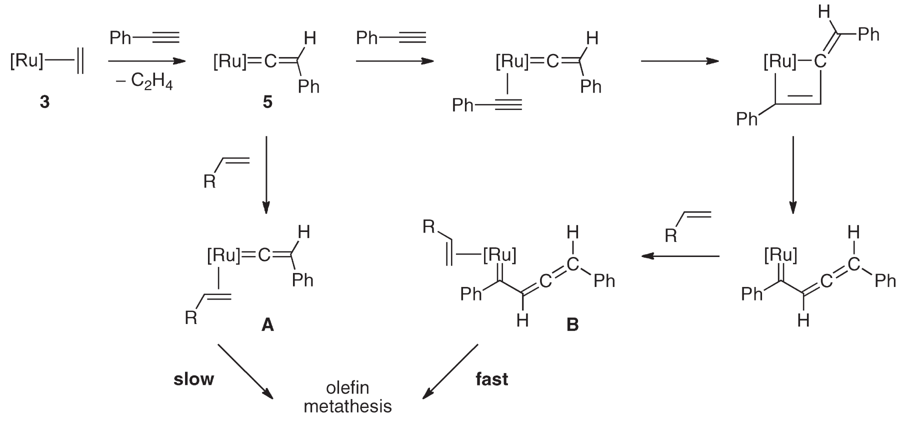
Scheme 9. Possible Activation of Complex 5 by AlCl$_3$



Mechanistic Indications. Except for the facile ROMP of norbornene, all the other catalytic tests that we performed required the use of a co-promoter to enhance the metathetical activity of complexes **5**−**10**. Recourse to aluminum chloride afforded a convenient way to initiate the ROMP of cyclooctene. The Lewis acid most likely favored the dissociation of a ligand from the saturated homobimetallic scaffold, thereby leading to a more reactive species able to coordinate the monomer. Experiments carried out with copper salts indicated that tricyclohexylphosphine was not involved in this activation process, whereas the good result obtained with silver triflate strongly suggested that halide abstraction was probably at stake. Therefore, we tentatively propose that aluminum chloride interacts with a bridging chloro ligand to afford cationic complex **12** and a highly reactive 14-electron species of type **13**, as illustrated for compound **5** in Scheme 9. The intimate details of the mechanism remain unclear. However, ESI-MS analyses of solutions prepared by titrating complex **5** with AlCl$_3$ (1.3 equiv) showed the presence of a major signal centered at $m/z = 577$, whose molecular weight and isotopic pattern matched those computed for the well-known cationic dimer **12**.[45] Additionally, ^{31}P NMR spectroscopy revealed that a main product containing a phosphine ligand resonated at 59.0 ppm, but the intermediacy of compound **13** remained otherwise elusive. Yet, it is noteworthy that a 14-electron species of the type [RuCl$_2$(=C=CHBu^t)(NHC)] was also postulated by Louie and Grubbs to be the key intermediate in catalytic systems generated in situ by adding 2 equiv of 1,3-dimesitylimidazolium chloride, sodium *tert*-butoxide, and *tert*-butylacetylene to the [RuCl$_2$(*p*-cymene)]$_2$ dimer (**1**).[14]

For the RCM of DEDAM, we reasoned that AlCl$_3$ would not be a suitable activator, because of its affinity for the diester functionality. In this case, addition of a small amount of phenylacetylene to homobimetallic ruthenium−phenylvinylidene precursor **5** provided an efficient workaround to boost its activity. A similar enhancement was also observed starting from ruthenium−ethylene complex **3**. Thus, we believe that the role of the terminal alkyne is 2-fold. First, it displaces rapidly and quantitatively the labile ethylene ligand of complex **3** to afford the homobimetallic vinylidene precursor **5** (cf. Scheme 3). A direct interaction between this compound and the olefinic substrate is able to generate a metathetically active species of type **A** (Scheme 10). However, this process is rather inefficient and slow. In the presence of excess phenylacetylene, complex **5** has the possibility to react with an alkyne

Scheme 10. Possible Mechanism for the Activation of Homobimetallic Ruthenium−Ethylene or −Vinylidene Complexes by Phenylacetylene



instead of an alkene partner. This second intervention should ease the required opening of a coordination site, because the alkyne is a better π-donor and a sterically less encumbered ligand than the alkene. Moreover, a subsequent enyne metathesis event would then lead to the formation of an alkylidene species of type **B**, which is a faster initiator than vinylidene intermediate **A**. As a matter of fact, previous work from our group had already shown that phosphino complex **3** and related NHC-based catalyst precursors efficiently promoted the enyne metathesis between phenylacetylene and ethylene.[21]

Conclusion

The labile ruthenium–ethylene complex **3** is a convenient starting material to prepare more elaborate homobimetallic ruthenium–arene architectures containing polyunsaturated carbon-rich fragments. Its reaction with various phenylacetylene derivatives in dichloromethane at room temperature afforded five new arylvinylidene complexes with substituents ranging from electron-donating (like the *para*-methoxy group in **6**) to strongly electron-withdrawing (such as the bis-*meta*-trifluoromethyl groups in **10**) in high yields. The synthesis of unsubstituted phenylvinylidene complex **5** was also successfully carried out in a single step starting from the widely available $[RuCl_2(p\text{-cymene})]_2$ dimer (**1**), tricyclohexylphosphine, and a small excess of phenylacetylene under microwave irradiation. This procedure is particularly attractive in terms of atom economy and efficiency. All the new compounds were fully characterized by various analytical techniques, and the influence of their remote aryl substituents on structural features was carefully investigated by IR, NMR, and XRD spectroscopies. A very good linear relationship was observed between the chemical shift of the vinylidene α-carbon atom and the Hammett σ-constants for *p*-OMe, *p*-Me, *p*-H, *p*-Cl, *p*-CF_3, and *m*-$(CF_3)_2$ groups. X-ray diffraction analysis showed that the unit cells of complexes **7**, **8**, and **9** contained two nonequivalent molecules, which differed primarily in the relative orientation of their *p*-cymene and vinylidene ligands. Comparison of the various bond lengths and angles showed that the introduction of electron-donating or -withdrawing groups on the aryl ring of the vinylidene ligand did not have any significant influence on the magnitude of its *trans* effect. Moreover, the distance between a ruthenium center and the carbon atom of the vinylidene ligand attached to it was mainly determined by the presence or the absence of a coaxial ligand and its donor strength, while the substituents on C_β were considerably less influential.

The catalytic activity of complexes **5**–**10** was probed in various types of olefin metathesis reactions. Unsubstituted phenylvinylidene compound **5** served as a lead structure for these experiments. Its reaction with norbornene, a typical strained cycloalkene, was investigated at temperatures ranging from 30 to 60 °C. In all cases, high molecular weight polymers with a broad polydispersity index and mostly *trans* double bonds were obtained almost quantitatively within 2 h. When the ROMP of cyclooctene was performed at temperatures ranging from 60 to 160 °C, only modest yields of polyoctenamer were isolated after 2 h. Thus, thermal activation was not sufficient to trigger the catalytic activity of complex **5** using a low-strain monomer. Alternatively, we found that aluminum chloride was a suitable cocatalyst to allow the formation of high molecular weight polyoctenamer with a rather narrow polydispersity index ($M_w/M_n = 1.25$) and an almost equimolar proportion of *cis* and *trans* double bonds within 2 h at 60 °C. No major changes were observed in the polymer yields and microstructures when complexes **6** and **7** bearing *para*-methoxy and *para*-methyl donor groups on their aryl rings were employed as catalyst precursors. On the other hand, compound **9** or **10** (and to a lesser extent **8**), bearing electron-withdrawing substituents, were significantly less active.

Model vinylidene derivative **5** and its ruthenium–ethylene parent (**3**) were equally inactive in the RCM of DEDAM, and they both required the addition of phenylacetylene to achieve the ring-closure of this α,ω-diene. Thus, the role of the terminal alkyne cocatalyst goes beyond the facile replacement of the η^2-alkene ligand with a vinylidene fragment. As a matter of fact, compounds **5**–**10** are highly stable, coordinatively saturated species that cannot enter a catalytic cycle without prior dissociation of a ligand. Recourse to $AlCl_3$ is believed to activate a μ-chloro bridge rather than a phosphine ligand and could result in the formation of the well-known cationic complex **12** and a metathetically active 14-electron species of the type $[RuCl_2(=C=CHPh)(PCy_3)]$ (**13**). The influence of phenylacetylene is less obvious to rationalize, although it can be reasonably assumed that an alkyne has a better chance than an alkene to find its way to the metal center, where it would allow an enyne metathesis to take place, thereby affording a highly active mono- or bimetallic ruthenium–alkylidene species.

Experimental Section

General Comments. Unless otherwise stated, all the syntheses were carried out under a dry argon atmosphere using standard Schlenk techniques. Solvents were distilled from appropriate drying agents and deoxygenated prior to use. The $[RuCl_2(p\text{-cymene})]_2$ dimer (**1**) and tricyclohexylphosphine were purchased from Strem. Homobimetallic ruthenium–ethylene and *tert*-butylvinylidene complexes (**3** and **5**) were prepared according to the literature.[17,22] All the other chemicals were obtained from Aldrich. A CEM Discover instrument was used for microwave-assisted syntheses. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 298 K with a Bruker DRX 400 spectrometer operating at 400.13 and 100.62 MHz, respectively. Chemical shifts are listed in parts per million downfield from TMS and are referenced from the solvent peaks or TMS. $^{31}P\{^1H\}$ NMR spectra were recorded at 298 K with a Bruker Avance 250 spectrometer operating at 101.25 MHz using an inlay capillary tube with 85% H_3PO_4 as external reference. Infrared spectra were recorded with a Perkin-Elmer Spectrum One FT-IR spectrometer. Elemental analyses were carried out in the Laboratory of Pharmaceutical Chemistry at the University of Liège. Gas chromatography was carried out with a Varian 3900 instrument equipped with a flame ionization detector and a WCOT fused silica column (stationary phase: CP-Sil 5CB, column length: 15 m, inside diameter: 0.25 mm, outside diameter: 0.39 mm, film thickness: 0.25 μm). Size-exclusion chromatography (SEC) was performed in THF at 45 °C with a SFD S5200 autosampler liquid chromatograph equipped with a SFD 2000 refractive index detector and a battery of 4 PL

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(45) (a) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233–241. (b) Arthur, T.; Stephenson, T. A. *J. Organomet. Chem.* **1981**, *208*, 369–387. (c) Tocher, D. A.; Walkinshaw, M. D. *Acta Crystallogr.* **1982**, *B38*, 3083–3085. (d) Brost, R. D.; Bruce, G. C.; Grundy, S. L.; Stobart, S. R. *Inorg. Chem.* **1993**, *32*, 5195–5200. (e) Čubrilo, J.; Hartenbach, I.; Lissner, F.; Schleid, T.; Niemeyer, M.; Winter, R. F. *J. Organomet. Chem.* **2007**, *692*, 1496–1504. (f) Sumiyoshi, T.; Gunnoe, T. B.; Petersen, J. L.; Boyle, P. D. *Inorg. Chim. Acta* **2008**, *361*, 3254–3262. (g) Mutseneck, E. V.; Reus, C.; Schödel, F.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Organometallics* **2010**, *29*, 966–975.

gel columns fitted in series (particle size: 5 μm; pore sizes: 10^5, 10^4, 10^3, and 10^2 Å; flow rate: 1 mL/min). The molecular weights (not corrected) are reported versus monodisperse polystyrene standards used to calibrate the instrument. Mass spectra were recorded with a Waters Q-TOF Ultima spectrometer (ESI+ mode, source temperature: 100 °C, capillary voltage: 3000 V, RF lens intensity: 100, source pressure: 3.3 mbar).

General Procedure for the Synthesis of Complexes 6−10. A phenylacetylene derivative (ca. 380 mmol, 2 equiv) was added to a solution of [(*p*-cymene)Ru(μ-Cl)$_3$RuCl(η^2-C_2H_4)(PCy$_3$)] (**3**) (150 mg, 190 μmol) in dichloromethane (7.5 mL), and the mixture was stirred for 2 h at room temperature under a static argon atmosphere. After evaporation of the solvent under reduced pressure, the residue was washed with *n*-pentane (3 × 5 mL) and dried overnight under high vacuum.

[(*p*-cymene)Ru(μ-Cl)$_3$RuCl(=C=CH−C_6H_4-4-OMe)(PCy$_3$)] (6): brown-beige solid (164 mg, 97% yield) obtained from 4-ethynylanisole (50 μL, 386 μmol). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.12−1.25 (m, 9 H, PCy$_3$), 1.35 (t, ^3J = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.51−1.74 (m, 15 H, PCy$_3$), 1.87 (m, 6 H, PCy$_3$), 2.12 (q, ^3J = 11.0 Hz, 3H, PCy$_3$), 2.28 (s, 3 H, CH$_3$, *p*-cym), 2.95 (sept, ^3J = 6.8 Hz, 1 H, C*H*(CH$_3$)$_2$), 3.73 (s, 3 H, OCH$_3$), 4.84 (d, $^4J_{PH}$ = 3.5 Hz, 1 H, Ru=C=CH), 5.40 (d, ^3J = 5.2 Hz, 2 H, CH$_{ar}$, *p*-cym), 5.57 (d, ^3J = 5.2 Hz, 1 H, CH$_{ar}$, *p*-cym), 5.65 (d, ^3J = 5.2 Hz, 1 H, CH$_{ar}$, *p*-cym), 6.72 (d, ^3J = 8.8 Hz, 2 H, CH$_{ar}$), 7.00 (d, ^3J = 8.8 Hz, 2 H, CH$_{ar}$) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ 18.5 (CH$_3$, *p*-cym), 21.9, 22.0 (CH(*C*H$_3$)$_2$), 26.4 (CH$_2$, PCy$_3$), 27.7 (d, $^3J_{PC}$ = 4 Hz, CH$_2$, PCy$_3$), 27.8 (d, $^3J_{PC}$ = 4 Hz, CH$_2$, PCy$_3$), 28.9 (d, $^2J_{PC}$ = 26 Hz, CH$_2$, PCy$_3$), 31.2 (*C*H(CH$_3$)$_2$), 35.2 (d, $^1J_{PC}$ = 24 Hz, CH, PCy$_3$), 55.2 (OCH$_3$), 78.2, 78.7, 79.5, 80.2 (CH$_{ar}$, *p*-cym), 97.2, 101.2 (C$_{ar}$, *p*-cym), 113.7 (Ru=C=*C*), 113.9, 122.1, 126.8 (C_6H_4), 157.3 (*C*-OCH$_3$), 357.5 (d, $^2J_{PC}$ = 19.4 Hz, Ru=C) ppm. ^{31}P NMR (101 MHz, CD_2Cl_2): δ 55.02 (s) ppm. IR (KBr): $\bar{\nu}$ 3065(w), 2928(s), 2849(m), 1631(s), 1573(w), 1507(s), 1444(m), 1293(w), 1244(s), 1176(m), 1033(m), 828(m) cm^{-1}. Anal. Calcd for $C_{37}H_{55}Cl_4O$-PRu_2 (890.76): C, 49.89; H, 6.22. Found: C, 49.77; H, 6.22.

[(*p*-cymene)Ru(μ-Cl)$_3$RuCl(=C=CH−C_6H_4-4-Me)(PCy$_3$)] (7): brown-beige solid (153 mg, 92% yield) obtained from 4-ethynyltoluene (50 μL, 394 μmol). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.13−1.24 (m, 12 H, PCy$_3$), 1.35 (t, ^3J = 6.7 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.50−1.74 (m, 14 H, PCy$_3$), 1.87 (m, 4 H, PCy$_3$), 2.14 (q, ^3J = 11.7 Hz, 3 H, PCy$_3$), 2.28 (s, 3 H, CH$_3$, *p*-cym), 2.30 (s, 3 H, CH$_3$, *p*-tolyl), 2.95 (sept, ^3J = 6.8 Hz, 1 H, C*H*(CH$_3$)$_2$), 4.85 (d, $^4J_{PH}$ = 3.3 Hz, 1 H, Ru=C=CH), 5.41 (d, ^3J = 5.5 Hz, 2 H, CH$_{ar}$, *p*-cym), 5.58 (d, ^3J = 5.5 Hz, 1 H, CH$_{ar}$, *p*-cym), 5.65 (d, ^3J = 5.5 Hz, 1 H, CH$_{ar}$, *p*-cym), 6.97 (s, 4 H, C_6H_4) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ 18.5 (CH$_3$, *p*-cym), 20.8 (CH$_3$, *p*-tolyl), 21.9, 22.0 (CH(*C*H$_3$)$_2$), 26.4 (CH$_2$, PCy$_3$), 27.7 (d, $^3J_{PC}$ = 4 Hz, CH$_2$, PCy$_3$), 27.8 (d, $^3J_{PC}$ = 4 Hz, CH$_2$, PCy$_3$), 29.0 (d, $^2J_{PC}$ = 27 Hz, CH$_2$, PCy$_3$), 31.3 (*C*H(CH$_3$)$_2$), 35.2 (d, $^1J_{PC}$ = 24 Hz, CH, PCy$_3$), 78.2, 78.7, 79.6, 80.2 (CH$_{ar}$, *p*-cym), 97.2, 101.2 (C$_{ar}$, *p*-cym), 114.0 (Ru=C=*C*), 125.9, 127.4, 128.9, 134.3 (C_6H_4), 356.4 (d, $^2J_{PC}$ = 19.4 Hz, Ru=C) ppm. ^{31}P NMR (101 MHz, CD_2Cl_2): δ 54.95 (s) ppm. IR (KBr): $\bar{\nu}$ 3068(w), 3046(w), 2922(s), 2848(s), 1630(s), 1606(m), 1509(m), 1445(m) 817(m), 490(m) cm^{-1}. Anal. Calcd for $C_{37}H_{55}Cl_4PRu_2$ (874.76): C, 50.80; H, 6.34. Found: C, 50.64; H, 6.29.

[(*p*-cymene)Ru(μ-Cl)$_3$RuCl(=C=CH−C_6H_4-4-Cl)(PCy$_3$)] (8): red-brown solid (139 mg, 82% yield) obtained from 4-ethynylchlorobenzene (52 mg, 381 μmol). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.13−1.24 (m, 12 H, PCy$_3$), 1.35 (t, ^3J = 6.3 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.48−1.74 (m, 14 H, PCy$_3$), 1.87 (m, 4 H, PCy$_3$), 2.14 (q, ^3J = 11.8 Hz, 3 H, PCy$_3$), 2.28 (s, 3 H, CH$_3$, *p*-cym), 2.95 (sept, ^3J = 6.8 Hz, 1 H, C*H*(CH$_3$)$_2$), 4.86 (d, $^4J_{PH}$ = 3.0 Hz, 1 H, Ru=C=CH), 5.41 (d, ^3J = 5.5 Hz, 2 H, CH$_{ar}$, *p*-cym), 5.58 (d, ^3J = 5.5 Hz, 1 H, CH$_{ar}$, *p*-cym), 5.65 (d, ^3J = 5.5 Hz, 1 H, CH$_{ar}$, *p*-cym), 7.03 (d, ^3J = 8.2 Hz, 2 H, C_6H_4), 7.10 (d, ^3J = 8.2 Hz, 2 H, C_6H_4) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ 18.6 (CH$_3$, *p*-cym), 21.9, 22.0 (CH(*C*H$_3$)$_2$), 26.4 (CH$_2$, PCy$_3$), 27.7 (d, $^3J_{PC}$ = 3 Hz, CH$_2$, PCy$_3$), 27.8 (d, $^3J_{PC}$ = 3 Hz, CH$_2$, PCy$_3$), 28.9 (d, $^2J_{PC}$ = 24 Hz, CH$_2$, PCy$_3$), 31.3 (*C*H(CH$_3$)$_2$), 35.3 (d, $^1J_{PC}$ = 24 Hz, CH, PCy$_3$), 78.3, 78.7, 79.5, 80.2 (CH$_{ar}$, *p*-cym), 97.2, 101.3 (C$_{ar}$, *p*-cym), 113.5 (Ru=C=*C*), 126.8, 128.2, 129.3, 130.0 (C_6H_4), 353.6 (d, $^2J_{PC}$ = 19.4 Hz, Ru=C) ppm. ^{31}P NMR (101 MHz, CD_2Cl_2): δ 54.92 (s) ppm. IR (KBr): $\bar{\nu}$ 3071(w), 2924(s), 2849(m), 1619(s), 1585(m), 1489(m), 1090(m), 833(m), 486(m) cm^{-1}. Anal. Calcd for $C_{36}H_{52}Cl_5PRu_2$ (895.18): C, 48.30; H, 5.86. Found: C, 48.05; H, 5.86.

[(*p*-cymene)Ru(μ-Cl)$_3$RuCl(=C=CH−C_6H_4-4-CF$_3$)(PCy$_3$)] (9): red-brown solid (160 mg, 90% yield) obtained from 4-ethynyl-α,α,α-trifluorotoluene (40 μL, 381 μmol). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.12−1.35 (m, 9 H, PCy$_3$), 1.33 (d, ^3J = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.52−2.19 (m, 24 H, PCy$_3$), 2.25 (s, 3 H, CH$_3$, *p*-cym), 2.93 (sept, ^3J = 6.8 Hz, 1 H, C*H*(CH$_3$)$_2$), 4.91 (d, $^4J_{PH}$ = 3.2 Hz, 1 H, Ru=C=CH), 5.42 (d, ^3J = 5.5 Hz, 2 H, CH$_{ar}$, *p*-cym), 5.58 (d, ^3J = 5.5 Hz, 1 H, CH$_{ar}$, *p*-cym), 5.65 (d, ^3J = 5.5 Hz, 1 H, CH$_{ar}$, *p*-cym), 7.18 (d, ^3J = 8.0 Hz, 2 H, C_6H_4), 7.35 (d, ^3J = 8.0 Hz, 2 H, C_6H_4) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ 18.6 (CH$_3$, *p*-cym), 21.9, 22.0 (CH(*C*H$_3$)$_2$), 26.3 (CH$_2$, PCy$_3$), 27.7 (d, $^3J_{PC}$ = 4 Hz, CH$_2$, PCy$_3$), 27.8 (d, $^3J_{PC}$ = 4 Hz, CH$_2$, PCy$_3$), 28.9 (d, $^2J_{PC}$ = 20 Hz, CH$_2$, PCy$_3$), 31.3 (*C*H(CH$_3$)$_2$), 35.2 (d, $^1J_{PC}$ = 23 Hz, CH, PCy$_3$), 78.3, 78.8, 79.6, 80.2 (CH$_{ar}$, *p*-cym), 97.2, 101.3 (C$_{ar}$, *p*-cym), 113.6 (Ru=C=*C*), 124.7 (q, $^1J_{CF}$ = 270 Hz, CF$_3$), 125.0 (q, $^3J_{CF}$ = 4 Hz, C_6H_4), 125.2 (C_6H_4), 125.7 (q, $^2J_{CF}$ = 33 Hz, *C*-CF$_3$), 136.7 (C_6H_4), 351.1 (d, $^2J_{PC}$ = 19 Hz, Ru=C) ppm. ^{31}P NMR (101 MHz, CD_2Cl_2): δ 54.84 (s) ppm. IR (KBr): $\bar{\nu}$ 3066(w), 2928(s), 2851(m), 1625(m), 1600(s), 1446(m), 1323(s), 1160(m), 1116(m), 1065(m), 845(m) cm^{-1}. Anal. Calcd for $C_{37}H_{52}Cl_4F_3PRu_2$ (928.73): C, 47.85; H, 5.64. Found: C, 47.13; H, 5.58.

[(*p*-cymene)Ru(μ-Cl)$_3$RuCl{=C=CH−C_6H_3-3,5-(CF$_3$)$_2$}(PCy$_3$)] (10): orange solid (158 mg, 83% yield) obtained from 4-ethynyl-3,5-bis(trifluoromethyl)benzene (67 μL, 381 μmol). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.05−1.30 (m, 12 H, PCy$_3$), 1.34 (d, ^3J = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.50−1.75 (m, 14 H, PCy$_3$), 1.80−1.95 (m, 4 H, PCy$_3$), 2.14 (q, ^3J = 11.9 Hz, 3 H, PCy$_3$), 2.26 (s, 3 H, CH$_3$, *p*-cym), 2.95 (sept, ^3J = 6.9 Hz, 1 H, C*H*(CH$_3$)$_2$), 5.01 (d, $^4J_{PH}$ = 3.3 Hz, 1 H, Ru=C=CH), 5.41 (m, 2 H, CH$_{ar}$, *p*-cym), 5.58 (d, ^3J = 5.8 Hz, 1 H, CH$_{ar}$, *p*-cym), 5.67 (d, ^3J = 5.8 Hz, 1 H, CH$_{ar}$, *p*-cym), 7.38 (s, 1 H, C_6H_3), 7.58 (s, 2 H, C_6H_3) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ 18.4 (CH$_3$, *p*-cym), 21.9, 22.0 (CH(*C*H$_3$)$_2$), 26.3 (CH$_2$, PCy$_3$), 27.7 (d, $^3J_{PC}$ = 3 Hz, CH$_2$, PCy$_3$), 27.8 (d, $^3J_{PC}$ = 3 Hz, CH$_2$, PCy$_3$), 28.9 (d, $^2J_{PC}$ = 35.5 Hz, CH$_2$, PCy$_3$), 31.3 (*C*H(CH$_3$)$_2$), 35.3 (d, $^1J_{PC}$ = 24.3 Hz, CH, PCy$_3$), 78.4, 78.7, 79.4, 80.2 (CH$_{ar}$, *p*-cym), 97.3, 101.4 (C$_{ar}$, *p*-cym), 113.2 (Ru=C=*C*), 126.8, 128.2, 129.3, 130.0 (C_6H_3), 348.5 (d, $^2J_{PC}$ = 18.6 Hz, Ru=C) ppm. ^{31}P NMR (101 MHz, CD_2Cl_2): δ 55.43 (s) ppm. IR (KBr): $\bar{\nu}$ 3067(w), 2930(m), 2852(m), 1622(m), 1598(s), 1447(m), 1376(s), 1277(s), 1176(s), 1131(s), 681(m) cm^{-1}. Anal. Calcd for $C_{38}H_{51}Cl_4F_6PRu_2$ (996.73): C, 45.79; H, 5.16. Found: C, 45.48; H, 5.18.

Microwave-Assisted Synthesis of [(*p*-cymene)Ru(μ-Cl)$_3$RuCl(=C=CH−C_6H_5)(PCy$_3$)] (5). A 10 mL pressure vial equipped with a magnetic stirring bar and capped with a septum was charged with [RuCl$_2$(*p*-cymene)]$_2$ (**1**) (120 mg, 196 μmol), tricyclohexylphosphine (55 mg, 196 μmol, 1 equiv), phenylacetylene (33 μL, 300 μmol, 1.5 equiv), and dichloromethane (3 mL). The reaction mixture was heated for 15 min at 105 °C under stirring in a microwave reactor with a 150 W maximum power. After cooling to room temperature, the solvent was removed on a rotary evaporator. The residue was washed with *n*-pentane (3 × 3 mL) and dried under high vacuum. Complex **5** was isolated as an orange-brown solid (156 mg, 93%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.08−1.29 (m, 9 H, PCy$_3$), 1.35 (t, ^3J = 6.6 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.45−1.79 (m, 15 H, PCy$_3$), 1.89 (m, 6 H, PCy$_3$), 2.14 (q, ^3J = 11.6 Hz, 3 H, PCy$_3$), 2.28 (s, 3 H, CH$_3$, *p*-cym), 2.95 (sept, ^3J = 6.8 Hz, 1 H, C*H*(CH$_3$)$_2$), 4.87 (d, $^4J_{PH}$ = 3.2 Hz, 1 H, Ru=C=CH), 5.42 (s, 2 H, CH$_{ar}$, *p*-cym), 5.59 (d, ^3J = 5.6 Hz, 1 H, CH$_{ar}$, *p*-cym), 5.66 (d, ^3J = 5.6 Hz, 1 H, CH$_{ar}$, *p*-cym), 6.92

(t, ^3J = 6.8 Hz, 1 H, *p*-CH, Ph), 7.07 (d, ^3J = 7.6 Hz, 2 H, *o*-CH, Ph), 7.15 (t, ^3J = 7.2 Hz, 2 H, *m*-CH, Ph) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ 18.6 (CH_3, *p*-cym), 21.8, 22.0 ($CH(CH_3)_2$), 26.3 (CH_2, PCy_3), 27.6 (d, $^3J_{PC}$ = 4 Hz, CH_2, PCy_3), 27.7 (d, $^3J_{PC}$ = 4 Hz, CH_2, PCy_3), 28.9 (d, $^2J_{PC}$ = 26 Hz, CH_2, PCy_3), 31.2 ($CH(CH_3)_2$), 35.2 (d, $^1J_{PC}$ = 24 Hz, CH, PCy_3), 78.3, 78.8, 79.6, 80.2 (CH_{ar}, *p*-cym), 97.1, 101.1 (C_{ar}, *p*-cym), 114.0 (Ru=C=*C*), 124.5, 125.5, 128.1, 131.1 (C_6H_5), 355.0 (d, $^2J_{PC}$ = 19.4 Hz, Ru=C) ppm. ^{31}P NMR (101 MHz, CD_2Cl_2): δ 54.21 (s) ppm. IR (KBr): $\bar{\nu}$ 3073(w), 3053(w), 2929(s), 2849(m), 1621(s), 1593(s), 1491(m), 1445(m), 1376(s), 1004(w), 756(m) cm^{-1}. Anal. Calcd for $C_{36}H_{53}Cl_4PRu_2$ (860.73): C, 50.23; H, 6.21. Found: C, 50.23; H, 6.30.

X-ray Crystallographic Studies. Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of cyclohexane into a CH_2Cl_2 solution of complexes **6**−**10**. Crystal data were collected on a Bruker APPEX II diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) from a fine-focus sealed tube source at 100 K (d = 0.95 Å for complexes **6** and **9**). Computing data and reduction was made with the APPEX II software.[46] The structure was solved using DIRDIF[47] and finally refined by full-matrix, least-squares based on F^2 by SHELXL.[48] An empirical absorption correction was applied using SADABS.[49] All non-hydrogen atoms were anisotropically refined, and the hydrogen atom positions were calculated and refined using a riding model. A highly disordered distribution of solvent around the inversion center in complex **6** was eliminated with SQUEEZE.[50] More details on the crystals, data collection parameters, and structure refinements are given in the Supporting Information.

Typical Procedure for the ROMP of Norbornene. A 50 mL round-bottom flask equipped with a magnetic stirring bar and capped with a three-way stopcock was charged with a homobimetallic ruthenium complex (15 μmol). Air was expelled by applying three vacuum/argon cycles before dry chlorobenzene (10 mL) and a 1.5 M solution of norbornene in chlorobenzene (2.5 mL, 3.75 mmol) were added with dried syringes under argon. The reaction mixture was stirred for 2 h in an oil bath at 60 °C. The conversion was monitored by gas chromatography using norbornane as an internal standard. The resulting gel was diluted with chloroform (2 × 10 mL) and slowly poured into methanol (500 mL) under vigorous stirring. The precipitated polynorbornene was filtered with suction, dried overnight under dynamic vacuum, and characterized by SEC and NMR.

Typical Procedure for the ROMP of Cyclooctene. A 10 mL pressure vial equipped with a magnetic stirring bar and capped with a septum was charged with a homobimetallic ruthenium complex (7.5 μmol). Air was expelled by applying three vacuum/argon cycles before dry chlorobenzene (2.5 mL) and cyclooctene (0.5 mL, 3.75 mmol) were added with dried syringes under argon. The reaction mixture was heated for 2 h at 140 °C under stirring in a microwave reactor with a 300 W maximum power. The conversion was monitored by gas chromatography using the cyclooctane impurity of cyclooctene as internal standard. The resulting gel was diluted with chloroform (10 mL) and slowly poured into methanol (250 mL) under vigorous stirring. The precipitated polyoctenamer was filtered with suction, dried overnight under dynamic vacuum, and characterized by SEC and NMR.

Alternatively, a 25 mL round-bottom flask equipped with a magnetic stirring bar and capped with a three-way stopcock was charged with a homobimetallic ruthenium complex (7.5 μmol) and a Lewis acid (7.5 μmol). Air was expelled by applying three vacuum/argon cycles before dry chlorobenzene (2.5 mL) and cyclooctene (0.5 mL, 3.75 mmol) were added with dried syringes under argon. The reaction mixture was stirred for 2 h in an oil bath at 60 °C. Analyses and workup were carried out as described above.

Self-Metathesis of Styrene. A homobimetallic ruthenium complex (4 μmol) and anhydrous aluminum chloride (1.1 mg, 8 μmol) were placed in a 15 mL Schlenk tube containing a magnetic stirring bar and capped with a septum. Air was expelled by three vacuum/argon cycles before 2 mL of a styrene solution (1 M in toluene, 2 mmol) was added with a dried syringe under argon. The reaction mixture was heated for 2 h in an oil bath at 85 °C under inert atmosphere. The conversion was monitored by gas chromatography using *n*-dodecane as internal standard.

RCM of Diethyl 2,2-Diallylmalonate. A homobimetallic ruthenium complex (4 μmol) was placed in a 15 mL Schlenk tube containing a magnetic stirring bar and capped with a septum. Air was expelled by three vacuum/argon cycles before 2 mL of a diethyl 2,2-diallylmalonate solution (0.1 M in toluene, 0.2 mmol) possibly containing 6 mol % of phenylacetylene was added with a dried syringe under argon. The reaction mixture was stirred in an oil bath at 85 °C. Conversion was monitored by GC using *n*-dodecane as internal standard.

Reaction of Complex 5 with $AlCl_3$. An NMR tube capped with a septum was charged with [(*p*-cymene)Ru(μ-Cl)$_3$RuCl(=C=CH−C_6H_5)(PCy_3)] (**5**) (28.4 mg, 33 μmol) and CD_2Cl_2 (0.6 mL) under Ar. A stock solution prepared by dissolving $AlCl_3$ (36.3 mg, 272 μmol) in CD_3CN (0.5 mL) was added in 20 μL portions with a microsyringe, and the reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy at 25 °C. The mixture obtained upon addition of 80 μL of stock solution (1.3 equiv of $AlCl_3$) was also analyzed by ESI-MS in toluene.

Acknowledgment. The financial support of the "Fonds de la Recherche Scientifique−FNRS", Brussels, is gratefully acknowledged for the purchase of major instrumentation. We thank Mr. Dario Bicchielli for his help with the synthesis and characterization of complex **6**, Ms. Itziar Otazo Aseguinolaza, Ms. Radostina Kalinova, and Mr. Alexandre Herman for their help with the ROMP catalytic tests, and Prof. Christo Jossifov (Institute of Polymers, Bulgarian Academy of Sciences) for stimulating discussions.

Supporting Information Available: Crystal data, detailed comparison of bond lengths and angles, and an X-ray crystallographic file in CIF format for complexes **6**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[46] *APPEX II*; Bruker AXS Inc.; Madison, WI, USA, 2004.

[47] Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Smits, J. M. M.; Garcia-Granda, S.; Gould, R. O. *DIRDIF-2007*; Radboud University: Nijmegen (The Netherlands), 2007.

[48] Sheldrick, G. M. *SHELX-97* (*SHELXS 97 and SHELXL 97*), *Programs for Crystal Structure Analyses*; University of Göttingen: Göttingen (Germany), 1998.

[49] Sheldrick, G. M. *SADABS, Programs for Scaling and Correction of Area Detection Data*; University of Göttingen: Göttingen (Germany), 1996.

[50] van der Sluis, P.; Spek, A. L. *Acta Crystallogr. Sect. A: Found. Crystallogr.* **1990**, *46*, 194–201.