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Homobimetallic Ruthenium Vinylidene, Allenylidene, and Indenylidene Complexes: Synthesis, Characterization, and Catalytic Studies

Xavier Sauvage,[a] Yannick Borguet,[a] Guillermo Zaragoza,[b] Albert Demonceau,[a] and Lionel Delaude[a,*]

[a] Center for Education and Research on Macromolecules, Institut de Chimie (B6a), Université de Liège, Sart-Tilman par 4000 Liège, Belgium
Fax: (+32)-4-366-3497; e-mail: l.delaude@ulg.ac.be
[b] Unidade de Difracción de Raios X, Edificio CACTUS, Universidade de Santiago de Compostela, Campus Sur, 15782 Santiago de Compostela, Spain

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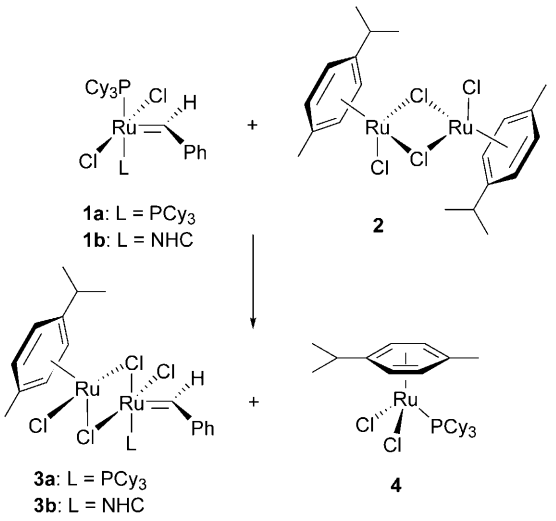
Abstract: Four homobimetallic ruthenium-(*p*-cymene) complexes bearing a tricyclohexylphosphine ligand and polyunsaturated carbon-rich fragments were obtained *via* a vinylidene-allenylidene-indenylidene cascade pathway from the ethylene complex $[(p\text{-cymene})Ru(\mu\text{-}Cl)_3RuCl(PCy_3)(\eta^2\text{-}C_2H_4)]$ (**7a**). All the products were isolated and fully characterized by IR and NMR spectroscopies. The molecular structure of the indenylidene complex **11** was determined by X-ray crystallographic analysis. The catalytic activity of the four complexes was probed in various types of olefin metathesis reactions and compared with those of a related homobimetallic ruthenium-benzylidene complex, as well as first, second, and third generation monometallic Grubbs catalysts. In the ring-closing metathesis (RCM) of diethyl diallylmalonate, the homobimetallic ruthenium-indenylidene complex **11** outperformed all the ruthenium-benzylidene complexes under investigation and was only slightly less efficient than its monometallic parent. Cross-metathesis experiments with ethylene showed that deactivation of ruthenium-benzylidene or indenylidene complexes was due to the rapid bimolecular decomposition of methylidene active species into ethylene complex **7a**. Vinylidene and allenylidene complexes were far less efficient catalyst precursors for ring-opening metathesis polymerization (ROMP) or RCM and remained inert under an ethylene atmosphere. Their catalytic activity was, however, substantially enhanced upon addition of an acidic co-catalyst that most likely promoted their *in situ* transformation into indenylidene species. Due to its straightforward synthesis and high metathetical activity, homobimetallic ruthenium-indenylidene complex **11** is a valuable intermediate for the preparation of the Hoveyda–Grubbs catalyst $[Cl_2Ru(PCy_3)(=CH\text{-}o\text{-}O\text{-}i\text{-}PrC_6H_4)]$ *via* stoichiometric cross-metathesis with 2-isopropoxystyrene. The procedure did not require any sacrificial phosphine and the transition metal not incorporated into the final product was easily recovered and recycled at the end of the process.

Keywords: alkenes; arene ligands; bridging ligands; catalyst design; metathesis; propargylic alcohols

Introduction

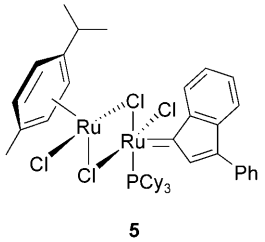
Owing to the advent of highly efficient, well-defined ruthenium catalysts, olefin metathesis has emerged as a powerful tool for assembling unsaturated hydrocarbon backbones in organic synthesis and in polymer chemistry.[1] Most catalytic systems investigated so far derive from the Grubbs first generation ruthenium-benzylidene complex $[RuCl_2(=CHPh)(PCy_3)_2]$ (**1a**) (PCy_3 is tricyclohexylphosphine).[2] Countless structural alterations have been made to this archetypal compound in order to tailor its activity,[3,4] stability,[5,6] solubility,[7] recoverability,[8] or latency[9] toward specific catalytic processes,[10] sometimes in an asymmetric fashion.[11] Although a single ruthenium center is preserved in most cases, a few homo- and heterobimetallic species have also been described. In a seminal contribution from 1998, Grubbs et al. reported the grafting of a second metal onto **1a** by reacting it with transition metal dimers containing bridging chloride ligands.[12] In particular, the $[RuCl_2(p\text{-cymene})]_2$ dimer (**2**) was reacted with complex **1a** to afford complex **3a** and a stoichiometric amount of by-product **4** (Scheme 1). In 1999, Herrmann and co-workers ex-

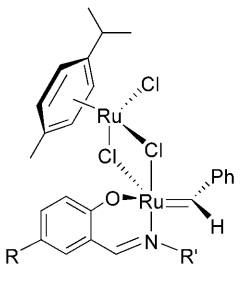


Scheme 1. Synthesis of homobimetallic ruthenium-benzylidene complexes **3a**, **b**.

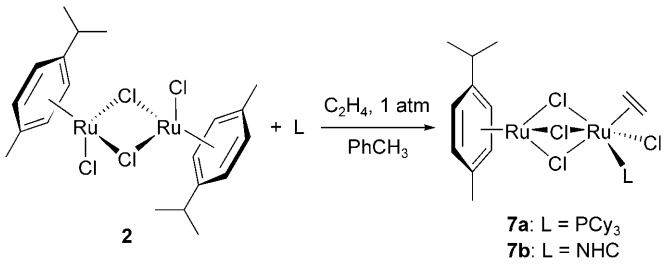
tended this methodology to the synthesis of bimetallic ruthenium-alkylidene complex **3b** bearing an N-heterocyclic carbene (NHC) instead of a phosphine ancillary ligand (Scheme 1).[13–16] In both complexes **3a** and **3b**, the presence of *two* μ-chloro bridges was postulated by analogy with the structure of the parent dimer **2**, but no crystal structure was determined to support this assumption.

A related homobimetallic complex obtained by reacting the ruthenium-arene dimer **2** with a monometallic adduct generated by treating $[RuCl_2(PPh_3)_3]$ with 1,1-diphenylpropargyl alcohol followed by phosphine exchange with PCy_3 was also investigated by Hill and Fürstner in 1999.[17,18] It was initially assumed to contain an *allenylidene* fragment. However, subsequent work from the groups of Nolan[19] and Fürstner[20] showed that this compound actually involved a ruthenium-*indenylidene* moiety formed by intramolecular rearrangement (see structure **5**). In yet another variation, Verpoort et al. prepared a series of homobimetallic ruthenium-benzylidene complexes bearing bidentate Schiff base ligands **6**.[21] Concomitant formation of ruthenium-arene complex **4** occurred in all cases.





R = H, NO_2 R' = Me, Aryl



Scheme 2. Synthesis of homobimetallic ruthenium-ethylene complexes **7a**, **b**.

In 2005, Severin and co-workers investigated the reaction of $[RuCl_2(p\text{-cymene})]_2$ with 1 equivalent of PCy_3 under an ethylene atmosphere. Under these conditions, the ruthenium-(*p*-cymene) dimer **2** afforded a new type of molecular scaffold **7a**, in which an $RuCl(\eta^2\text{-}C_2H_4)(PCy_3)$ fragment was connected *via three* μ-chloro bridges to a ruthenium-arene moiety, as evidenced by X-ray diffraction analysis (Scheme 2).[22] The only by-product formed was one equivalent of *p*-cymene. In view of the enhancements brought by the replacement of phosphines with NHCs in monometallic ruthenium-arene catalyst precursors for olefin metathesis[23,24] and atom transfer radical reactions,[25] we adopted the same strategy to synthesize two new homobimetallic complexes of type **7b** bearing NHCs instead of phosphine ligands.[26] Catalytic tests showed that the replacement of PCy_3 with carbene ligands induced a major shift of reactivity. Indeed, complexes **7b** were found to be highly suitable for promoting olefin metathesis, whereas complex **7a** was essentially inactive under the same experimental conditions. Results from this study also indicated that the ethylene ligand was highly labile and that adding a small amount of terminal alkyne to the reaction media had a beneficial influence on the metathetical activity.[26] These observations prompted us to further investigate the role of the alkyne co-catalyst.

In this contribution, we explore the chemistry of new homobimetallic ruthenium-arene complexes bearing vinylidene, allenylidene, and indenylidene ligands prepared from complex **7a** and propargyl alcohol derivatives. We also compare their catalytic activities toward several types of olefin metathesis reactions and we show that they are valuable intermediates for the safe and efficient one-pot synthesis of the Hoveya–Grubbs alkoxybenzylidene catalyst $[Cl_2Ru(PCy_3)(=CH\text{-}o\text{-}O\text{-}i\text{-}PrC_6H_4)]$.

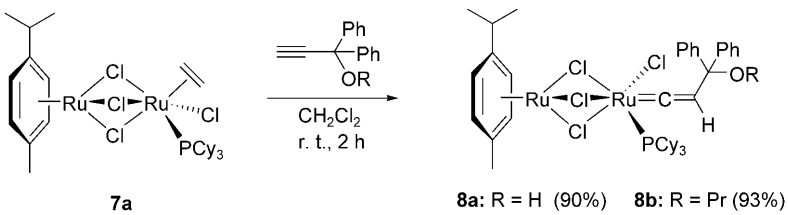
Results and Discussion

Synthesis and Characterization of Homobimetallic Ruthenium Complexes

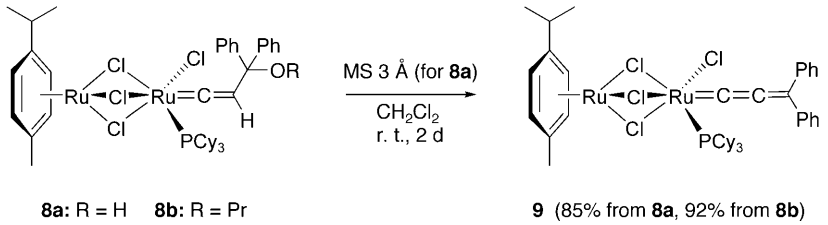
By analogy with the preparation of monometallic ruthenium-alkylidene complexes bearing the metathetically active Ru=CH−CH=CPh$_2$ or Ru=CHPh moieties from [RuCl$_2$(PPh$_3$)$_3$] and 1,1-diphenyl-2-cyclopropene[27] or phenyldiazomethane,[2] respectively, we first investigated the reaction of homobimetallic ruthenium-ethylene complex **7a** with these two carbene precursors. Preliminary experiments along these lines were conducted in dichloromethane at room temperature. Disappointingly, there was no sign of evolution after a few hours and only unidentified decomposition products were detected by ^{31}P NMR spectroscopy when the reaction media were kept for longer periods of time. We then turned our attention to the use of propargylic alcohol derivatives, since they are well known to afford polyunsaturated carbon-rich ligands by reaction with ruthenium centers.[17–20,28,29] Thus, complex **7a** was reacted with a small excess of 1,1-diphenyl-2-propyn-1-ol in dichloromethane at room temperature (Scheme 3). Within 2 h, a clean and quantitative reaction had occurred, as evidenced by the disappearance of the initial phosphine resonance at 44.3 ppm and the emergence of a new signal located at 54.4 ppm in CH_2Cl_2 spiked with CD_2Cl_2. After solvent evaporation and washing, homobimetallic ruthenium-vinylidene complex **8a** was isolated in 90% yield. Apart from its ^{31}P NMR signature, characteristic spectroscopic features included a sharp line at 1645 cm^{-1} ($\nu_{C=C}$) and a broad absorption centered at 3416 cm^{-1} (ν_{OH}) on IR spectroscopy, a doublet at 4.78 ppm with a coupling constant $^4J_{P,H}$ = 3.5 Hz for the vinylidene proton on ^{1}H NMR spectroscopy, and a highly deshielded doublet at 345.9 ppm with a coupling constant $^2J_{P,C}$ = 18.1 Hz for the Ru=C carbon nucleus on ^{13}C NMR.

Inspired by a report from Dixneuf et al. who showed that the reaction of allyl or propyl propargylic ethers with cationic ruthenium-arene complexes proceeded *via* retro-ene cleavage to afford monometallic alkenyl-carbene-ruthenium species,[30] we decided to investigate the reaction of complex **7a** with 1,1-diphenylpropynyl *n*-propyl ether. This substrate was prepared by alkylation of 1,1-diphenylpropynol with *n*-bromopropane in the presence of sodium hydride according to standard procedures.[30–32] At room temperature in dichloromethane, its reactivity toward ruthenium-ethylene complex **7a** closely matched the one observed with 1,1-diphenylpropynol and resulted in the formation of vinylidene complex **8b** in almost quantitative yield (Scheme 3). Spectroscopic evidence for an Ru=C=CHR unit included a sharp, medium-intensity IR band at 1669 cm^{-1} ($\nu_{C=C}$) and a doublet at 4.00 ppm with a coupling constant $^4J_{P,H}$ = 3.8 Hz for the vinylidene proton. The α-carbon atom resonated as a doublet with a coupling constant $^2J_{P,C}$ = 16.5 Hz in ^{13}C{^{1}H} NMR and was located much further downfield (339.5 ppm) than the C$_\beta$ remote end (s, 110.3 ppm). In ^{31}P{^{1}H} NMR, a unique singlet was observed at 54.0 ppm.

Extended ^{31}P NMR monitoring revealed that dichloromethane solutions of complexes **8a**, **b** were not fully stable at room temperature. Hence, ^{13}C NMR experiments that required overnight acquisitions were performed at −40 °C. At this temperature, however, carbon atoms coupled to the phosphorus nucleus displayed significantly broadened peaks. Signs for a slow albeit irreversible transformation were most visible for complex **8b** that spontaneously expelled *n*-propanol to afford homobimetallic ruthenium-allenylidene complex **9** after 2–4 days (Scheme 4). The exact duration necessary to achieve a full conversion varied from one experiment to another and is most likely influenced by the presence of acidic trace impurities that could assist the departure of the propoxide group. Yet, the reaction proceeded cleanly and complex **9** was isolated in almost quantitative yield by simple filtration and washing. Support in favour of an allenylidene group came from the presence of a $\nu_{C=C=C}$ absorption at 1918 cm^{-1} on IR spectroscopy and three ^{13}C{^{1}H} characteristic resonances for the Ru=C=C=CPh$_2$ spine located at 301.5, 237.3, and 147.1 ppm, the former being a doublet with a coupling constant $^2J_{P,C}$ = 18.1 Hz in CD_2Cl_2 at 25 °C. Moreover, both ^{1}H and ^{13}C NMR spectra showed that the two phenyl rings were equivalent. Thus, we were eventually able to isolate the homobimetallic ruthenium-allenylidene complex initially postulated by Hill and Fürstner in 1999,[17,18] although subsequent studies



Scheme 3. Synthesis of homobimetallic ruthenium-vinylidene complexes **8a**, **b**.



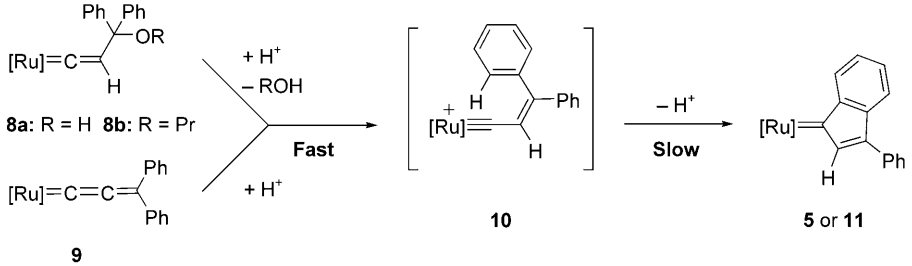
Scheme 4. Synthesis of homobimetallic ruthenium-allenylidene complex **9**.

proved that these authors actually had obtained the phenylindenylidene species depicted as **5** instead.[20]

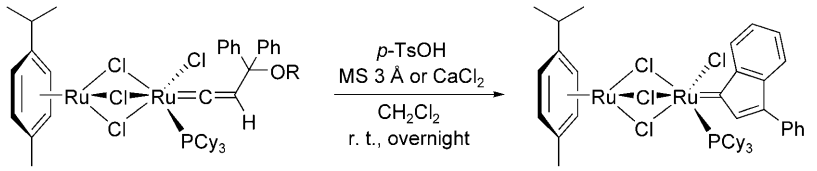
In the case of γ-hydroxyvinylidene complex **8a**, slow conversion into allenylidene product **9** was also observed in dichloromethane at room temperature (Scheme 4). Under these conditions, the dehydration was, however, accompanied by side-reactions leading to unidentified by-products and was therefore of little synthetic value. Since we suspected the released water to be responsible for this mischief, we first tried to percolate a dichloromethane solution of complex **8a** through a short column packed with acidic alumina. Unfortunately, due to the strong affinity of product **9** towards the stationary phase, elution was largely inefficient and only poor yields were attained. Trapping water with molecular sieves 3 Å proved to be a much more satisfactory strategy. In the presence of this drying agent, 2 days were still necessary to achieve a full conversion of vinylidene complex **8a** into allenylidene product **9**, but the isolated yield climbed to 85% and side-reactions were suppressed.

Detailed mechanistic studies by the groups of Dixneuf[33] and Schanz[29] have recently highlighted the role of acids on the rearrangement of allenylidene units into indenylidene groups in various monometallic ruthenium complexes, either neutral or cationic. These findings prompted us to investigate the reaction of homobimetallic ruthenium-allenylidene complex **9** with a stoichiometric amount of trifluoroacetic acid. Upon addition of the acid to the complex dissolved in CD_2Cl_2 at −50 °C, an instantaneous colour change from dark red to yellow occurred and the $^{31}P\{^1H\}$ NMR absorption of **9** located at 54.1 ppm was replaced by a new downfield signal at 68.0 ppm. These observations strongly suggest the formation of a cationic ruthenium-carbyne complex (**10**) (Scheme 5). This intermediate remained stable for several hours in CD_2Cl_2 at −50 °C but quickly decomposed into a complex mixture of unidentified products upon warming to room temperature, thereby precluding its isolation and full characterization. ^1H and $^{13}C\{^1H\}$ NMR spectra recorded at −50 °C were difficult to interpret, due to line broadening and poor signal-to-noise ratio. It was nevertheless possible to identify a doublet at 6.24 ppm with a coupling constant $^4J_{P,H} = 2.0$ Hz in ^1H NMR and a doublet at 311.3 ppm with a coupling constant $^2J_{P,C} = 23.6$ Hz in $^{13}C\{^1H\}$ NMR for the Ru≡C–CH motif.

Addition of 1 equivalent of trifluoroacetic acid to a cold CD_2Cl_2 solution of ruthenium-vinylidene complexes **8a**, **b** led to the same experimental observations that were made starting from allenylidene derivative **9** and also pointed to the instant formation of carbyne complex **10** (Scheme 5). The only difference was the presence of supplementary peaks due to H_2O (for **8a**) or *n*-PrOH (for **8b**) in the ^1H NMR spectra. In the latter case, integration of the various ^1H signals confirmed the quantitative release of 1 equivalent of alcohol. The formation of *n*-PrOH was also evidenced by ^{13}C NMR spectroscopy. Due to the rapidity of the transformation, no evidence for the transient formation of allenylidene complex **9** was detected, although it cannot be ruled out. Once again, the labile intermediate **10** observed at −50 °C did not persist at room temperature and led to several unidentified products upon decomposition. When a small amount of anhydrous calcium chloride was added to the NMR tube containing a CD_2Cl_2 solution of complex **8a** or **8b** at −50 °C prior to the introduction of trifluoroacetic acid and warming to room temperature,



Scheme 5. Proposed reaction path for the formation of indenylidene complexes **5** or **11**.



Scheme 6. Synthesis of homobimetallic ruthenium-indenylidene complex **11**.

however, a cleaner reaction slowly occurred, as shown by the progressive replacement of the ^{31}P signal at 68.0 ppm by a single new line at 41.1 ppm. This resonance had previously been assigned to the ruthenium-indenylidene complex **5** (Scheme 5).[17] Thus, addition of a drying agent effectively prevented side-reactions and nicely complemented the recourse to an acidic promoter for inducing a direct vinylidene-to-indenylidene interconversion.

When performing the transformation on a somewhat larger scale, we successfully employed *para*-toluenesulfonic acid monohydrate as acidic promoter (Scheme 6). This solid reagent was found more convenient to handle and to weigh precisely than trifluoroacetic acid. We also employed molecular sieves 3 Å as dehydrating agent instead of calcium chloride when starting from hydroxy compound **8a**. Reaction mixtures were stirred overnight in dichloromethane at room temperature. Homobimetallic ruthenium-indenylidene complex **11** was isolated in 86–87% yield from both **8a**, **b** after filtration and work-up. Its IR and NMR spectra were identical to those reported earlier in the literature for complex **5**.[17,20] Distinctive absorption bands for the indenylidene group were observed at 1947 and 1621 cm^{-1} on IR spectroscopy, while the Ru=C carbon atom gave a doublet at 309.7 ppm with a coupling constant $^2J_{P,C} = 15.4$ Hz in $^{13}C\{^1H\}$ NMR.

Structural Analysis of Complex 11

Solid state analysis of complex **11** by X-ray crystallography confirmed that the (*p*-cymene)Ru unit was indeed connected to the Ru(Cl)(PCy_3)(indenylidene) fragment *via* three μ-chloro bridges (Figure 1). A typical piano stool geometry was observed for the (arene)$RuCl_3$ moiety, with three Ru–Cl bonds of almost equal lengths (2.41–2.44 Å). The other ruthenium atom lay in a highly distorted octahedral environment with Ru–Cl bond lengths varying between 2.44 and 2.67 Å for the three face-bridging chloro ligands, whereas the fourth terminal halogen was located much closer to the metal center at a 2.3604(10) Å distance. The Ru=C distance between the metal and the indenylidene fragment [1.874(3) Å] was similar to those observed in monometallic complexes bearing phosphine[34] or NHC ligands.[19] From these data, it can be inferred that the genuine structure of compound **5** actually involved a ruthenium-*indenylidene* moiety linked *via three* μ-chloro bridges to the second metal center. The structure of homobimetallic ruthenium-benzylidene complexes **3a**, **b** should probably also be revised to account for the presence of three bridging chlorine atoms instead of two, but we have not been able to obtain X-ray crystal structures to support this assumption yet.

The profound influence exerted by the indenylidene ligand on the chloro atom *trans* to it is responsible for the significantly longer Ru2–Cl3 distance [2.6657(10) Å] compared with other Ru–Cl bonds in the crystal structure of complex **11**. All these measurements are in line with those recorded previously by Severin et al. for various other homobimetallic ruthenium-arene complexes bearing three μ-chloro bridges.[22,35] Based on the data acquired by the Swiss group, the *trans* effect of the indenylidene unit in complex **11** may be ranked slightly superior to that of

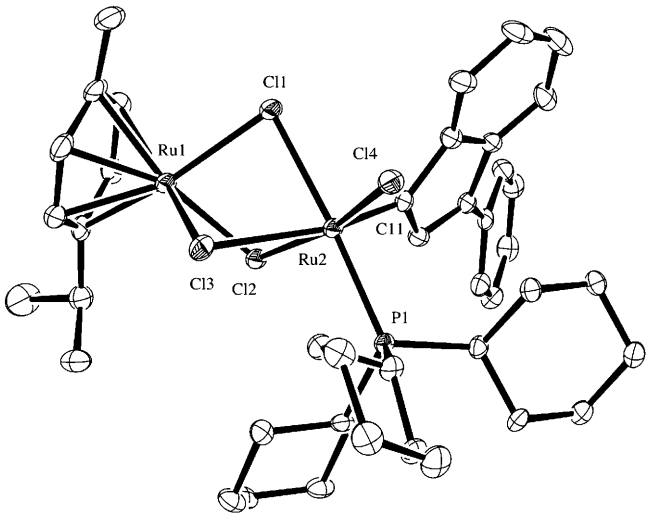


Figure 1. ORTEP representation of complex **11** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for the sake of clarity. Selected bond lengths [Å] and angles [deg]: Ru1–Cl1 2.4375(9), Ru1–Cl2 2.4352(9), Ru1–Cl3 2.4124(11), Ru2–P1 2.3473(9), Ru2–Cl1 2.5044(10), Ru2–Cl2 2.4436(10), Ru2–Cl3 2.6658(10), Ru2–Cl4 2.3604(10), Ru2–C11 1.874(3); Cl3–Ru2–C11 162.28(8),Cl2–Ru2–Cl4 167.99(2), P1–Ru2–Cl4 88.87(3).

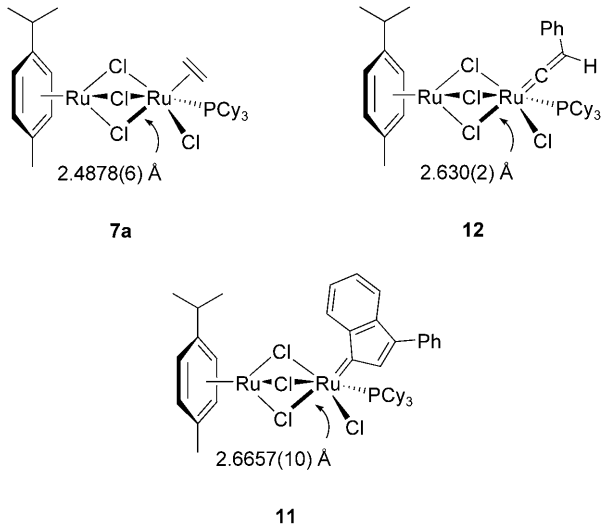


Figure 2. Trans effect of various carbon-rich ligands in homobimetallic ruthenium-arene complexes (data for complexes **7a** and **12** from refs.[22,35b] respectively).

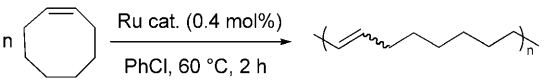
a vinylidene group and considerably higher than the one exerted by the ethylene ligand in complex **7a** (Figure 2).

It should be pointed out that compound **11** is 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 μ-chloro bridges. Thus, only one pair of enantiomers was obtained as a racemic mixture. This observation also applied to precursors **8a**, **b** and **9**. Furthermore, all the homobimetallic complexes investigated in this study were configurationally stable on the NMR time scale. Indeed, the four aromatic protons on the *p*-cymene ligand were nonequivalent and resonated as four separate doublets. Likewise, the two methyl groups of the isopropyl side chain resolved as two separate doublets.

Catalytic Studies

Back in 1999, Herrmann and co-workers showed that bimetallic ruthenium-benzylidene complexes **3a**, **b** were more active catalysts for the ring-opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene than their monometallic counterparts. Thus, significantly higher rate constants were recorded with catalyst precursor **3b** ($k_{rel}=13$) and to a lesser extent with species **3a** ($k_{rel}=2.4$) compared to the monometallic first generation Grubbs catalyst **1a** ($k_{rel}=1$).[13] Various homo- and heterobimetallic ruthenium-alkylidene complexes were also successfully employed to promote the ROMP of cyclooctene and norbornene or norbornadiene derivatives,[16] the self-metathesis of *cis*-2-pentene,[12] and the ring-closing metathesis (RCM) of α,ω-dienes.[15,36] For this last application, they displayed excellent activities in the formation of tri- or even tetrasubstituted cycloalkene products, a performance that could not be achieved with the monometallic complex **1a**. In sharp contrast with these trends, homobimetallic ruthenium-indenylidene compound **5** (now **11**) was repeatedly found to be a less efficient catalyst than its monometallic parent in the ring-closing metathesis of several dienes.[18,20,37]

To the best of our knowledge, no literature data are available concerning the metathetical activity of homobimetallic ruthenium-vinylidene or -allenylidene species. Thus, we decided to probe the ability of complexes **8a**, **b** and **9** as catalyst precursors for the ROMP of cyclooctene [Eq. (1)]. In our laboratory,



(1)

this reaction serves as a benchmark to appraise new catalytic systems for olefin metathesis.[24,38] Polymerizations were carried out in chlorobenzene at 60 °C and the monomer-to-catalyst ratio was 250. For the sake of comparison, complexes **3a** and **11** were also tested under identical conditions. These two compounds displayed very similar behaviours (Table 1). Within 2 h, they both afforded a quantitative conversion of cyclooctene into high molecular weight polyoctenamer. Moreover, the polymers obtained had the same polydispersity index ($M_w/M_n=1.7$) and a predominantly *trans* double bond content ($\sigma_{cis}\cong 0.2$). In

Table 1. ROMP of cyclooctene catalyzed by various homobimetallic ruthenium complexes.[a]

Complex	*p*-TsOH	Monomer Conversion [%][b]	Yield [%]	10^{-3} M_n[c]	M_w/M_n[c]	σ_{cis}[d]
3a	–	>99	84	93	1.7	0.20
11	–	>99	89	114	1.7	0.22
8a	–	45	37	199	1.9	0.59
8b	–	70	60	138	2.4	0.56
9	–	63	48	88	1.8	0.58
8a	1 equiv.	>99	88	80	2.2	0.26
8b	1 equiv.	>99	91	75	2.0	0.24
9	1 equiv.	>99	89	95	2.1	0.24

[a] *Experimental conditions:* Ru complex (0.03 mmol), *p*-TsOH (0.03 mmol) and cyclooctene (7.5 mmol) in PhCl (5 mL) for 2 h at 60 °C.
[b] Determined by GC using the cyclooctane impurity of cyclooctene as an internal standard.
[c] Determined by GPC in THF with polystyrene calibration.
[d] Fraction of *cis* double bonds within the polyoctenamer, determined by ^{13}C NMR.

sharp contrast with these results, homobimetallic ruthenium-vinylidene and allenylidene complexes (**8a**, **b** and **9**) were far less efficient for the ROMP of cyclooctene. Isolated polymer yields did not exceed 60% after 2 h at 60 °C and very high molecular weight were reached in some instances, indicating that only few active species had been generated. More important, the unsaturated polyoctenamers contained a significantly higher proportion of *cis* double bonds ($\sigma_{cis} \cong 0.6$) than those obtained from catalyst precursors **3a** and **11**. This difference of microstructure denotes the intervention of two separate types of active species, depending on the nature of the carbon-rich ligand present on the precatalyst employed. Visual inspection of the reaction media sustained this dichotomy. The benzylidene and indenylidene complexes led to orange solutions – believed to contain alkylidene active species – that quickly jellified, whereas the vinylidene and allenylidene catalyst precursors gave a dark red colouration when dissolved with the cycloolefin monomer in chlorobenzene at 60 °C. Although their viscosity progressively increased, these solutions remained fluid during the 2 h allowed for the polymerization to proceed. Noteworthily, monomer consumption kept increasing slowly even after they were quenched with chloroform containing traces of butylated hydroxytoluene (BHT).

During the course of their investigations on the ROMP of cyclooctene mediated by cationic ruthenium-allenylidene complexes, Dixneuf et al. had shown that polymerization rates were significantly enhanced by the addition of strong acids, such as trifluoromethanesulfonic acid.[33] This co-catalyst induced the intramolecular rearrangement of the allenylidene ligand into an indenylidene group, as discussed above (*cf.* Scheme 5). We have applied the same strategy to our benchmark reaction by adding a stoichiometric amount of *p*-toluenesulfonic acid monohydrate to homobimetallic ruthenium-vinylidene and allenylidene complexes **8a**, **b** and **9**. Results listed in Table 1 clearly demonstrated the validity of this approach. The acid effectively altered the course of the polymerization. Full monomer consumption occurred within 2 h at 60 °C and led to high yields of polyoctenamer containing mostly *trans* double bonds. This microstructure closely reflected the one observed when benzylidene or indenylidene complexes **3a** and **11** served as initiators. Besides, the orange colour of the reaction media also revealed that alkylidene active species had been formed in significant amounts from the vinylidene or allenylidene precursors. Thus, *p*-toluenesulfonic acid is a convenient protic source to activate vinylidene or allenylidene complexes *in situ* and the presence of crystallization water does not interfere with the catalytic system.

In order to better rank the catalytic activities of homobimetallic ruthenium complexes **3a**, **8a**, **9** and **11**

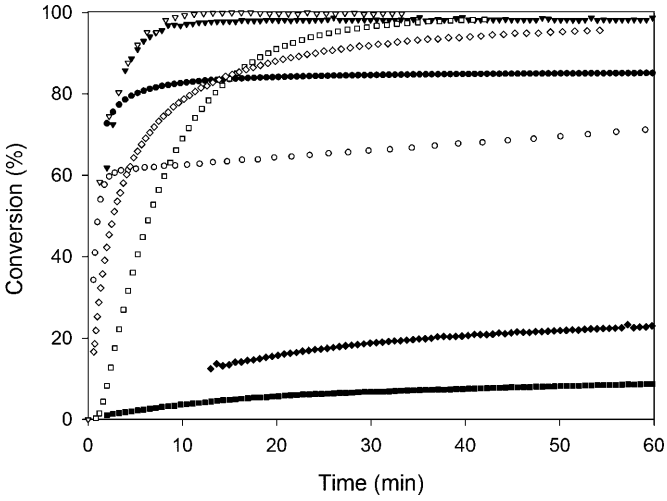
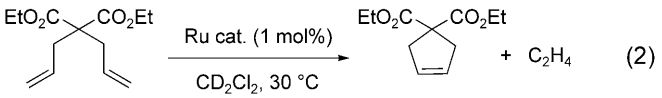


Figure 3. Time course of the RCM of diethyl 2,2-diallylmalonate using various mono- and bimetallic ruthenium catalysts (1 mol%) in CD_2Cl_2 at 30 °C (**1a**: ○, **3a**: ●, **8a**: ■, **9**: ◆, **11**: ▼, **13**: □, **14**: ◇, **15:** ▽).

and to compare them with common monometallic systems currently available, we have carried out the RCM of diethyl 2,2-diallylmalonate using a standard protocol defined by Grubbs and co-workers for evaluating olefin metathesis catalysts.[39] Thus, reactions were performed in CD_2Cl_2 at 30 °C using 1 mol% of catalyst and the conversion was monitored by ^1H NMR spectroscopy [Eq. (2)]. Under these conditions, homobimetallic ruthenium-indenylidene complex **11** turned out to be more efficient than its benzylidene analogue **3a**. Indeed, both species displayed a very similar high initial activity, but the conversion of diethyl diallylmalonate stopped at 85% with **3a** whereas precursor **11** afforded a 98% yield of the corresponding cyclopentene diester within 15 min (Figure 3). As expected, homobimetallic vinylidene and allenylidene precursors lagged farther behind, as shown for complexes **8a** and **9** that afforded the RCM product in 8 and 23% yields, respectively, after 60 min. However, these two catalyst precursors were also less sensitive to deactivation and conversions kept steadily increasing with time. Ultimately, a quantitative reaction was recorded with **8a** and **9** after 48 h at 30 °C.



To quantify the activities of the various complexes under scrutiny, we have determined the rate constants observed by assuming a first order behaviour in the RCM of diethyl 2,2-diallylmalonate (DEDAM) at

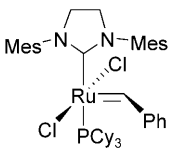
Table 2. Pseudo-first order rate constants observed for the RCM of diethyl 2,2-diallylmalonate catalyzed by various mono- and bimetallic ruthenium complexes at 30 °C.

Complex	k_{obs} [10^{-6} s^{-1}]	Reference
3a	9600	this work
11	8000	this work
8a	8	this work
9	77	this work
13	2200	[39]
14	4100[a]	[39]
15	9700	this work

[a] Value calculated for the first 50% of conversion.

30 °C. The formalism proposed by Grubbs et al. was employed to extract the rate constants from the plot of ln([DEDAM]) *vs.* time.[12,39,40] Based on the kinetic data obtained (Table 2), the activity of homobimetallic ruthenium catalysts **3a**, **8a**, **9** and **11** followed the order: indenylidene ≈ benzylidene ⩾ allenylidene > vinylidene.

Comparison of our results with previous work from the literature confirmed that homobimetallic ruthenium-benzylidene complex **3a** was more active than the first generation Grubbs catalyst **1a**[12] (Figure 3). It even displayed a higher initial activity than the second and third generation NHC-based ruthenium-alkylidene species **13**[4] and **14**.[41] However, its decomposition occurred more rapidly and prevented completion of the reaction. The accumulation of ethylene in the septum-capped NMR tube used to monitor the conversion is likely to play a key role in this degradation (*vide infra*), but carrying out the RCM in a closed system was mandatory to respect the standard protocol proposed by Grubbs et al. to evaluate metathesis catalysts.[39] Under these experimental conditions, homobimetallic ruthenium-indenylidene precursor **11** was more resistant to deactivation and outperformed all the ruthenium-benzylidene complexes under investigation (Figure 3 and Table 2). In accordance with earlier observations,[18,20,37] it was nevertheless slightly less efficient than its monometallic parent **15**, which afforded a full conversion of diethyl diallylmalonate into the corresponding RCM product within a few minutes at room temperature.[32]



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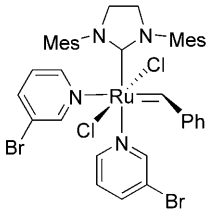

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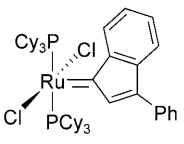
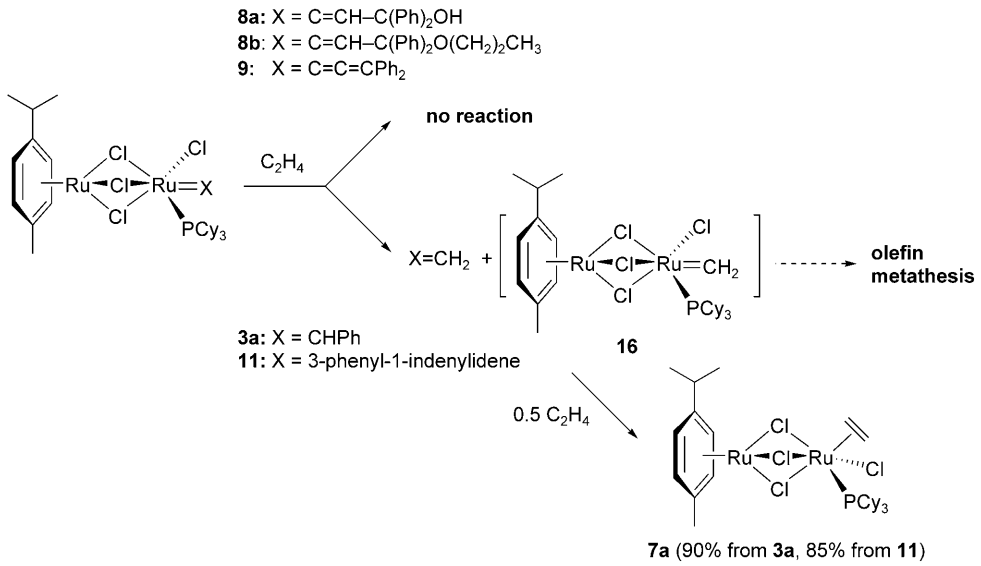


15

We next investigated the self-metathesis of styrene in the presence of homobimetallic ruthenium complexes **3a**, **8a**, **b**, **9**, and **11**. Experiments were carried out by adding 0.002 molar equivalent of catalyst to a stock solution of the olefin (1 M in toluene) stirred in an oil bath at 85 °C under an inert atmosphere [Eq. (3)]. Consumption of styrene and formation of stilbene (mostly the *trans* isomer) were monitored by GC. With all five catalysts under scrutiny, reactions were sluggish and conversions levelled off without going past the 10% threshold. With complexes **3a** and **11**, this plateau was reached within 30 min at 85 °C. In accordance with previous data obtained for ROMP and RCM, allenylidene and vinylidene complexes **8a**, **b** and **9** reacted much more slowly. Up to 2 days were needed before conversion stopped increasing. Adding a stoichiometric amount of *p*-toluenesulfonic acid monohydrate to these systems enhanced kinetics but did not alter the final stilbene yield that remained unchanged at *ca.* 10%. These poor results are most likely due to the rapid decomposition of the propagating species.[36] Indeed, homobimetallic ruthenium-methylidene species are expected to be the key intermediates present in the reaction media after the first catalytic cycle. Detailed investigations by Grubbs and co-workers showed that a sterically bulky environment was required to stabilize homo- and heterobimetallic ruthenium-alkylidene compounds. Attempts to generate [(*p*-cymene)ClRu(μ-Cl)$_2$RuCl(PCy_3)(=CH_2)] from [$RuCl_2$(*p*-cymene)]$_2$ (**2**) and [$RuCl_2(PCy_3)_2$(=CH_2)] failed and afforded an uncharacterized ruthenium-ethylene complex instead.[12]

(3)

These observations prompted us to take a closer look at the cross-metathesis of complexes **3a**, **8a**, **b**, **9**, and **11** with ethylene. Preliminary experiments were performed in CD_2Cl_2 or C_6D_6 and monitored by ^1H and ^{31}P NMR spectroscopies. No sign of reaction was detected with complexes **8a**, **b** and **9**, which remained stable in the presence of C_2H_4 for more than two days at 25 or 60 °C. Conversely, when solutions of complexes **3a** and **11** were placed under an ethylene atmosphere, a clean structural change occurred within 20 min, as evidenced by the replacement of the initial phosphorus absorptions (48.5 ppm in C_6D_6 at 60 °C for **3a**, 41.1 ppm in CD_2Cl_2 at 25 °C for **11**) by a new single resonance located at 43.6 ppm in CD_2Cl_2 or 44.3 ppm in C_6D_6. Parallel examination of the reaction media by ^1H NMR showed the release of styrene or 1-methylene-1*H*-indene from the benzylidene or indenylidene fragments, respectively, and the emergence of two new doublets at 4.07 and 4.56 ppm as-



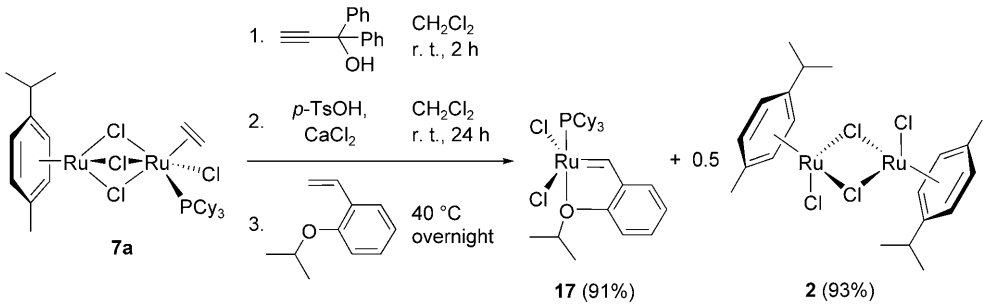
Scheme 7. Reaction of homobimetallic ruthenium complexes with ethylene.

signed to a ruthenium-ethylene moiety. These spectroscopic features strongly suggested the formation of ruthenium-ethylene complex **7a**.[22] To validate this hypothesis, we have carried out the reaction of complexes **3a** and **11** with ethylene on a preparative scale (Scheme 7). Syntheses were performed in toluene at 40 °C for 1 h. After solvent evaporation, the residue was extracted with *n*-pentane to afford 1 equivalent of the cross-metathesis product, styrene or 1-methylene-1*H*-indene. In the latter case, GC-MS analysis revealed the presence of small amounts of isomeric side-products that were not further characterized. Full NMR analysis of the remaining orange solid unambiguously demonstrated that it was pure complex **7a**. Hence, metathetically active benzylidene or indenylidene catalyst precursors **3a** and **11** are converted into methylidene species **16** when the ethylene concentration is high enough. Although highly unstable, this intermediate undergoes a remarkably clean and quantitative decomposition into ruthenium-ethylene complex **7a**. This transformation must proceed *via* a bimolecular pathway, but the mechanistic details remain unknown.

Preparative Application

The most straightforward route to ruthenium-alkylidene metathesis catalysts involves the reaction of suitable metal precursors with diazo compounds.[2] However, the instability of these highly labile reagents gives rise to major safety issues and severely limits their availability. Alternative synthetic pathways are thereby eagerly sought. One strategy implies the direct introduction of an alkylidene fragment onto an Ru(0) or Ru(II) center from a vinyl or propargyl chloride,[42] a *gem*-dichloro compound,[43] or a terminal alkyne.[44] Sulfur ylides generated *in situ* from sulfonium salts were also used as carbenoid precursors along these lines.[45] A second strategy takes advantage of the metathetical activity of ruthenium-indenylidene species to convert them into alkylidene derivatives *via* cross-metathesis with an appropriate alkene introduced in stoichiometric proportion or in excess. Although a further step is required to reach the desired product, this method has several practical assets, owing to the ease of formation and stability of Ru-indenylidene complexes. Thus, Blechert et al. prepared the second-generation Hoveyda–Grubbs catalyst from $[RuCl_2(PPh_3)_2(3\text{-phenyl-1-indenylidene})]$ *via* phosphine-NHC exchange followed by cross-metathesis with (*E*)-1-(hepta-1,6-dienyl)-2-isopropoxybenzene.[46] When a mixed PCy_3/NHC indenylidene complex served as starting material for similar reactions, copper(I) chloride was added in slight excess to help remove the phosphine.[47] Nolan and co-workers further refined the concept by devising a one-pot procedure for the synthesis of Grubbs catalyst **1a** starting from $[RuCl_2(PPh_3)_3]$ and 1,1-diphenylpropargyl alcohol, followed by phosphine exchange with PCy_3, and cross-metathesis with excess styrene.[48] In a slightly less efficient variation, Fürstner et al. converted a tricyclohexylphosphine-bearing indenylidene complex into a Hoveyda-type catalyst *via* enyne metathesis with 1-ethynyl-2-isopropoxybenzene in the presence of silver(I) chloride as phosphine scavenger.[49]

Since the reaction of homobimetallic ruthenium-indenylidene complex **11** with excess styrene afforded the highly unstable methylidene complex **16** that eventually decomposed into ethylene complex **7a** rather than the corresponding benzylidene complex **3a** (*vide supra*), we chose to react complex **11** with a



Scheme 8. One-pot synthesis of Hoveyda–Grubbs catalyst **17** from complex **7a**.

two-fold excess of 2-isopropoxystyrene, reasoning that the styrenyl ether would stabilize the alkylidene cross-metathesis product *via* oxygen chelation. Indeed, a preliminary experiment carried out overnight in toluene at 70 °C led to the quantitative formation of Hoveyda–Grubbs catalyst **17** and ruthenium-arene dimer **2** (0.5 equivalent). This was the first time that we observed cleavage of the μ-chloro bridges and clean formation of a monometallic product from the series of homobimetallic compounds under investigation. Formation of a stable chelate with oxygen is most likely responsible for opening one of the chloro bridges, thereby weakening the whole assembly and causing its dismantlement.

Building on this result, we set up a one-pot procedure for the synthesis of complex **17** starting from bimetallic precursor **7a**, without the need to isolate intermediate indenylidene species **11** (Scheme 8). Thus, ethylene complex **7a** was first converted into γ-hydroxyvinylidene complex **8a** by addition of 1,1-diphenylpropynol in dichloromethane. After 2 h at room temperature, solvent evaporation helped drive the reaction to completion and afforded a solid residue that was brought back to air. *p*-Toluenesulfonic acid monohydrate and anhydrous calcium chloride were added to the flask and its inert atmosphere was restored by applying three vacuum/nitrogen cycles. Dichloromethane was syringed in and the resulting suspension was stirred for 24 h at room temperature. Instant formation of cationic carbyne species **10** led to a yellow colouration that slowly turned dark red, as indenylidene complex **11** formed. Next, neat 2-isopropoxystyrene was added with a microsyringe and the mixture was stirred overnight at 40 °C. After solvent evaporation, selective extractions and flash chromatography were applied to separate alkoxybenzylidene catalyst **17** from the ruthenium dimer **2** and organic by-products. Gratifyingly, ^{31}P NMR monitoring throughout the process indicated that each step occurred cleanly and quantitatively, thereby affording high yields of pure organometallic products. The procedure did not require any sacrificial phosphine. This point is of particular importance, since tricyclohexylphosphine is costly and removing it from a ruthenium center often requires the addition of a scavenger such as CuCl or AgCl. A second advantage of the process is that dimer **2** was easily separated from complex **17** by selective extraction and could be recycled into starting material **7a** (*cf.* Scheme 2).

Conclusions

The labile ruthenium-ethylene complex **7a**, which is readily obtained from commercially available $[RuCl_2(p\text{-cymene})]_2$ (**2**), tricyclohexylphosphine and ethylene,[22] is a convenient starting material to prepare more elaborate homobimetallic ruthenium-arene architectures containing polyunsaturated carbon-rich ligands. Thus, reaction of **7a** with propargyl alcohol derivatives afforded quantitative yields of vinylidene complexes **8a**, **b** within 2 h at room temperature. Although they were stable enough to be fully characterized, these adducts underwent a slow albeit irreversible transformation into ruthenium-allenylidene complex **9** in solution. Elimination of *n*-propanol from the γ-propoxyvinylidene unit in **8b** proceeded cleanly and selectively without the need for any additive. Dehydration of the γ-hydroxyvinylidene ligand of **8a** was better accomplished in the presence of 3 Å molecular sieves to suppress side-reactions. Although its structure was erroneously reported in 1999,[17,18,20] complex **9** had never been isolated so far. In the presence of an acidic promoter, it rearranged into the homobimetallic ruthenium-indenylidene compound **11**, whose molecular structure was unambiguously determined by X-ray diffraction analysis. A direct vinylidene-to-indenylidene interconversion was also successfully carried out in the presence of a drying agent and a strong acid, thereby affording complex **11** in three steps and 72% overall yield from $[RuCl_2(p\text{-cymene})]_2$, one equivalent of PCy_3, and 1,1-diphenylpropynol. This procedure is particularly attractive in terms of atom economy, since it does not require the use of a sacrificial phosphine, nor the formation of any ruthenium-containing side-product such as **4** (*cf.* Scheme 1).

The catalytic activity of complexes **8a**, **b**, **9**, and **11** was probed in various types of olefin metathesis reactions and compared with those of homobimetallic ruthenium-benzylidene complex **3a**, as well as first (**1a**), second (**13**), and third generation (**14**) monometallic Grubbs catalysts. For the RCM of diethyl diallylmalonate, ruthenium-indenylidene complex **11** outperformed all the ruthenium-benzylidene complexes under investigation and was only slightly less efficient than its monometallic parent **15**. Cross-metathesis experiments with ethylene showed that deactivation of ruthenium-alkylidene or indenylidene complexes **3a** and **11** was due to the rapid bimolecular decomposition of methylidene active species **15** into ethylene complex **7a**. Vinylidene and allenylidene complexes **8a**, **b** and **9**, on the other hand, were far less efficient olefin metathesis initiators and remained inert under an ethylene atmosphere. Their catalytic activity was, however, substantially enhanced upon addition of an acidic co-catalyst that most likely promoted their *in situ* transformation into indenylidene species.

Due to its straightforward synthesis and high metathetical activity, homobimetallic ruthenium-indenylidene complex **11** was deemed an attractive intermediate to convert into alkoxyalkylidene species *via* stoichiometric cross-metathesis with 2-isopropoxystyrene. Thus, a convenient one-pot procedure was devised for the preparation of Hoveyda–Grubbs catalyst **17** from ethylene complex **7a** *via* a vinylidene-allenylidene-indenylidene cascade pathway. Taking into account the optimized synthesis of precursor **7a** from ruthenium-(*p*-cymene) dimer **2** in a preliminary step, monometallic catalyst **17** was obtained in 85% overall yield. No large excess of organic reagents was required and the transition metal not incorporated into the final product could easily be recovered and recycled at the end of the process.

Experimental Section

General Information

All reactions were carried out with rigorous exclusion of air using standard Schlenk techniques. Organic solvents were dried by standard procedures and distilled under argon prior to use. 1,1-Diphenylpropynol, *p*-toluenesulfonic acid monohydrate, and 3 Å molecular sieves (8–12 mesh beads) were purchased from Aldrich and used as received. Anhydrous calcium chloride (2–5 mm granules) was purchased from Mallinckrodt Baker and finely powdered immediately before use. 2-Isopropoxystyrene,[50] complex **3a**,[12] and complex **7a**[22] were prepared according to literature. ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Bruker DRX 400 or a Bruker Avance 250 spectrometer at 25 °C unless otherwise specified. Chemical shifts are expressed in parts per million and are referenced to solvent residual peaks (^{1}H, $^{13}C\{^{1}H\}$) or external H_3PO_4 ($^{31}P\{^{1}H\}$). All assignments are tentative, based on additivity rules[51] and comparison between related structures. Infrared spectra were recorded on a Perkin–Elmer Spectrum One FT-IR instrument. GC analyses were carried out on a Varian 3900 gas chromatograph equipped with a CP-Sil 5 CB capillary column and an FID detector. Gel permeation chromatography was performed in THF at 45 °C on a SFD S5200 autosampler liquid chromatograph equipped with a SFD 2000 refractive index detector and a battery of 4 PL gel columns fitted in series. The molecular weights (not corrected) are reported versus monodisperse polystyrene standards used to calibrate the instrument. Elemental analyses were carried out in the Laboratory of Pharmaceutical Chemistry at the University of Liège.

Synthesis of 1,1-Diphenylpropynyl *n*-Propyl Ether

To a 100-mL Schlenk tube containing a solution of 1,1-diphenylpropynol (3 g, 14 mmol) in DMF (20 mL) at −78 °C, 95% sodium hydride (0.51 g, 20 mmol) was added portionwise in 5 min. The resulting suspension was stirred at room temperature until the gas evolution stopped. It was cooled again at −78 °C before 1-bromopropane (3 g, 24 mmol) was added. The reaction mixture was stirred overnight at room temperature. It was diluted with diethyl ether (40 mL), washed with brine (3×30 mL), dried over $MgSO_4$ and concentrated on a rotary evaporator to give a pale yellow oil, which was purified by column chromatography on silica gel with petroleum ether. Pure 1,1-diphenylpropynyl *n*-propyl ether was isolated as a colourless oil, which crystallized upon standing; yield: 3.01 g (86%); mp 40–41 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.59$ (d, 4H, $J = 7.5$ Hz, Ph), 7.37–7.23 (m, 6H, Ph), 3.46 (t, 2H, $^{3}J_{H,H} = 6.3$ Hz, $OCH_2CH_2CH_3$), 2.95 (s, 1H, alkyne), 1.70 (qt, 2H, $^{3}J_{H,H} = 7.5$ Hz and 6.3 Hz, $OCH_2CH_2CH_3$), 0.99 (t, 3H, $^{3}J_{H,H} = 7.5$ Hz, $OCH_2CH_2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 143.6$ (s, C_{ipso}), 128.3 (s, CH_{meta}), 127.7 (s, CH_{para}), 126.7 (s, CH_{ortho}), 83.7 (s, $HCCCPh_2$), 79.8 (s, $HCCCPh_2$), 77.4 (s, $HCCCPh_2$), 66.4 (s, $OCH_2CH_2CH_3$), 23.3 (s, $OCH_2CH_2CH_3$), 11.0 (s, $OCH_2CH_2CH_3$).

Synthesis of [(*p*-Cymene)Ru(μ-Cl)$_3$RuCl(PCy$_3$)(=C=CH−C(Ph)$_2$OH)] (8a)

1,1-Diphenylpropynol (31 mg, 0.15 mmol) was added to a solution of complex **7a** (100 mg, 0.13 mmol) in CH_2Cl_2 (10 mL) and the mixture was stirred for 2 h at room temperature. The solvent was removed under reduced pressure. The residue was washed with diethyl ether (3×5 mL) and dried under high vacuum to afford complex **8a** as a red powder; yield: 113 mg (90%). IR (Nujol): ν = 1645 (C=C), 3416 cm^{-1} (OH); ^{1}H NMR (250 MHz, CD_2Cl_2, 298 K): $\delta =$ 7.47 (d, 2H, $^{3}J_{H,H} = 7.5$ Hz, Ph), 7.32 (d, 2H, $^{3}J_{H,H} = 7.5$ Hz, Ph), 7.30–7.20 (m, 6H, Ph), 5.66 (d, 1H, $^{3}J_{H,H} = 5.5$ Hz, CH cymene), 5.59 (d, 1H, $^{3}J_{H,H} = 5.5$ Hz, CH cymene), 5.45 (d, 1H, $^{3}J_{H,H} = 5.5$ Hz, CH cymene), 5.43 (d, 1H, $^{3}J_{H,H} = 5.5$ Hz, CH cymene), 4.78 (d, 1H, $^{4}J_{P,H} = 3.5$ Hz, Ru=C=CH), 3.54 (s, 1H, OH), 2.97 [sept, 1H, $^{3}J_{H,H} = 7.0$ Hz, $CH(CH_3)_2$], 2.32 (s, 3H, CH_3), 2.13–1.45 (m, 24H, PCy_3), 1.38 [d, 3H, $^{3}J_{H,H} =$ 7.0 Hz, $CH(CH_3)_2$], 1.37 [d, 3H, $^{3}J_{H,H} = 7.0$ Hz, $CH(CH_3)_2$], 1.35–1.00 (m, 9H, PCy_3); ^{13}C NMR (101 MHz, CD_2Cl_2, 233 K): $\delta = 345.9$ (d, $^{2}J_{P,C} = 18.1$ Hz, Ru=*C*=CH), 148.9, 148.5 (s, C phenyl), 127.4, 127.3, 126.1, 125.9, 125.5, 121.0 (s, CH

phenyl), 120.99 (s, Ru=C=*C*H), 100.0, 96.8 (s, C cymene), 80.0, 78.9, 77.7, 77.1 (s, CH cymene), 73.5 (s, CPh_2), 35.0 (d, $^1J_{P,C}=24.3$ Hz, CH PCy_3), 30.6 [s, *C*H$(CH_3)_2$], 29.1 (s, CH_2 PCy_3), 26.9 (d, $^2J_{PC}=11.0$ Hz, CH_2 PCy_3), 25.6 (s, CH_2 PCy_3), 21.3 [s, CH(*C*H$_3)_2$], 18.3 (s, CH_3); ^{31}P NMR (101 MHz, CD_2Cl_2, 298 K): $\delta=54.4$; anal. calcd. for $C_{43}H_{59}Cl_4OPRu_2$: C 53.42, H 6.15; found: C 53.48, H 6.20.

Synthesis of [(*p*-Cymene)Ru(μ-Cl)$_3$RuCl(PCy$_3$)(=C=CH-C(Ph)$_2$OCH$_2$CH$_2$CH$_3$)] (8b)

1,1-Diphenylpropynyl *n*-propyl ether (40 mg, 0.15 mmol) was added to a solution of complex **7a** (100 mg, 0.13 mmol) in CH_2Cl_2 (10 mL) and the mixture was stirred for 2 h at room temperature. The solvent was removed under reduced pressure. The residue was washed with *n*-pentane (3×5 mL) and dried under high vacuum to afford complex **8b** as an orange powder; yield: 122 mg (93%). IR (Nujol): $\nu=1669$ cm^{-1} (C=C); ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): $\delta=7.96$ (d, 1H, $^3J_{H,H}=7.5$ Hz, Ph), 7.67 (m, 4H, Ph), 7.34–7.13 (m, 5H, Ph), 5.63 (d, 1H, $^3J_{H,H}=5.0$ Hz, CH cymene), 5.55 (d, 1H, $^3J_{H,H}=5.0$ Hz, CH cymene), 5.41 (s, 2H, CH cymene), 4.00 (d, 1H, $^4J_{P,H}=3.8$ Hz, Ru=C=CH), 3.43 (qt, 2H, $^3J_{H,H}=7.8$ Hz and 6.6 Hz, $OCH_2CH_2CH_3$), 2.96 [sept, 1H, $^3J_{H,H}=6.8$ Hz, C*H*$(CH_3)_2$], 2.32 (s, 3H, CH_3), 2.20–1.00 (m, 33H, PCy_3), 1.62 (q, 2H, $^3J_{H,H}=6.6$ Hz, $OCH_2CH_2CH_3$), 1.37 [d, 3H, $^3J_{H,H}=6.8$ Hz, CH(C*H*$_3)_2$], 1.36 [d, 3H, $^3J_{H,H}=6.8$ Hz, CH(C*H*$_3)_2$], 1.00 (t, 3H, $^3J_{H,H}=7.8$ Hz, $OCH_2CH_2CH_3$); ^{13}C NMR (100 MHz, CD_2Cl_2, 233 K): $\delta=339.5$ (d, $^2J_{P,C}=16.5$ Hz, Ru=*C*=CH), 146.6, 146.3 (s, C phenyl), 128.7, 128.4, 127.7, 127.4, 126.2, 125.6 (s, CH phenyl), 110.3 (s, Ru=C=*C*H), 99.9, 96.6 (s, C cymene), 82.0 (s, CPh_2), 80.0, 78.8, 77.9, 77.6 (s, CH cymene), 64.2 (s, O*C*H$_2$CH$_2$CH$_3$), 33.9 (d, $^1J_{P,C}=24.3$ Hz, CH PCy_3), 30.6 [s, *C*H$(CH_3)_2$], 29.1 (s, CH_2 PCy_3), 27.2 (d, $^2J_{P,C}=11.0$ Hz, CH_2 PCy_3), 25.8 (s, CH_2 PCy_3), 22.9 (OCH$_2$*C*H$_2$CH$_3$), 21.5, 21.3 [s, CH(*C*H$_3)_2$], 18.3 (s, CH_3 cymene), 10.6 (s, OCH$_2$CH$_2$*C*H$_3$); ^{31}P NMR (101 MHz, CD_2Cl_2, 298 K): $\delta=54.0$; anal. calcd. for $C_{46}H_{65}Cl_4OPRu_2$: C 54.76, H 6.49; found: C 54.10, H 6.48.

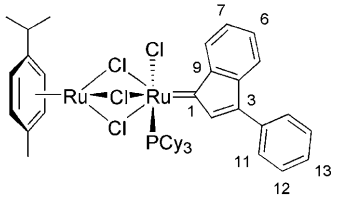
Synthesis of [(*p*-Cymene)Ru(μ-Cl)$_3$RuCl(PCy$_3$)(=C=C=CPh$_2$)] (9)

A solution of complex **8a** (200 mg, 0.21 mmol) in CH_2Cl_2 (30 mL) was stirred for 2 days at room temperature in the presence of 3 Å molecular sieve (3.2 g). During this period, the colour of the solution changed from orange to dark red and the molecular sieves became pulverulent. The resulting suspension was decanted and the supernatant solution was cannulated into another flask under argon. The solvent was removed under reduced pressure and the residue was washed with diethyl ether (2×20 mL) followed by *n*-pentane (2×20 mL). It was dried under high vacuum to afford complex **9** as a dark red powder; yield: 169 mg (85%). IR (Nujol): $\nu=1918$ cm^{-1} (C=C=C); ^{1}H NMR (250 MHz, CD_2Cl_2, 298 K): $\delta=7.95$ (d, 4H, $^3J_{H,H}=7.5$ Hz, Ph), 7.67 (d, 2H, $^3J_{H,H}=7.5$ Hz, Ph), 7.34 (d, 4H, $^3J_{H,H}=7.5$ Hz, Ph), 5.65 (d, 1H, $^3J_{H,H}=5.5$ Hz, CH cymene), 5.57 (d, 1H, $^3J_{H,H}=5.5$ Hz, CH cymene), 5.42 (d, 1H, $^3J_{H,H}=5.5$ Hz, CH cymene), 5.40 (d, 1H, $^3J_{H,H}=5.5$ Hz, CH cymene), 3.02 [sept, 1H, $^3J_{H,H}=6.8$ Hz, C*H*$(CH_3)_2$], 2.33 (s, 3H, CH_3), 2.13–1.45 (m, 24H, PCy_3), 1.40 [d, 3H, $^3J_{H,H}=6.8$ Hz, CH(C*H*$_3)_2$], 1.39 [d, 3H, $^3J_{H,H}=6.8$ Hz, CH(C*H*$_3)_2$], 1.35–1.00 (m, 9H, PCy_3); ^{13}C NMR (101 MHz, CD_2Cl_2, 298 K): $\delta=301.5$ (d, $^2J_{P,C}=18.1$ Hz, Ru=*C*=C=CPh$_2$), 237.3 (s, Ru=C=*C*=CPh$_2$), 147.1 (s, Ru=C=C=*C*Ph$_2$), 141.5, 129.0, 128.8, 128.6 (s, Ph), 101.2, 96.6 (s, C cymene), 79.9, 79.2, 78.8, 78.5 (s, CH cymene), 35.0 (d, $^1J_{P,C}=24.3$ Hz, CH PCy_3), 31.2 [s, *C*H$(CH_3)_2$], 29.1 (s, CH_2 PCy_3), 28.6 (s, CH_2 PCy_3), 27.8 (d, $^2J_{P,C}=10$ Hz, CH_2 PCy_3), 27.6 (d, $^2J_{P,C}=11$ Hz, CH_2 PCy_3), 26.4 (s, CH_2 PCy_3), 22.0, 21.9 [s, CH(*C*H$_3)_2$], 18.5 (s, CH_3); ^{31}P NMR (101 MHz, CD_2Cl_2, 298 K): $\delta=54.1$; anal. calcd. for $C_{43}H_{57}Cl_4PRu_2$: C 54.43, H 6.06; found: C 54.61, H 6.26.

Complex **9** was also obtained by stirring a solution of complex **8b** (100 mg, 0.1 mmol) in CH_2Cl_2 (10 mL) for 2–4 days at room temperature. During this period, the initially orange solution became dark red. It was concentrated to *ca.* 1 mL under reduced pressure and *n*-pentane (10 mL) was added. The supernatant solution was removed with a cannula and the precipitate was washed with *n*-pentane (3×5 mL). It was dried under high vacuum to afford the title compound a dark red powder; yield: 87 mg (92%).

Synthesis of [(*p*-Cymene)Ru(μ-Cl)$_3$RuCl(PCy$_3$)(3-phenyl-1-indenylidene)] (11)

A solution of complex **8a** (100 mg, 0.1 mmol) and *p*-toluenesulfonic acid monohydrate (40 mg, 0.21 mmol) in CH_2Cl_2 (10 mL) was stirred overnight in the presence of 3 Å molecular sieves (1.6 g) at room temperature. During this period, the dark yellow solution slowly became dark orange. It was filtered on sintered glass and the solvent was removed under vacuum. The remaining brown solid was washed with cold *n*-pentane (5 mL) and dried under high vacuum to afford complex **11** as an orange brown powder; yield: 86 mg (86%); IR (Nujol): $\nu=1947$, 1621 cm^{-1}; ^{1}H NMR (250 MHz, CD_2Cl_2, 298 K): $\delta=8.84$ (d, 1H, $^3J_{H,H}=7.0$ Hz, H-8), 7.82 (d, 2H, $^3J_{H,H}=7.3$ Hz, H-11), 7.55 (m, 1H, H-6), 7.41 (m, 4H, H-12, H-7, and H-13), 7.20 (d, 1H, H-5), 6.75 (s, 1H, H-2), 5.54 (d, 1H, $^3J_{H,H}=5.8$ Hz, CH cymene), 5.34 (d, 1H, $^3J_{H,H}=5.8$ Hz, CH cymene), 5.27 (d, 1H, $^3J_{H,H}=5.8$ Hz, CH cymene), 5.12 (d, 1H, $^3J_{H,H}=5.8$ Hz, CH cymene), 2.87 [sept, 1H, $^3J_{H,H}=6.8$ Hz, C*H*$(CH_3)_2$], 2.12 (s, 3H, CH_3), 2.05–0.90 (m, 24H, PCy_3), 1.35 [d, 2H, $^3J_{H,H}=6.8$ Hz, CH(C*H*$_3)_2$], 1.30 [d, 2H, $^3J_{H,H}=6.8$ Hz, CH(C*H*$_3)_2$]; ^{13}C NMR (101 MHz, CD_2Cl_2, 298 K): $\delta=309.7$ (d, $^2J_{P,C}=15.4$ Hz, C1), 144.8 (s, C9), 143.7 (s, C4), 141.1 (d, $^3J_{P,C}=3.9$ Hz, C2), 140.0 (s, C3) , 136.3 (s, C10), 130.4 (s, C8), 130.0 (s, C12), 129.4 (s, C7), 129.2 (s, C6), 128.6 (C13), 126.1 (C11), 117.9 (s, C5), 100.4 and 96.4 (s, C cymene), 80.2, 79.8, 79.1, 78.11 (s, CH cymene), 37.0 (d, $^1J_{P,C}=23.2$ Hz, CH, PCy_3), 31.1 [s, *C*H$(CH_3)_2$], 29.7 (s, CH_2, PCy_3), 29.3 (s, CH_2, PCy_3), 28.2 (d, $^2J_{P,C}=8.6$ Hz, CH_2, PCy_3), 27.5 (d, $^2J_{P,C}=11.9$ Hz, CH_2,



PCy_3), 26.4 (s, CH_2, PCy_3), 22.4, 21.6 [s, $CH(CH_3)_2$], 18.3 (s, CH_3); ^{31}P NMR (101 MHz, CD_2Cl_2, 298 K): $\delta = 41.1$; anal. calcd. for $C_{43}H_{57}Cl_4PRu_2$: C 54.43, H 6.06; found: C 55.85, H 6.50.

Complex **11** was also obtained by stirring a solution of complex **8b** (100 mg, 0.1 mmol) and *p*-toluenesulfonic acid monohydrate (40 mg, 0.21 mmol) in CH_2Cl_2 (10 mL) overnight at room temperature in the presence of anhydrous $CaCl_2$ (1.6 g). During this period, the dark yellow solution slowly became red. After decantation, it was transferred with a cannula into another flask under argon and the solvent was removed under vacuum. The remaining red solid was washed with cold *n*-pentane (5 mL) and dried under high vacuum to afford the title compound as an orange brown powder; yield: 82 mg (87%).

X-Ray Diffraction Analysis of Complex 11

Orange-red crystals of complex **11** suitable for X-ray diffraction analysis were obtained by slow evaporation of a CD_2Cl_2 solution. Crystal data were collected on a Bruker APPEX II Diffractometer using graphite-monochromated Mo-Kα radiation ($k = 0.71073$ Å) from a fine-focus sealed tube source at 100 K. Computing data and reduction was made with the APPEX II software.[52] The structure was solved using DIRDIF,[53] and finally refined by full-matrix, least-squares based on F^2 by SHELXL.[54] An empirical absorption correction was applied using SADABS.[55] All non-hydrogen atoms were anisotropically refined and the hydrogen atom positions were included in the model by electronic density or were geometrically calculated and refined using a riding model. A highly disordered distribution of solvent (CD_2Cl_2) was eliminated with SQUEEZE.[56]

Crystal data for [(*p*-cymene)Ru(μ-Cl)$_3$RuCl(PCy$_3$)(3-phenyl-1-indenylidene)] (11): $C_{43}H_{57}Cl_4PRu_2$, $M = 948.8$, monoclinic, $a = 28.116(8)$, $b = 12.837(4)$, $c = 28.345(13)$ Å, $\beta = 107.431(17)°$, $V = 9760(6)$ Å^3, $T = 100(2)$ K, space group $I2/a$, $Z = 8$, μ(Mo-Kα) = 0.71073 Å, 126928 reflections collected, 11638 independent reflections, $R_{int} = 0.068$, R_1 [$I > 2\sigma(I)$] = 0.0356, R_1 (all data) = 0.0564, wR_2 [$I > 2\sigma(I)$] = 0.0887, wR_2 (all data) = 0.0972.

CCDC 706396 contains the supplementary crystallographic data (excluding structure factors) for the structure reported in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax.: (internat.) +44–1223/336–033].

ROMP of Cyclooctene

A 25-mL round-bottom flask containing a magnetic stirring bar and capped with a three-way stopcock was charged with a homobimetallic ruthenium complex (0.03 mmol) and possibly *p*-toluenesulfonic acid monohydrate (6 mg, 0.03 mmol). The reactor was purged of air by applying three vacuum/argon cycles before dry chlorobenzene (5 mL) was added. The solution was warmed to 60 °C in a thermostated oil bath and cyclooctene (1 mL, 7.5 mmol) was added *via* a syringe. The reaction mixture was stirred for 2 h at 60 °C. The conversion was monitored by gas chromatography using the cyclooctane impurity of cyclooctene as an internal standard. The resulting gel was diluted with $CHCl_3$ containing traces of butylated hydroxytoluene (2 × 10 mL) and slowly poured into MeOH (500 mL) under vigorous stirring. The precipitated polyoctenamer was dried under high vacuum and characterized by GPC and NMR spectroscopy.

RCM of Diethyl 2,2-Diallylmalonate

Under inert atmosphere, a NMR tube with a screw-cap septum was charged with a freshly prepared stock solution of catalyst (10^{-3} M in CD_2Cl_2, 0.8 mL, 0.0008 mmol). The sample was heated to 30 °C in the NMR probe before diethyl 2,2-diallylmalonate (19.3 μL, 19.2 mg, 0.08 mmol) was added with a microsyringe under inert atmosphere. Experimental data points were collected using Bruker automation software. The conversion of diethyl 2,2-diallylmalonate was computed from the integrals obtained for allyl methylene protons in the starting material ($\delta = 2.61$, dt) and the product ($\delta = 2.98$, s).

Self-Metathesis of Styrene

A 25-mL round-bottom flask containing a magnetic stirring bar and capped with a three-way stopcock was charged with a homobimetallic ruthenium complex (0.04 mmol) and possibly *p*-toluenesulfonic acid monohydrate (8 mg, 0.04 mmol). The reactor was purged of air by applying three vacuum/argon cycles before styrene (20 mL of a 1 M solution in toluene, 20 mmol) was added with a dried syringe under argon. The solution was stirred at 85 °C in a thermostated oil bath under inert atmosphere. The conversion was monitored by GC using *n*-dodecane as internal standard.

Reaction of Complexes 3a and 5 with Ethylene

A Schlenk tube containing a magnetic stirring bar was charged with a homobimetallic ruthenium complex (0.05 mmol) and toluene (1 mL). The solution was stirred for 1 h at 40 °C under an ethylene atmosphere (0.5 bar). It quickly became orange and a solid precipitated. After cooling to room temperature, *n*-pentane (5 mL) was added to the suspension and the supernatant liquid was filtered off with a cannula. The remaining solid was washed with *n*-pentane (3 × 5 mL) and dried under high vacuum to afford [(*p*-cymene)Ru(μ-Cl)$_3$RuCl(PCy$_3$)(C_2H_4)] (**7a**) as an orange powder; yield: 36 mg (90% from **3a**), 34 mg (85% from **11**). ^1H, ^{13}C, and ^{31}P NMR spectra were identical to those reported earlier in the literature.[22]

One-Pot Synthesis of [Cl$_2$Ru(PCy$_3$)(=CH-*o*-O-*i*-PrC$_6$H$_4$)] (17) from Complex 7a

1,1-Diphenylpropynol (93 mg, 0.45 mmol) was added to a solution of complex **7a** (0.3 g, 0.39 mmol) in CH_2Cl_2 (30 mL) and the mixture was stirred for 2 h at room temperature. The solvent was removed under reduced pressure. To the residue were added *p*-toluenesulfonic acid monohydrate (0.11 g, 0.6 mmol), anhydrous $CaCl_2$ (4.8 g) and CH_2Cl_2 (30 mL). The orange suspension was stirred for 24 h at room temperature. It turned yellow after a few min and became dark red after 24 h. Next, 2-isopropoxystyrene (10 mg, 0.6 mmol) was added with a microsyringe and the mixture was stirred overnight at 40 °C. Elimination of CH_2Cl_2 under reduced pressure afforded a pale orange solid. This crude

product mixture was transferred into a Büchner funnel. Complex **17** was first extracted by adding small portions of hot cyclohexane until the initially brown washings remained colourless. The solid cake was then extracted with CH_2Cl_2 (25 mL) to afford an orange solution of $[RuCl_2(p\text{-cymene})]_2$ (**2**). The cyclohexane extracts were evaporated on a rotary evaporator. The residue was further purified by flash chromatography on a plug of silica gel using cyclohexane as eluant until unsaturated organic by-products were no longer detected by UV light on a TLC plate. Hoveyda–Grubbs complex **17** was then removed from the column using a 3/1 v/v mixture of cyclohexane/CH_2Cl_2 as eluant. Evaporation of the solvent under reduced pressure afforded pure complex **17** as a brown solid; yield: 210 mg (91%). Its ^1H, ^{13}C, and ^{31}P NMR spectra were identical to those reported earlier in the literature.[5] The $[RuCl_2(p\text{-cymene})]_2$ dimer **2** was recovered as an orange-red solid by evaporation of the CH_2Cl_2 solution under reduced pressure followed by recrystallization from toluene; yield: 220 mg (93%).

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