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# Homobimetallic Ruthenium-Ethylene, Vinylidene, Allenylidene, and Indenylidene Catalysts for Olefin Metathesis

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**Summary:** Following the discovery of bimetallic ruthenium scaffold (**1**), two new homobimetallic ruthenium-N-heterocyclic carbene complexes (**2**,**3**) were synthesized and found highly suitable for promoting ROMP, RCM, and CM reactions. Results from this study indicated that the ethylene ligand was highly labile and that adding a small amount of a terminal alkyne to the reaction media had a beneficial influence on the metathetical activity. These observations prompted us to further investigate the role of the alkyne co-catalyst. Thus, homobimetallic ruthenium-arene complexes bearing vinylidene (**4**,**5**), allenylidene (**6**), and indenylidene (**7**) ligands were prepared from complex **1** and propargyl alcohol derivatives. Their catalytic activities were probed in several types of olefin metathesis reactions, and they were found valuable intermediates for the safe and efficient one-pot synthesis of the Hoveya–Grubbs isopropoxybenzylidene catalyst (**8**).

**Keywords:** arene ligands; N-heterocyclic carbene; olefin metathesis; organometallic catalysts; phosphine ligands

## Introduction

The vast majority of well-defined ruthenium complexes investigated so far for promoting olefin metathesis derive from the Grubbs first generation ruthenium-benzylidene catalyst $[RuCl_2(=CHPh)(PCy_3)_2]$.[1] However, other related 16-electron species such as ruthenium-vinylidene,[2–4] allenylidene,[4,5] or indenylidene[6,7] complexes, have also proven efficient promoters for alkene metathesis and related reactions. In most cases, a single ruthenium center is present, although a few homo and heterobimetallic species were also reported.[8–12]

Ruthenium-arene complexes belong to a separate category of organometallic compounds. These 18-electron species with a distinctive piano-stool geometry have been known in the literature for more than 40 years.[13–17] Most representatives of this class of half-sandwich compounds were designed to include unfunctionalized arene ligands, such as benzene, *para*-cymene (1-methyl-4-isopropylbenzene), or hexamethylbenzene that can be easily removed upon thermal,[18] or photochemical[19–23] activation to release highly active, coordinatively unsaturated species. Thus, monometallic ruthenium-arene complexes are versatile and efficient catalyst precursors for various important organic transformations, including olefin metathesis.[24,25]

## Results and Discussion

In 2005, Severin and co-workers investigated the reaction of $[RuCl_2(p\text{-cymene})]_2$ with 1 equiv. of $PCy_3$ under an ethylene atmosphere. Under these conditions, the ruthenium dimer afforded a new type of molecular scaffold, in which a $RuCl(\eta^2\text{-}C_2H_4)(PCy_3)$ fragment was connected via three μ-chloro bridges to a ruthenium-(*p*-

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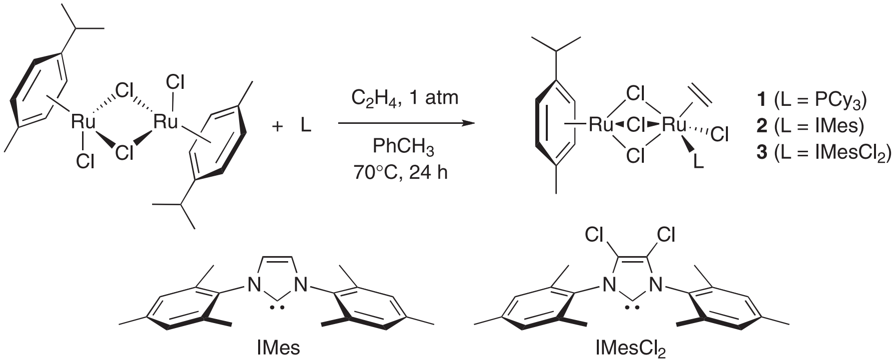
cymene) moiety.[26] The resulting homobimetallic complex (**1**) displayed an outstanding catalytic activity in atom transfer radical additions, but was not effective at promoting olefin metathesis. In view of the enhancements brought by the replacement of phosphines by N-heterocyclic carbenes (NHCs) in monometallic ruthenium-arene catalyst precursors,[22,23] we decided to investigate the effect of similar modifications in the bimetallic series. Thus, in 2007, we reported on the synthesis and catalytic activity of two new homobimetallic ruthenium-arene complexes of general formula $[(p\text{-cymene})\,\mathrm{Ru}(\mu\text{-Cl})_3\mathrm{RuCl}(\eta^2\text{-C}_2\mathrm{H}_4)(\mathrm{NHC})]$, where NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (**2**) or 1,3-bis(2,4,6-trimethylphenyl)-4,5-dichloroimidazolin-2-ylidene (**3**).[27] These compounds were isolated in high yields upon heating a toluene solution of $[\mathrm{RuCl}_2(p\text{-cymene})]_2$ with 1 equiv. of carbene ligand under an ethylene atmosphere (Scheme 1).

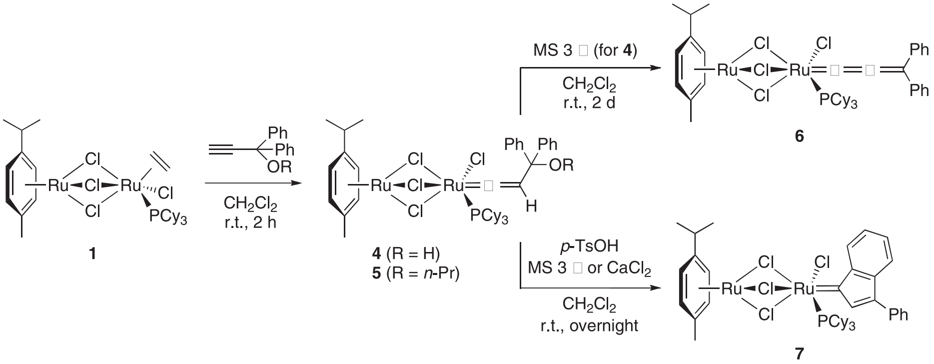
Contrary to monometallic ruthenium-arene complexes of the $[\mathrm{RuCl}_2(p\text{-cymene})(\mathrm{L})]$ type (L = phosphine or NHC ligand), complexes **2** and **3** did not require the addition of a diazo compound nor visible light illumination to initiate the ring-opening metathesis polymerization (ROMP) of norbornene or cyclooctene. When $\alpha,\omega$-dienes were exposed to **2** or **3**, a mixture of cycloisomerization and ring-closing metathesis (RCM) products was obtained in a non-selective way. Addition of a terminal alkyne co-catalyst enhanced the metathetical activity while completely repressing the cycloisomerization process. Thus, quantitative conversions of diethyl 2,2-diallylmalonate and *N,N*-diallyltosylamide were achieved within 2 h at room temperature using 2 mol% of catalyst precursor **2** and 6 mol% of phenylacetylene.

The positive influence of phenylacetylene on catalytic systems derived from complexes **2** and **3** prompted us to further investigate the reaction of alkynes with the labile ruthenium-ethylene complex **1** (Scheme 2).[28] Hence, treatment of $[(p\text{-cymene})\mathrm{Ru}(\mu\text{-Cl})_3\mathrm{RuCl}(\eta^2\text{-C}_2\mathrm{H}_4)(\mathrm{PCy}_3)]$ with a slight excess of propargyl alcohol derivatives afforded quantitative yields of vinylidene complexes **4** and **5** within 2 h at room temperature. Although these products were stable enough to be fully characterized by various analytical techniques, they underwent a slow albeit irreversible transformation into ruthenium-allenylidene complex **6** in solution. Elimination of *n*-propanol from the $\gamma$-propoxyvinylidene unit in **5** proceeded cleanly and selectively without the need for any additive. Dehydration of the $\gamma$-hydroxyvinylidene ligand of **4** was better accomplished in the presence of 3 Å molecular sieves to suppress side-reactions.

Although its structure was erroneously reported in 1999,[9,10,29] complex **6** had never been isolated before. In the presence of an acidic promoter, it rearranged into the homobimetallic ruthenium-indenylidene



**Scheme 1.**
Synthesis of homobimetallic ruthenium-ethylene complexes **1**–**3**.

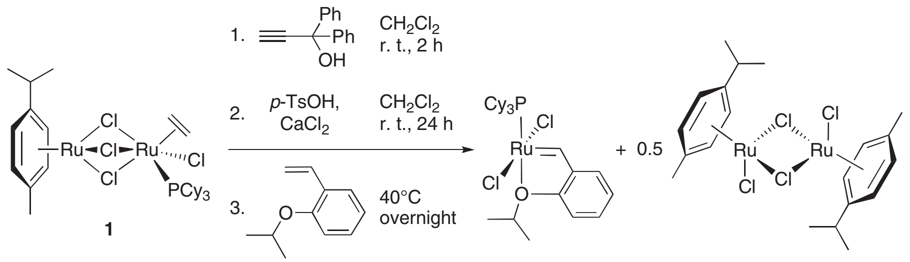


**Scheme 2.**
Synthesis of homobimetallic ruthenium-vinylidene (4,5), allenylidene (6), and indenylidene (7) complexes from ethylene complex 1.

compound **7**, 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 **7** in three steps and 72% overall yield from $[RuCl_2(p\text{-cymene})]_2$, 1 equiv. of $PCy_3$, and 1,1-diphenylpropynol.

The catalytic activity of complexes **4–7** was probed in various types of olefin metathesis reactions and compared with those of first, second, and third generation monometallic Grubbs catalysts. For the ring-closing metathesis of diethyl diallylmalonate, ruthenium-indenylidene complex **7** outperformed all these ruthenium-benzylidene complexes. Cross-metathesis (CM) experiments with ethylene showed that deactivation of bimetallic ruthenium-alkylidene or indenylidene complexes was due to the rapid bimolecular decomposition of methylidene active species into ethylene complex **1**. Vinylidene and allenylidene complexes **4–6**, 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 **7** was deemed an attractive intermediate to convert into an alkoxyalkylidene species *via* stoichiometric cross-metathesis with 2-isopropoxystyrene. Thus, a convenient one-pot procedure was devised for the preparation of the Hoveyda–Grubbs catalyst (**8**) from ethylene complex **1** *via* a vinylidene-allenylidene-indenylidene cascade pathway (Scheme 3). Taking into



**Scheme 3.**
One-pot synthesis of the Hoveyda–Grubbs catalyst (8) from homobimetallic ruthenium-ethylene complex 1.

account the optimized synthesis of precursor **1** from [RuCl$_2$($p$-cymene)]$_2$ in a preliminary step, monometallic catalyst **8** was obtained in 85% overall yield. No large excess of organic reagents was required and the transition metal not incorporated into the final product was easily recovered and recycled at the end of the process.

## Conclusion

Homobimetallic ruthenium-arene complexes bearing phosphine or NHC ancillary ligands are versatile and efficient catalyst precursors for olefin metathesis. Their synthesis can be achieved in a few steps starting from the widely available [RuCl$_2$($p$-cymene)]$_2$ dimer. Hence, ruthenium-arene complexes provide a convenient platform for catalytic engineering and ligand fine-tuning, as we have shown by carefully adjusting the nature of the ancillary ligands or carbon-rich fragment. Because all these 18-electron species lack a vacant coordination site and the mandatory alkylidene fragment needed for metathesis, their major drawback is a poor initiation efficiency. This may be a critical issue, for instance when controlled polymerizations are required. However, the ability to trigger the catalytic process upon addition of a co-catalyst or via photochemical irradiation is also a highly desirable feature for some practical applications. Combining the best of both worlds into a single, easily accessible catalytic system is our next challenge.

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