[18] A related phase structure should be present in the SmA phases of a TTF derivative with four branched lateral chains (R. A. Bissell, N. Boden, R. J. Bushby, C. W. G. Fishwick, E. Holland, B. Movaghar, G. Ungar, *Chem. Commun.* **1998**, 113.) and was suggested for 1,4,5,8-tetraalkyl-substituted derivatives of anthracene and anthraquinone (S. Norvez, F. G. Tournilhac, P. Bassoul, P. Hersonn, *Chem. Mater.* **2001**, *13*, 2552).

[19] In this case, which would correspond to laminated SmC or $SmC_A$ structures, the aromatic cores would be tilted with respect to the direction of the periodicity within the aromatic sublayers, but parallel to the layer planes of the bulk organization.

[20] To distinguish such phases from conventional smectic phases, in which the calamitic molecules are arranged perpendicular to or tilted with respect to the layer planes, it is proposed to designate such phases as laminated mesophases (Lam), whereby a subscript designates the organization within the ordered sublayers ($Lam_A$ = laminated SmA phase, see Figure 2i). In principle, the $SmA_b$ and SmA phases of **2**–**4** can alternatively be described as a laminated nematic phase ($Lam_N$) and laminated isotropic phases ($Lam_{Iso}$), respectively, but the phase symmetry of these phases is the same as in conventional $SmA_b$ and SmA phases, so that this-well established nomenclature should still be used in these cases.

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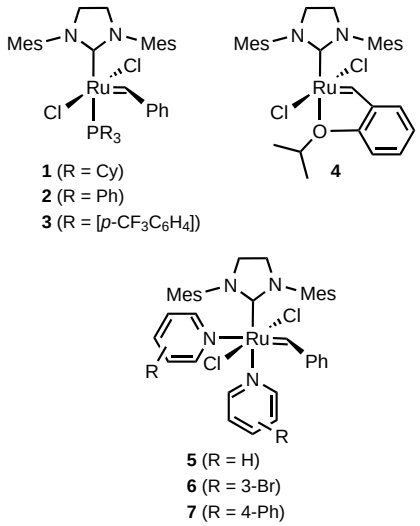
[24] A crystalline SmG-like organization of aromatic cores was proposed for the aromatic layers of 1,4,5,8-tetraalkyl-substituted derivatives of anthracene and anthraquinone.[18b]

## A Practical and Highly Active Ruthenium-Based Catalyst that Effects the Cross Metathesis of Acrylonitrile**

Jennifer A. Love, John P. Morgan, Tina M. Trnka, and Robert H. Grubbs*

The N-heterocyclic carbene-coordinated ruthenium benzylidene complex $[(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh]$ (**1**) is a highly active catalyst for a wide variety of olefin-metathesis reactions,[1] including those with sterically demanding[2] and electron-deficient olefins (Scheme 1).[3] In spite of recent advances, there are several processes that remain challenging,




Scheme 1. Ruthenium-based olefin metathesis catalysts. Mes = 2,4,6-trimethylphenyl.

such as olefin cross metathesis (CM) with directly functionalized olefins.[4] For example, acrylonitrile CM has only been successful with Schrock's arylimido molybdenum alkylidene catalyst[5] and the ether-tethered ruthenium alkylidene derivative $[(H_2IMes)(Cl)_2Ru{=}CH(o\text{-}i\text{PrOC}_6H_4)]$ (**4**).[6,7] Phosphane-ligated ruthenium catalysts have given poor results for this transformation,[3a,5c,6c,8,9] except for one report of efficient CM between purified acrylonitrile and 1-decene mediated by **1**.[10] We have determined that dissociation rates of ligands are related to catalyst efficiency during CM with acrylonitrile. On this basis, we have developed a new, highly efficient ruthenium complex to perform acrylonitrile CM with unpurified acrylonitrile; this catalyst is the *fastest initiator* of any ruthenium-based catalyst reported to date.[11]

Previous studies have shown that precatalysts of the type $[L_2X_2Ru{=}CHR]$ initiate by dissociating one L-type ligand before entering the catalytic cycle (Scheme 2);[12] in complexes **1**–**3**, L is a phosphane ($PR_3$), and in complex **4**, L is a tethered ether ligand (*i*PrO). Importantly, complexes **1**–**4** all provide the *same* propagating species (**A** and **B**) after a *single* turnover.[13] If either **A** or **B** is trapped by L, dissociation of L must occur before catalysis can continue. The relative affinity of **A** and/or **B** for the olefin in preference to L (i.e., favoring propagation) controls how long these species remain in the catalytic cycle. Consequently, the differences in activity between catalysts **1**–**4** depend on their rates of initiation and rebinding of L, both of which can be tuned by the nature of L.[12b,14–16]

Complexes **1**–**4** are all active for a variety of metathesis processes, such as CM, ring-closing metathesis (RCM), and ring-opening-metathesis polymerization (ROMP). However, the situation involving acrylonitrile CM is more complex; CM between acrylonitrile and allylbenzene proceeds efficiently with **4** (68% yield) but not with **1**–**3** (21%, 35%, and 36% yields, respectively; Table 1).[17] Clearly, this difference cannot simply be an issue of precatalyst initiation; **2** and **4** have roughly the same initiation rates and initiation is faster with **3** than **1**, **2**, or **4** Table 2. The difference is also not a result of

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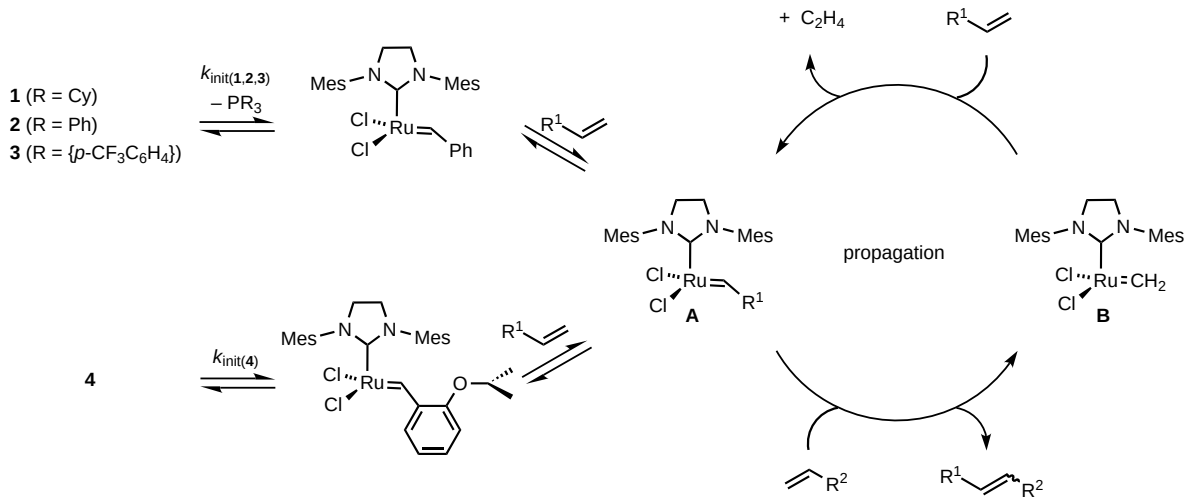



Scheme 2. Mechanism of olefin cross metathesis.

Table 1. Cross metathesis of acrylonitrile with allylbenzene.[a]

| Catalyst | Yield [%] | $E/Z$[b] |
|---|---|---|
| **1** | 21 | 1:1.7 |
| **2** | 35 | 1:4 |
| **3** | 36 | 1:1.8 |
| **4** | 68 | 1:1.9 |
| **5** | 26 | 1:1.2 |
| **6** | 67 | 1:1.8 |
| **7** | 29 | 1:1.8 |

[a] Conditions for CM: acrylonitrile (1.0 equiv), allylbenzene (2.5 equiv, 0.2 M in $CH_2Cl_2$), ruthenium catalyst (2.5 mol%), 40 °C, 12 h. [b] Ratios determined by means of $^1$H NMR spectroscopy.

Table 2. Initiation rate constants of various ruthenium alkylidene complexes.[a]

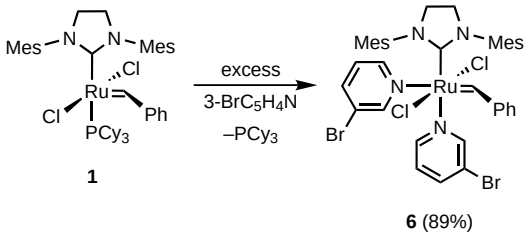
| Catalyst | $k_{init}$ (at 5 °C) [$\times 10^{-3}$ s$^{-1}$] |
|---|---|
| **1** | $0.0032 \pm 0.0006$[b] |
| **2** | $1.8 \pm 0.1$[b] |
| **3** | $35 \pm 9$[b] |
| **4** | $2.6 \pm 0.1$[c] |
| **5** | $> 200$[d] |
| **6** | $> 4000$[d] |
| **7** | $> 200$[d] |

[a] Experimental details are given in the Supporting Information, unless otherwise indicated. [b] Ref. [12b]. [c] Ref. [14]. [d] Lower limit estimate.

changes in the propagating species because **1**–**4** converge to the *same* intermediate after a *single* turnover (Scheme 2). Furthermore, a cyano-substituted alkylidene is observed in solution during CM of acrylonitrile using **1**. This species has a slower initiation rate than **1**, which suggests that a cyanocarbene intermediate, if trapped by phosphane, only reenters the catalytic cycle with difficulty. Consequently, the activity of complexes **1**–**4** in acrylonitrile CM must be strongly influenced by the rates of both dissociation and rebinding of L.

We have shown that an improvement in initiation without a substantial increase in the rate of rebinding of L improves the rate of catalysis.[12,14] We previously noted that the pyridine ligands in $[(H_2IMes)(py)_2(Cl)_2Ru{=}CHPh]$ (**5**, py = pyridine) can be readily replaced with phosphanes; even the electron-deficient phosphane P(*p*-$CF_3C_6H_4)_3$ reacts with **5** to provide **3**.[18,19] On this basis, it was anticipated that pyridine-ligated complexes would be useful catalysts in acrylonitrile CM.

A variety of bispyridine complexes can be prepared by adding an excess of the appropriate pyridine to **1**. These reactions are complete within minutes, require little or no solvent, and can be easily performed with commercial, unpurified reagents. For example, reaction of **1** (0.5 g) with 3-bromopyridine (10 equiv) provides $[(H_2IMes)(3\text{-Br-py})_2(Cl)_2Ru{=}CHPh]$ (**6**) within minutes (Scheme 3).[20] The product is isolated in 89% yield simply by precipitation with pentane and without further purification. In comparison, the synthesis of **4** is considerably less efficient and more time-consuming, especially because chromatography is required for purification and not all reagents are commercially available.[6,7]




Scheme 3. Synthesis of bispyridine complex **6**.

We attempted to measure the initiation rates of **5**–**7** by using both NMR spectroscopy and UV/Vis kinetic studies (Table 2).[15] The reaction of complex **6** with ethyl vinyl ether was complete within 0.5 seconds at 5 °C; this is by far the fastest initiation measured in a ruthenium-based system. The rate constants ($k_{init}$) for **5**–**7** increase linearly with olefin concentration even with up to 3750 equivalents of olefin, which suggests that these reaction conditions do not approach saturation kinetics.[21] We consider the values obtained under these nonsaturation conditions as lower-limit estimates for the initiation rate constants of **5**–**7**.[22] In particular, complex **6** initiates the reaction at least three orders of magnitude faster than **4** and at least six orders of magnitude faster than **1**! The

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superior initiation properties of **6** over those of **3** and **4** is further illustrated by their relative activities in the ROMP of cyclooctadiene (cod; Figure 1).[12b,14,16a,23]

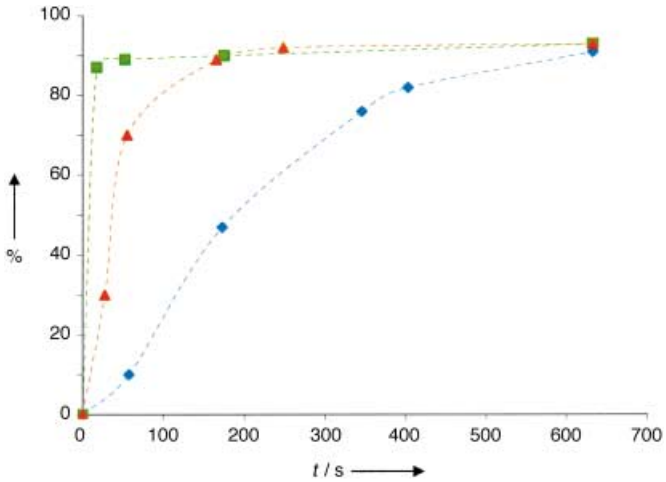


Figure 1. ROMP of cod at 10 °C with catalysts **3**, **4**, and **6** (cod/Ru 3000:1, [Ru] = 0.5 mM in $CD_2Cl_2$). The progress of the reaction was monitored by $^1H$ NMR spectroscopy. ▲ complex **3**; ◆ complex **4**; ■ complex **6**. Dotted lines are intended as visual aids and are not curve fits.

Complexes **5**–**7** were compared for their ability to mediate CM between acrylonitrile and allylbenzene (Table 1). Although complexes **5** and **7** provide only modest yields of cross product (26% and 29%, respectively), the 3-bromopyridine derivative **6** provides a respectable yield of 67%, similar to that obtained with **4**. From these results, we conclude that the complexes with pyridine and 4-phenylpyridine ligands (**5** and **7**, respectively) do not achieve a sufficient steady-state concentration of the propagating species for CM to occur readily. Complex **6** is a considerably better catalyst, presumably because dissociation of the electron-deficient 3-bromopyridine ligand is extremely rapid and/or because rebinding is slow, both of which contribute to favorable turnover conditions.

We have shown that tuning the electronics of the L-type ligand can provide a catalyst that is capable of performing acrylonitrile CM with high efficiency. $[(H_2IMes)(3\text{-Br-py})_2(Cl)_2Ru{=}CHPh]$ is an exceptionally fast initiator for the metathesis of simple olefins and is synthetically accessible in one step from commercially available starting materials.

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