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Communications

Ruthenium Alkylidenes: Fast Initiators for Olefin Metathesis

Joseph E. Williams, Mary J. Harner, and Michael B. Sponsler*

Department of Chemistry, Syracuse University, Syracuse, New York 13244

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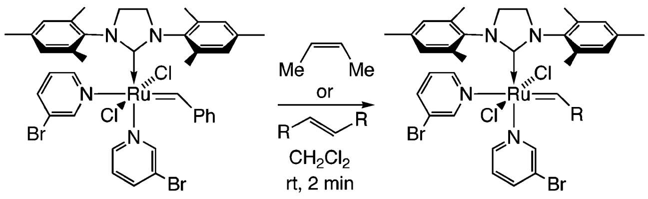
Summary: A family of ruthenium alkylidene complexes, $(H_2IMes)RuCl_2(=CHR)(3\text{-bromopyridine})_2$, where R = Me, Et, nPr, as well as the corresponding PCy_3 complexes, $(H_2IMes)RuCl_2(=CHR)(PCy_3)$, have been prepared. The PCy_3 alkylidene complexes exhibit much higher stoichiometric reactivity than does the analogous benzylidene complex, reflecting faster dissociation of PCy_3 from the alkylidene complexes.

Olefin metathesis has emerged over the past decade as a powerful tool in organic synthesis.[1] In particular, Grubbs' first-[2] and second-generation catalysts[3] have found extensive use in both polymer and small-molecule syntheses.[1,4] The second-generation catalyst $(H_2IMes)RuCl_2(=CHPh)(PCy_3)$ (**1P**) displays high catalytic reactivity despite a low initiation rate, corresponding to the loss of PCy_3. This makes it less suitable for some reactions, such as stoichiometric formation of new ruthenium complexes.[5] A pyridine complex,[6] the 3-bromopyridine complex $(H_2IMes)RuCl_2(=CHPh)(3\text{-bromopyridine})_2$ (**1B**),[7] other PR_3 complexes,[8] and phosphonium alkylidenes[9] have been used as fast-initiating versions of this catalyst. In analogy with the observation that the first-generation ethylidene[2] and propylidene catalysts[10] are more reactive than the benzylidene catalyst, we herein report alkylidene analogues of **1P** and **1B**, all of which have been found to undergo faster initiation.

Scheme 1



1B

2B (R = Me), 84%
3B (R = Et), 89%
4B (R = *n*Pr), 92%

Reaction of **1B** with *cis*-2-butene in CH_2Cl_2 afforded ethylidene **2B**, as shown in Scheme 1. The propylidene and butylidene complexes (**3B** and **4B**) were prepared

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* To whom correspondence should be addressed. E-mail: sponsler@syr.edu. Fax: 315-443-4070.

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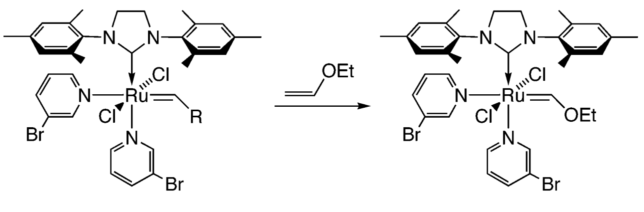
(9) Romero, P. E.; Piers, W. E.; McDonald, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6161−6165.

(10) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543−6554.

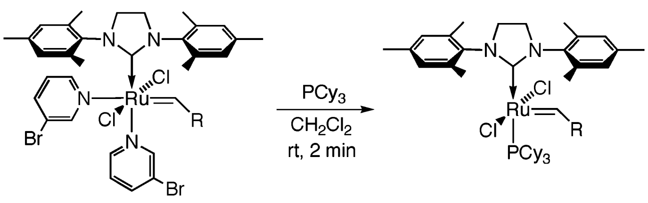
10.1021/om050040h CCC: $30.25

Scheme 2



1B-4B **5B**

Scheme 3



2B-4B

2P (R = Me), 68%
3P (R = Et), 71%
4P (R = *n*Pr), 58%
(yields from **1B**)

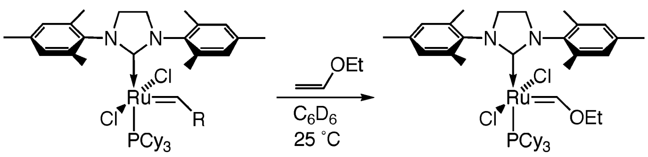
in a similar fashion by using *trans*-3-hexene and *trans*-4-octene, respectively. All three reactions proceeded in high yield.

Complexes **2B**−**4B** possess reactivity with alkenes similar to that of **1B**, showing complete reaction within 2 min.[11] For example, treatment of **1B**−**4B** with ethyl vinyl ether gave a fast and complete conversion to the Fischer carbene **5B**[12] (Scheme 2).

Complexes **2B**−**4B** are less stable in solution than is **1B**, all three decomposing[13] in solution with loss of alkylidene to give the same orange product containing H_2IMes, 3-bromopyridine, and Cl, as determined from spectral data (^{1}H and ^{13}C NMR, MS). Complex **4B** decomposes the fastest, followed closely by **2B**, with **3B** showing significantly better stability.[14] Decomposition of the complexes **1B**−**4B** was greatly accelerated by the presence of 1-alkenes, such as 1-pentene. For example, **1B** fully decomposed in seconds in the presence of ethylene.

Complexes **2B**−**4B** were each treated with PCy_3 (usually immediately after formation) to provide the phosphine complexes **2P**−**4P**, as shown in Scheme 3.[15] All three reactions proceeded in good yield.

Scheme 4



1P-4P **5P**

Table 1. Rate Constants (10^{-4} s^{-1}) for Reaction with Ethyl Vinyl Ether (1.0 M)[a]

	amt of compd	
compd	0.01 M	0.03 M
1P	1.1	0.95[b]
2P		6.2
3P	14[c]	9.3
4P	27	9.8

[a] Each sample (in C_6D_6 at 25 °C) was kept in the NMR probe throughout the run. Analysis was done by ^{1}H NMR integration. [b] This value agrees with the value obtained from the phosphine exchange Eyring analysis in ref 10: 0.89 × 10^{-4} s^{-1} at 25 °C for **1P** (0.04 M in toluene-d_8). The rate-determining step of both reactions is presumed to be loss of phosphine. [c] With an ethyl vinyl ether concentration of 0.10 M, the observed rate constant was 11 × 10^{-4} s^{-1}. With an ethyl vinyl ether concentration of 2.0 M, the observed rate constant was 13 × 10^{-4} s^{-1}.

Complexes **3P**−**4P** were also prepared directly from **1P** in analogy to Scheme 1, but the reaction took several hours. While **2P**−**4P** were stable in solution for many days at 0 °C, interconversion reactions were observed in the presence of alkenes. With 10 equiv of *trans*-3-hexene at room temperature, **3P** was converted to an equilibrium mixture of 75% **2P** and 25% **3P** over a period of 1−2 days. When a solution of **4P** was likewise kept at room temperature for 1 week in the presence of 10 equiv of *trans*-4-octene, small amounts of **2P** and **3P** were observed to grow in. These interconversion reactions are presumably a result of Ru−H-catalyzed alkene isomerization, a process that has been observed in metathesis reactions of **1P**.[13c,16] A hydride ^{1}H NMR signal was observed at −25.03 ppm (d, J = 21 Hz) in the isomerization of **3P**, consistent with known hydride decomposition products of **1P**.[13c,17]

Stoichiometric metathesis rates for the reaction of complexes **1P**−**4P** with ethyl vinyl ether to give **5P**[18] (Scheme 4) were measured by ^{1}H NMR integration. All reactions showed first-order kinetics and gave the rate constants shown in Table 1. Stoichiometric reactions of **3P** with *trans*-4-octene, giving **4P**, and of **4P** with *trans*-hexene. giving **3P**, were observed to proceed smoothly at rates similar to those in Table 1, consistent with a rate-determining loss of PCy_3 for all of these reactions.

As clearly shown by Table 1, the reactivity of the benzylidene **1P** is much lower than that of **2P**−**4P**. At 0.01 M, the half-life of **4P** was 4.3 min, while the half-life for **1P** was 105 min. Complexes **2P**−**4P** lose PCy_3 faster than does **1P**, as evidenced by the stoichiometric rates, and the difference is much greater than was observed for first-generation diphosphine catalysts. The propylidene/benzylidene rate ratio for phosphine ex-

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[11] ^{1}H NMR spectra taken within 2 min of addition show complete conversion.

[12] The identity of this complex was confirmed through addition of PCy_3, affording complex **5P**.[18]

[13] Decomposition of metathesis-active ruthenium catalysts has been studied recently: (a) van Rensburg, W. J.; Steynberg, P. J.; Meyer, W. H.; Kirk, M. M.; Forman, G. S. *J. Am. Chem. Soc.* **2004**, *126*, 14332−14333. (b) Hong, S. H.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2004**, *126*, 7414−7415. (c) Dinger, M. B.; Mol, J. C. *Eur. J. Inorg. Chem.* **2003**, 2827−2833.

[14] While decomposition was evident almost immediately by ^{1}H NMR for complexes **4B** and **2B**, decomposition of **3B** was observable only after approximately 3 h. Complexes **4B** and **2B** were fully decomposed overnight. In comparison, **1B** was stable in this time frame.

[15] The ^{1}H and ^{31}P NMR spectra of complex **2P** were reported in: Chatterjee, A. K.; Sanders, D. P.; Grubbs, R. H. *Org. Lett.* **2002**, *4*, 1939−1942. The complex was generated by reaction of **1P** with *cis*-2-butene, propene, or 2-methyl-2-butene. Note added in proof: Complexes **2P**, **2B**, and **3P** have appeared in a very recent report: Lehman, S. E., Jr.; Wagener, K. B. *Organometallics* **2005**, published ASAP.

[16] Sworen, J. C.; Pawlow, J. H.; Case, W.; Lever, J.; Wagener, K. B. *J. Mol. Catal. A: Chem.* **2003**, *194*, 69−78.

[17] Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T.-L.; Ding, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546−2558.

[18] Louie, J.; Grubbs, R. H. *Organometallics* **2002**, *21*, 2153−2164.

change in $(PCy_3)_2RuCl_2({=}CHR)$ at 25 °C is calculated from a reported Eyring analysis[10] to be 1.6, while the metathesis rate ratio for **3P**/**1P** is 10 or more (10−13, depending on concentration).

Increasing the concentration of the complex decreased the rate, probably due to an increased rate of phosphine reassociation. This would imply that the alkene concentration is not high enough for saturation kinetics, even with an alkene/complex ratio of 33−100. Support for this was obtained in two other ways. First, reducing the alkene concentration 10-fold (alkene/complex ratio of 10) reduced the rate for **3P** by 25%.[19] Second, following the protocol of Grubbs and co-workers,[10] we measured rates for **3P** and ethyl vinyl ether with different concentrations of added PCy_3. By plotting $1/k_{obs}$ vs $[PCy_3]/[alkene]$, we obtained as the slope the relative rate constants for binding of PCy_3 and ethyl vinyl ether to the unsaturated, 14-electron complex. The value obtained for **3P** was 2600, representing a strong preference for binding of PCy_3. This contrasts with the reported value of 1.25 for **1P**,[10] representing a relatively equal preference for PCy_3 and alkene. Thus, while the alkylidenes initiate more rapidly than the benzylidene, their greater tendency to rebind PCy_3 also has implications for their use in catalysis.

The catalytic activity of **3P** was tested in the ring-opening metathesis polymerization (ROMP) of dicyclopentadiene.[20] A solution of 0.6 mol % **3P** in 1/1 dicyclopentadiene/CH_2Cl_2 caused gelation at ambient temperature in less than 2 min. In comparison, **1P** required ca. 3 min to cause gelation.

Interestingly, complex **3P** showed no activity in the ring-closing metathesis (RCM) of diethyl diallylmalonate,[21] under conditions for which **1P** gave complete reaction after 6 h.[22] The stoichiometric reaction of **3P** with diethyl diallylmalonate, forming the methylidene $(H_2IMes)RuCl_2({=}CH_2)(PCy_3)$ and the ring-closed cyclopentene product, proceeded completely at a rate similar to that for the other stoichiometric reactions of **3P**. A possible explanation for the lack of catalysis is that the faster PCy_3 dissociation of **3P** leads to a higher PCy_3 concentration and faster deactivation of the propagating methylidene catalyst, $(H_2IMes)RuCl_2({=}CH_2)$.[23]

Reaction of complexes **2B**−**4B** with acetylene resulted in the formation of polyacetylene (PA), as reported for **1B**.[24] Complex **3P** also results in the formation of polyacetylene, though in lower yields. In side-by-side runs with 2.5 mg of catalyst, **1P** gave 4.5 mg of PA while **3P** gave 2.7 mg of PA. Under similar conditions, **1B** gave 25.8 mg of PA and **2B** gave 14.4 mg of PA.

In summary, we have prepared and studied a number of ruthenium alkylidene complexes that react quickly in stoichiometric olefin metathesis reactions and show some promise as catalysts. The decomposition reactions are still under study.

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Supporting Information Available: Text and figures giving experimental details, kinetic plots, and ^1H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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[19] Increasing the ethyl vinyl ether concentration from 1.0 to 2.0 M decreased the rate slightly from 14×10^{-4} to 13×10^{-4} s^{-1}. This likely indicates that near-saturation conditions exist at these higher concentrations. The small decrease can be attributed to either a solvent effect (2.0 M corresponds to a 1/2 alkene/C_6D_6 ratio) or experimental error.

[20] Woodson, C. S.; Grubbs, R. H. U.S. Patent 5 939 504, 2000; *Chem. Abstr.* **2000**, *132*, 123053.

[21] Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953−956.

[22] Reactions were run with 0.1 mol % catalyst (0.01 mM) in C_6D_6 at 25 °C.

[23] Deactivation can occur through either coordination or decomposition.[13b] The CH_2 ^1H NMR signal for $(H_2IMes)RuCl_2({=}CH_2)(PCy_3)$ was observed in the attempted catalytic reactions of **3P**, consistent with deactivation by coordination. Another possible explanation is that **3P** might contain an impurity that prevents catalysis.

[24] Schuehler, D. E.; Williams, J. E.; Sponsler, M. B. *Macromolecules* **2004**, *37*, 6255−6257.