

Articles

Metathesis of Electron-Rich Olefins: Structure and Reactivity of Electron-Rich Carbene Complexes

Janis Louie and Robert H. Grubbs*

Arnold and Mabel Beckman Laboratories of Chemical Synthesis,
Division of Chemistry and Chemical and Chemical Engineering,
California Institute of Technology, Pasadena, California 91125

Received December 5, 2001

The addition of excess $\text{H}_2\text{C}=\text{C}(\text{H})\text{ER}$ to $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{C}(\text{H})\text{R}$ (**1a,b**) afforded a series of well-defined ruthenium carbene complexes, $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{C}(\text{H})\text{ER}$ (ER = OEt (**5**), SEt (**6**), SPh (**7**), N(carbazole) (**8**), N(pyrrolidinone) (**9**)) in yields ranging from 66 to 90%. Such complexes containing an electron-donating group on the carbene carbon are often referred to as Fischer-type carbenes. Replacement of one phosphine ligand with 1,3-dimesitylimidazolylidene (IMes) afforded the respective mixed-ligand complexes $(\text{IMes})(\text{PCy}_3)\text{Cl}_2\text{Ru}=\text{C}(\text{H})\text{ER}$ (**11–14**) in 48–89% yield. Alternatively, addition of $\text{H}_2\text{C}=\text{C}(\text{H})\text{OEt}$ to $(\text{H}_2\text{IMes})(\text{PCy}_3)\text{Cl}_2\text{Ru}=\text{C}(\text{H})\text{Ph}$ (**3a**; H_2IMes = 1,3-dimesityl-4,5-dihydroimidazolylidene) afforded $(\text{H}_2\text{IMes})(\text{PCy}_3)\text{Cl}_2\text{Ru}=\text{C}(\text{H})\text{OEt}$ (**15**) in 93% yield. The crystal structures of complexes **5**, **7–9**, and **11** were determined and found to be structurally similar to the parent ruthenium alkylidene ($[\text{Ru}]=\text{C}(\text{H})\text{R}$) complexes. In solution, the chemical shift of the $[\text{Ru}]=\text{C}(\text{H})\text{ER}$ resonance in ^1H NMR spectra was found to be inversely related to the electronegativity of the α -heteroatom; however, no trends were evident in the ^{31}P or ^{13}C NMR spectra. Intramolecular coordination of the pendant amide carbonyl group to the Ru center established a temperature-dependent equilibrium between complexes **9** and **14** and their cyclometalated forms. All Ru electron-rich complexes initiated the ring-opening metathesis polymerization (ROMP) of strained cyclic olefins and the ring-closing metathesis (RCM) of diethyl diallylmalonate. A general trend in the relative reactivities and thermal stabilities of the $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{C}(\text{H})\text{ER}$ complexes followed the order $\text{C} > \text{N} > \text{S} > \text{O}$. In addition, complexes coordinated with an N-heterocyclic carbene ligand (e.g., $(\text{IMes})(\text{PCy}_3)\text{Cl}_2\text{Ru}=\text{C}(\text{H})\text{ER}$) displayed enhanced activities in olefin metathesis and were thermally more stable than their bis(phosphine) analogues. Finally, the thermal decomposition product of $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{C}(\text{H})\text{OEt}$ was isolated and determined by X-ray analysis to be $(\text{PCy}_3)_2\text{ClRu}(\text{H})\text{CO}$ (**10**).

Introduction

Over the past decade, the development of Ru-based olefin metathesis catalysts has led to their use in a variety of organic and polymer synthesis applications.¹ The catalysts with the general structure $\text{LL}'\text{X}_2\text{Ru}=\text{CHR}$ have received the bulk of the attention because they are generally robust and functional group tolerant and because a variety of synthetic pathways exist. In addi-

tion, extensive synthetic,² mechanistic,³ and theoretical⁴ investigations have continually improved the performance of the catalysts and expanded their overall applicability. For example, early systems such as $(\text{PPh}_3)_2\text{Cl}_2\text{Ru}=\text{C}(\text{H})\text{C}(\text{H})=\text{CPh}_2$ were only effective in the ring-opening metathesis polymerization (ROMP) of highly strained olefins (e.g. norbornene) and displayed rather limited thermal stability.⁵ The incorporation of more bulky and electron-donating phosphines (e.g. PCy_3) afforded catalysts, $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHR}$ (**1a–c**; Figure 1), that are active in a wide variety of ring-closing metath-

(1) (a) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413–4450. (b) Fürstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3012–3043. (c) Schuster, M.; Blechert, S. *Angew. Chem., Int. Ed.* **1997**, *36*, 2036–2056.

(2) (a) Schwab, P.; France, M. B.; Ziller, R. H.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039–2041. (b) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100–110. (c) Wilhelm, T. E.; Belderrain, T. R.; Brown, S. N.; Grubbs, R. H. *Organometallics* **1997**, *16*, 3867–3869. (d) Belderrain, T. R.; Grubbs, R. H. *Organometallics* **1997**, *16*, 4001–4003. (e) Wolf, J.; Stüer, W.; Grünwald, C.; Werner, H.; Schwab, P.; Schulz, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1124–1128. (f) Weskamp, T.; Kohl, F. J.; Herrmann, W. A. *J. Organomet. Chem.* **1999**, *582*, 362–365. (g) Jafarpour, L.; Nolan, S. P. *Organometallics* **2000**, *19*, 2055–2057.

(3) (a) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887–3897. (b) Smith, A. B., III; Adams, C. M.; Kozmin, S. A. *J. Am. Chem. Soc.* **2001**, *123*, 990–991. (c) Aldhart, C.; Volland, M. A. O.; Hofmann, P.; Chen, P. *Helv. Chim. Acta* **2000**, *83*, 3306–3311.

(4) (a) Dölker, N.; Frenking, G. *J. Organomet. Chem.* **2001**, *617–618*, 225–232. (b) Adlhart, C.; Hinderling, C.; Baumann, H.; Chen, P. *J. Am. Chem. Soc.* **2000**, *122*, 8204–8214. (c) Spivak, G. J.; Coalter, J. N.; Oliván, M.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 999–1001.

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

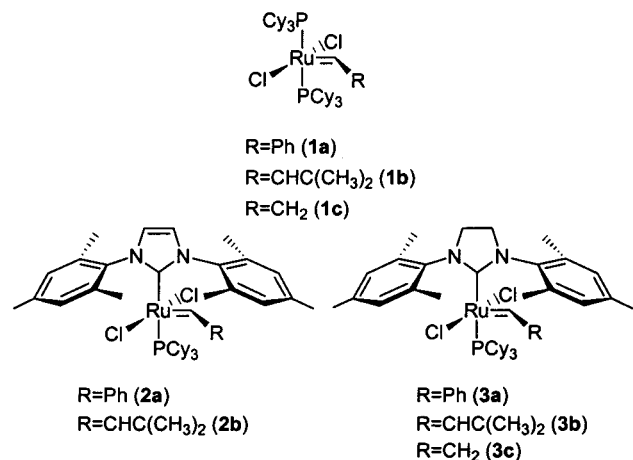


Figure 1. First- and second-generation ruthenium alkylidenes.

esis (RCM), cross-metathesis (CM), and ROMP applications.⁶ However, they are limited to olefinic substrates that are not sterically hindered or that do not possess functionality in the α -position (such as unsaturated esters and amides). This limitation was recently overcome through incorporation of large, electron-donating imidazolylidene ligands.⁷ The new catalysts (IMes)(PCy₃)Cl₂Ru=C(H)R (**2a,b**) and (H₂IMes)(PCy₃)Cl₂Ru=C(H)R (**3a,b**) (IMes = 1,3-dimesitylimidazolylidene; H₂IMes = 1,3-dimesityl-4,5-dihydroimidazolylidene) have enabled the preparation of not only α -functionalized olefins but also di-, tri-, and tetrasubstituted olefins.⁸ In addition, the increased activity of these catalysts has not resulted in the loss of functional group tolerance and inertness toward air and moisture.

The recent results with acrylates and related systems suggested that Ru electron-rich carbene complexes derived from functionalized olefins such as enols,⁹ enamines,¹⁰ and vinyl sulfides⁹ were relatively unreactive in metathetical [2 + 2] reactions with olefins.^{11,12}

(6) (a) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858–9859. (b) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446–452. (c) O'Leary, D. J.; Blackwell, H. E.; Washenfelder, R. A.; Grubbs, R. H. *Tetrahedron Lett.* **1998**, *39*, 7427–7430. (d) O'Leary, D. J.; Blackwell, H. E.; Washenfelder, R. A.; Miura, K.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 1091–1094.

(7) (a) Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2490–2492. (b) Weskamp, T.; Kohl, F. J.; Hieringer, W.; Gleich, D.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2416–2419. (c) Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674–2678. (d) Scholl, M.; Deng, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953–956.

(8) (a) Ackermann, L.; Fürstner, A.; Weskamp, T.; Kohl, F. J.; Herrmann, W. A. *Tetrahedron Lett.* **1999**, *40*, 4787–4790. (b) Chatterjee, A. K.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 1751–1753. (c) Chatterjee, A. K.; Morgan, J. P.; Scholl, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 3783–3784. (d) Lee, C. W.; Grubbs, R. H. *Org. Lett.* **2000**, *2*, 2145–2147. (e) Fürstner, A.; Thiel, O. R.; Ackerman, L.; Schanz, H.-J.; Nolan, S. P. *J. Org. Chem.* **2000**, *65*, 2204–2207. (f) Briot, A.; Bujard, M.; Gouverneur, V.; Nolan, S. P.; Mioskowski, C. *Org. Lett.* **2000**, *2*, 1517–1519. (g) Choi, T.-L.; Chatterjee, A. K.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2001**, *40*, 1277–1279.

(9) Fischer, P. In *The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulphur Analogues*; Patai, S., Ed.; Wiley: Chichester, U.K., 1980; Vol. 1, pp 761–820 and references therein.

(10) (a) Hickmott, P. W. *Tetrahedron* **1982**, *38*, 1975–2050. (b) *The Chemistry of Enamines*; Rappoport, Z., Ed.; Wiley: Chichester, U.K., 1994; Vols. 1 and 2.

(11) Coalter, J. N.; Caulton, K. G. *New J. Chem.* **2001**, *25*, 679–684.

(12) For some early-transition-metal Fischer-type carbenes that undergo metathesis, see: (a) Katz, T. J.; Acton, N. *Tetrahedron Lett.* **1976**, *47*, 4251–4254. (b) Katz, T. J.; Lee, S. J.; Shippey, M. A. *J. Mol. Catal.* **1980**, *8*, 219–226.

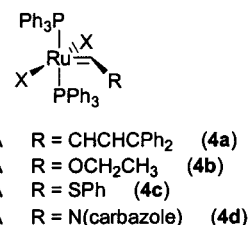


Figure 2. Triphenylphosphine-ligated ruthenium alkylidenes.

For example, an early report demonstrated that the ruthenium alkylidenes (PPh₃)₂(TFA)₂Ru=C(H)R (**4a**) reacted with vinyl ethers, amines, and sulfides to afford the Ru Fischer-type complexes (PPh₃)₂(TFA)₂Ru=C(H)ER (**4b–d**, ER = OEt, SPh, N(carbazole); Figure 2), which were subsequently found to be inert toward olefins.¹³ In fact, ethyl vinyl ether is commonly used to quench Ru-based ring-opening metathesis polymerizations, affording a methylene-terminated polymer and the Ru Fischer-type carbene (PCy₃)₂Cl₂Ru=C(H)OEt.¹⁴

However, a number of recent reports have indicated that [Ru]=C(H)OR type complexes may indeed be active olefin metathesis catalysts.¹⁵ Although a few Ru Fischer-type carbenes have been synthesized and characterized, a detailed study of their fundamental structures and reactivity is required.^{13,15b–d,16} In addition to reactivity, the thermal stability of Ru Fischer-type complexes has not been examined, even though they are believed to be more thermally stable than their alkylidene counterparts.^{15c} To address the effect of directly modifying the electronic nature of the carbene carbon, we have prepared and characterized a series of well-defined carbenes (PCy₃)₂Cl₂Ru=C(H)ER and (L)(PCy₃)Cl₂Ru=C(H)ER (L = IMes, H₂IMes; ER = OR, SR, NR). As will be discussed below, the complexes contain structural (solution and solid-state) and thermal characteristics similar to those of Ru alkylidenes. More importantly, these catalysts were found to be active in a variety of olefin metathesis reactions. These results define the requirements for the efficient metathesis of functionalized olefins such as enols, enamines, and vinyl sulfides.

Results and Discussion

Synthesis and Characterization of Bis(phosphine) Ru Electron-Rich Carbene Complexes. The reaction between various vinyl ethers and (PCy₃)₂Cl₂

(13) Wu, Z.; Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 5503–5511.

(14) (a) Maynard, H. D.; Grubbs, R. H. *Macromolecules* **1999**, *32*, 6917–6924. (b) Weck, M.; Mohr, B.; Maughon, B. R.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 6430–6437. (c) In addition, there has been one report that involves the use of a derivatized vinyl ether as a means to add an end cap to a metathesis polymer; see: Gordon, E. J.; Gestwicki, J. E.; Strong, L. E.; Kiessling, L. L. *Chem. Biol.* **2000**, *7*, 9–16.

(15) (a) Katayama, H.; Urushima, H.; Ozawa, F. *Chem. Lett.* **1999**, 269–370. (b) Katayama, H.; Urushima, H.; Ozawa, F. *J. Organomet. Chem.* **2000**, *606*, 16–25. (c) Katayama, H.; Urushima, H.; Nishioka, T.; Wada, C.; Nagao, M.; Ozawa, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 4513–4515. (d) van der Schaaf, P. A.; Kolly, R.; Kirner, H.-J.; Rime, F.; Mühlebach, A.; Hafner, A. *J. Organomet. Chem.* **2000**, *606*, 65–74.

(16) (a) Coalter, J. N., III; Spivak, G. J.; Gérard, H.; Clot, E.; Davidson, E. R.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1998**, *120*, 9388–9389. (b) Huang, D.; Bollinger, J. C.; Streib, W. E.; Foltling, K.; Young, V., Jr.; Eisenstein, O.; Caulton, K. G. *Organometallics* **2000**, *19*, 2281–2290.

Download English Version:

<https://daneshyari.com/en/article/5409873>

Download Persian Version:

<https://daneshyari.com/article/5409873>

[Daneshyari.com](https://daneshyari.com)