

SYNLETT Spotlight 159

Grubbs' Metathesis Catalyst – A Versatile Catalysts for Non-Metathetic Reactions

Compiled by Anuradha Mukherjee



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

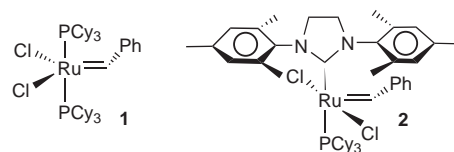
Anuradha Mukherjee was born in 1975 in Asansol, India. After having obtained her MSc in Chemistry from Burdwan University, she started working for her PhD at the National Chemical Laboratory, Pune. Since 2004 she has been following her research interest in the synthesis of late transition metal catalysts with new pyrazolyl-based ligands for C-C and C-N cross-coupling reactions at the Indian Association for the Cultivation of Science, Kolkata.

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Introduction

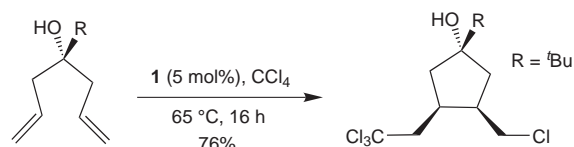
Grubbs' ruthenium-based catalysts (**1** and **2**) have demonstrated remarkable efficiency in olefin metathesis over the past ten years.¹ However, non-metathetic applications appeared very recently that deserve special attention and broaden the synthetic utility of Grubbs' catalysts.² The complexes were shown to catalyze the Kharasch addition, the removal of allyl groups from amines, the atom-transfer radical polymerization,³ the hydrogenation of olefins, the transfer hydrogenation of ketones,⁴ the dehydrogenative oxidation of alcohols, the dehydrogenative condensation of alcohols, isomerization, hydrosilylation of alkynes, cycloaddition and the hydro-silylation of carbonyls.⁵ The aim of this article is to give some examples of these advances, with special focus on practical concerns.

Catalyst **1** is prepared by treatment of phenyl diazomethane with $\text{RuCl}_2(\text{PPh}_3)_3$ complex, followed by replacement of PPh_3 with PCy_3 .⁶ The replacement of one PCy_3 ligand by an imidazol-based N-heterocyclic carbene (NHC) from complex **1** affords catalyst **2** in quantitative yield.⁷ Both catalysts are very stable to air and moisture.

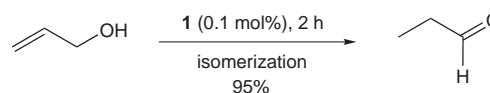


Abstracts

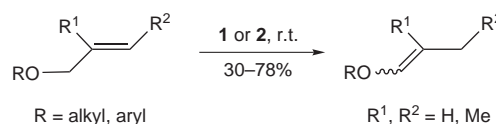
(A) Complex **1** promotes the atom-transfer radical addition. Radical cyclization occurs with high diastereoselectivity.⁸



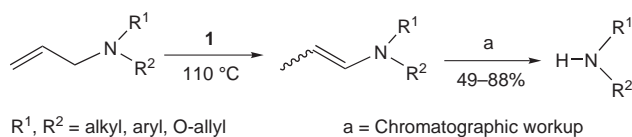
(B) Grubbs-type carbene **1** (ca. 1:1000) catalyzes the isomerization of allyl alcohol and affords propionaldehyde in a very high yield. The methyl derivative, 3-buten-2-ol, leads to the corresponding 2-butanone.⁹



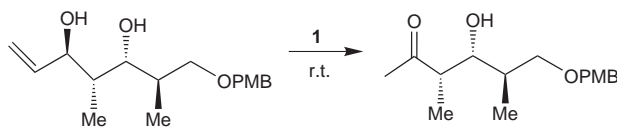
(C) Isomerization of unsaturated oxygen and nitrogen-containing compounds takes place in presence of Grubbs' carbenes at ambient temperature in moderate yield.¹⁰



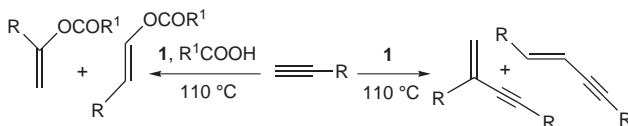
(D) Grubbs' carbene efficiently catalyzes the deprotection of tertiary allylic amines. In addition to the novelty of the method, it is general, selective, and synthetically simple. Significantly, the catalytic system directs the reaction toward the selective deprotection of allylamines in the presence of allylic ethers.¹¹



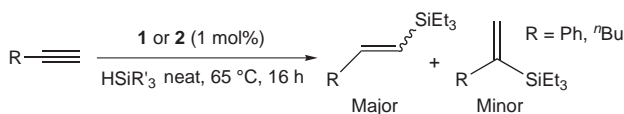
(E) Alk-1-en-3-ols under exposure to complex **1** afford an allylic alcohol to methyl ketone transformation even at room temperature.¹²



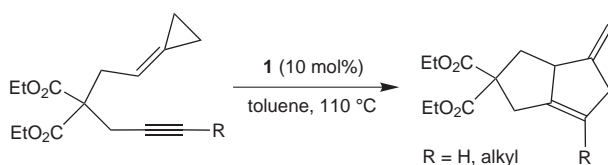
(F) The catalytic activity of Grubbs' first-generation catalyst towards dimerization, vinylation or nucleophilic attack of carboxylic acids on terminal alkynes was observed very recently. The preference for dimerization or vinylation is strongly dependent on the nature of the terminal alkyne.¹³



(G) Complexes are shown to be effective catalysts for the inter- and intramolecular hydrosilylation of alkynes.¹⁴



(H) Very recently, it was observed that Grubbs' carbene complexes can catalyze [3C+2C] cycloaddition processes.¹⁵



References and Notes

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