

SYNLETT Spotlight 145

Dirhodium Tetraacetate: An Effective Catalyst in Organic Synthesis

Compiled by Pranab Haldar



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

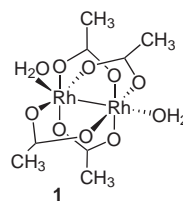
Pranab Haldar was born in Midnapur, India. He received his M.Sc. (Chemistry) degree in 2001 from Banaras Hindu University (India). He is currently working on his Ph.D. thesis under the supervision of Prof. J. K. Ray at Indian Institute of Technology (Kharagpur), India. He received 'Young Scientist' award of the Indian Chemical Society in 2002. His research interests focus on synthesis of bioactive *N*-aryl- γ -lactam derivatives and pyrroles and development of environmentally benign methodologies for the synthesis of aza-heterocycles.

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Introduction

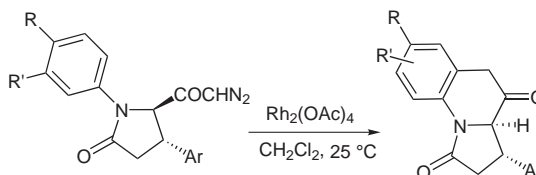
Unlike free carbenes, Rh(II)-catalyzed carbenoids often undergo highly regio- and stereoselective intra- and intermolecular insertion into a sigma bond. Although many transition-metal complexes afford carbenoids, only those of Rh(II) have shown general applicability due to their higher selectivity. The pioneering development of Rh(II) acetate by Teyssie and co-workers¹ has resulted in highly chemo-, regio- and stereoselective reactions of α -diazocarbonyl compounds via a variety of reactivity modes. Subsequently, an extensive library of successful transformations rapidly evolved, ranging from Rh(II)-catalyzed OH² and NH³ insertion to cyclopropanation of olefins⁴ and aromatic systems.⁵

Rh(II)-catalyzed reactions can often be performed in the presence of water. Because of the high partition of Rh₂(OAc)₄ in the water phase, the catalyst can be effectively reused,⁶ permitting the development of a more environmentally benign process. Dirhodium tetraacetate is conveniently prepared by refluxing RhCl₃·3H₂O and sodium acetate/acetic acid in ethanol and is now also commercially available. The Rh₂(OAc)₄ core has approximately D_{4h} symmetry, with the Lewis base adducts H₂O in **1** coordinating to the sites *trans* to the Rh–Rh bond.

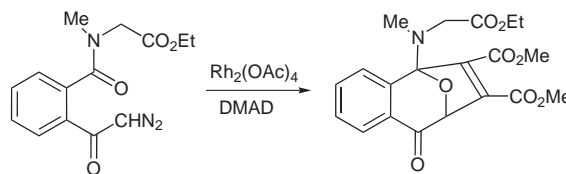


Abstracts

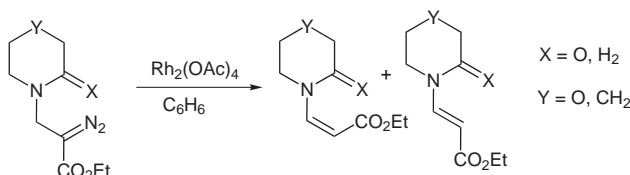
(A) Rh(II)-catalyzed regioselective intramolecular and regioselective intermolecular CH insertion into aliphatic and aromatic C–H bonds is a very powerful methodology for the synthesis of a diverse range of organic compounds.⁷



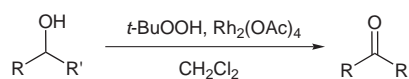
(B) Rh₂(OAc)₄ is a very useful catalyst for two-component-cycloaddition as well as three-component 1,3-dipolar cycloaddition reactions.⁸



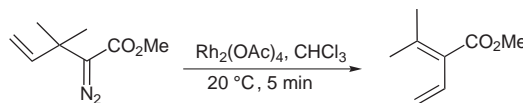
(C) On treatment with catalytic rhodium(II) acetate, cyclic diazoamides and diazoamines furnished the corresponding cyclic enamides and Z enamines, respectively.⁹



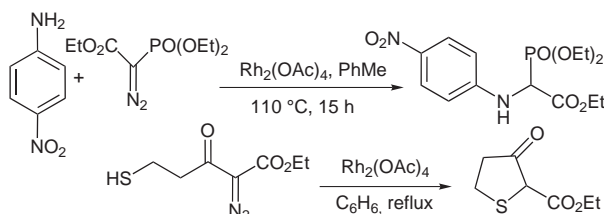
(D) Allylic and benzylic alcohols were oxidized to the corresponding carbonyl compounds using *tert*-butyl hydroperoxide in stoichiometric amounts and $\text{Rh}_2(\text{OAc})_4$ as catalyst (1 mol%) in dichloromethane at ambient temperature.¹⁰



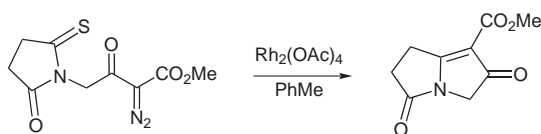
(E) Intramolecular 1,2-insertions into C–C bonds by Rh(II) carbenoids have been used for the synthesis of substituted dienes.¹¹



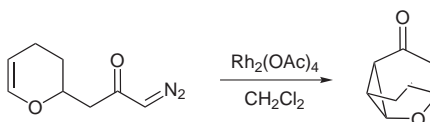
(F) Rh(II) carbenoids react with amines, alcohols or thiols to yield the product of a formal intra- or intermolecular X–H bond (X = N/O/S) insertion via the formation of a ylide intermediate.¹²



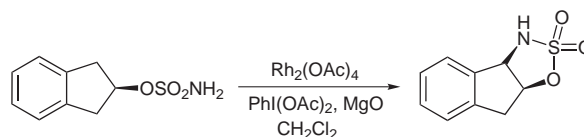
(G) Rh(II) carbenoids react readily with lone pairs giving the corresponding ylides, which are valuable intermediates, capable of undergoing a broad range of synthetically useful transformations.¹³



(H) $\text{Rh}_2(\text{OAc})_4$ is an effective catalyst for the intra- and intermolecular cyclopropanation reactions through the decomposition of diazocarbonyl compounds.¹⁴



(I) Du Bois et al. reported the Rh(II)-catalyzed oxidative cyclization of sulfamate and carbamate esters.¹⁵



References

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