SYNLETT
Spotlight 145

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

Dirhodium Tetraacetate: An Effective Catalyst in Organic Synthesis

Compiled by Pranab Haldar

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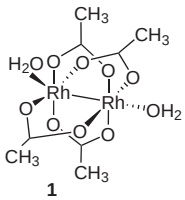
Introduction

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-workers[1] 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 OH[2] and NH[3] insertion to cyclopropanation of olefins[4] and aromatic systems.[5,]

Rh(II)-catalyzed reactions can often be performed in the presence of water. Because of the high partition of $Rh_2(OAc)_4$ 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 $RhCl_3{\cdot}3H_2O$ and sodium acetate/acetic acid in ethanol and is now also commercially available. The $Rh_2(OAc)_4$ core has approximately D_{4h} symmetry, with the Lewis base adducts H_2O in **1** coordinating to the sites *trans* to the Rh–Rh bond.



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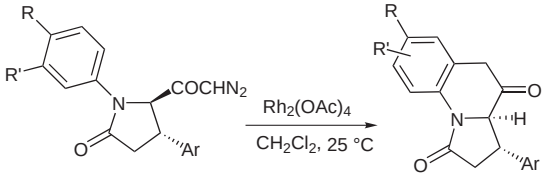
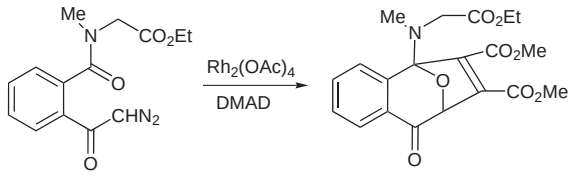
Abstracts

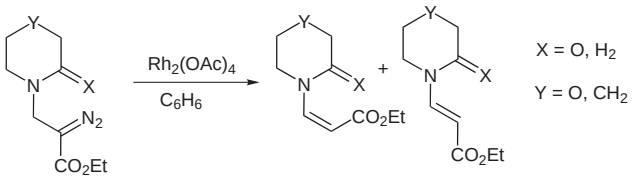
(A) Rh(II)-catalyzed regioselective intramolecular and regiospecific intermolecular CH insertion into aliphatic and aromatic C–H bonds is a very powerful methodology for the synthesis of a diverse range of organic compounds.[7]



(B) $Rh_2(OAc)_4$ 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, repectively.[9]



SYNLETT 2005, No. 20, pp 3169–3170
Advanced online publication: 28.11.2005
DOI: 10.1055/s-2005-922755; Art ID: V14705ST
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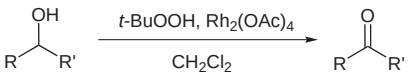
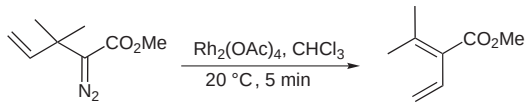
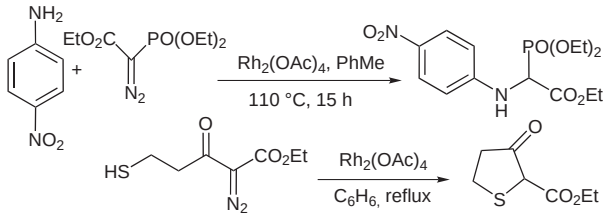
(D) Allylic and benzylic alcohols were oxidized to the corresponding carbonyl compounds using *tert*-butyl hydroperoxide in stoichiometric amounts and $Rh_2(OAc)_4$ as catalyst (1 mol%) in dichloromethane at ambient temperature.[10]



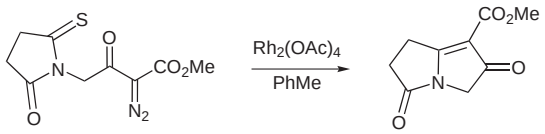
(E) Intramolecular 1,2-insertions into C–C bonds by Rh(II) carbenoids have been used for the synthesis of substituted dienes.[11]



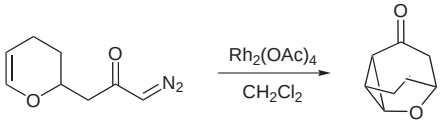
(F) Rh(II) carbenoids react with amines, alcohols or thiols to yield the product of a formal intra- or intermolecular X–H bond (X = N/O/S) insertion via the formation of an ylide intermediate.[12]



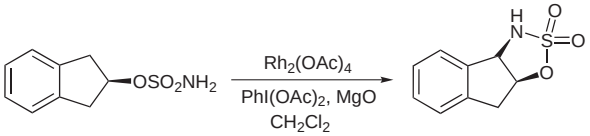
(G) Rh(II) carbenoids react readily with lone pairs giving the corresponding ylides, which are valuable intermediates, capable of undergoing a broad range of synthetically useful transformations.[13]



(H) $Rh_2(OAc)_4$ 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]



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