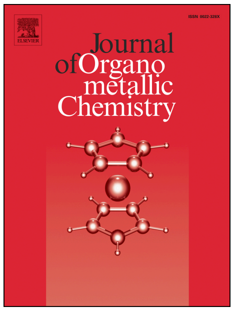

Insertion of carbenoids into X-H bonds catalyzed by the cyclobutadiene rhodium complexes

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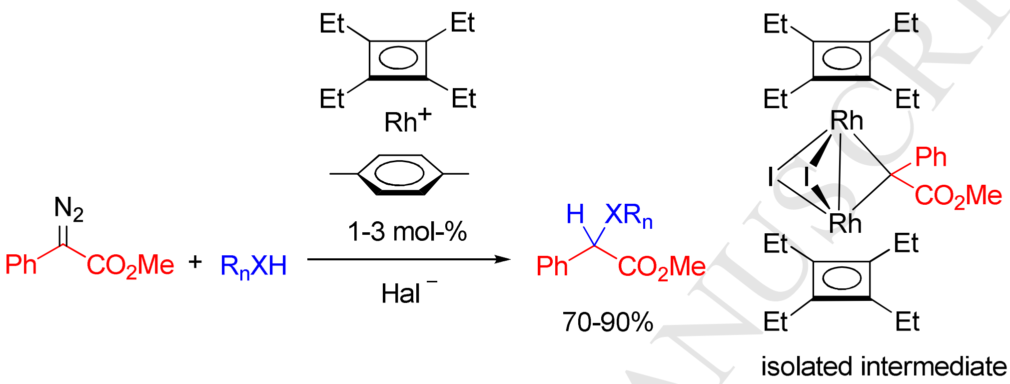
Dedicated to Academician I. P. Beletskaya in recognition of her fundamental contribution to the development of organometallic chemistry and catalysis

Graphical Abstract



Graphical Abstract Synopsis

Cyclobutadiene rhodium complexes catalyze the formation of carbenoid species from diazo acetates and subsequent insertion of carbenoids into X-H bonds (X = B, N, O, Si). The isolated intermediate complex unexpectedly has a binuclear structure with a bridging carbene ligand.

Abstract

The cyclobutadiene rhodium complex $[(C_4Et_4)RhCl]_2$ (generated from $[(C_4Et_4)Rh(p\text{-xylene})]PF_6$ and $BnNEt_3Cl$) catalyzes reaction of methyl α-diazophenylacetate with R_nX-H compounds to give the insertion products methyl 2-R_nX-2-phenylacetates in 70–90% yields (R_nX-H = methanol, *tert*-butylamine, 2,6-diisopropylaniline, morpholine, diallylamine, triethylsilane, triethylamine-borane). The stoichiometric reaction of $[(C_4Et_4)RhI]_2$ with methyl α-diazophenylacetate gives the intermediate complex $(C_4Et_4)_2Rh_2(\mu\text{-}I)_2$(μ-1-carboxymethyl-1-phenylmethylene), which has a binuclear structure with bridging iodide and carbene ligands. This result indicates that catalytically active carbene species may have more complex structures than the commonly assumed $L_nM{=}CR_2$.

Keywords: diazo compound, carbene, rhodium, cyclobutadiene, catalysis, pi-complex