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

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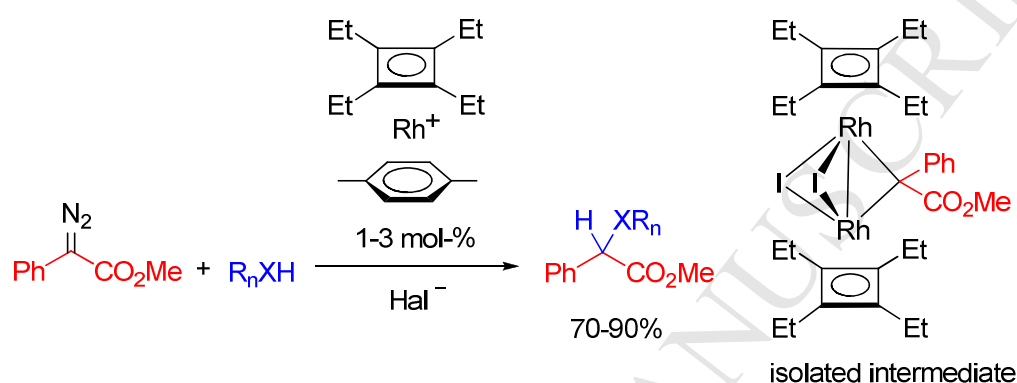
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*Dedicated to Academician I. P. Beletskaya in recognition of her fundamental contribution to the development of organometallic chemistry and catalysis*

### 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 ( $\text{X} = \text{B}, \text{N}, \text{O}, \text{Si}$ ). The isolated intermediate complex unexpectedly has a binuclear structure with a bridging carbene ligand.

### Abstract

The cyclobutadiene rhodium complex  $[(\text{C}_4\text{Et}_4)\text{RhCl}]_2$  (generated from  $[(\text{C}_4\text{Et}_4)\text{Rh}(\text{p-xylene})]\text{PF}_6$  and  $\text{BnNEt}_3\text{Cl}$ ) catalyzes reaction of methyl  $\alpha$ -diazophenylacetate with  $\text{R}_n\text{X-H}$  compounds to give the insertion products methyl 2- $\text{R}_n\text{X}$ -2-phenylacetates in 70–90% yields ( $\text{R}_n\text{X-H}$  = methanol, *tert*-butylamine, 2,6-diisopropylaniline, morpholine, diallylamine, triethylsilane, triethylamine-borane). The stoichiometric reaction of  $[(\text{C}_4\text{Et}_4)\text{RhI}]_2$  with methyl  $\alpha$ -diazophenylacetate gives the intermediate complex  $(\text{C}_4\text{Et}_4)_2\text{Rh}_2(\mu\text{-I})_2(\mu\text{-1-carboxymethyl-1-phenylmethylene})$ , 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  $\text{L}_n\text{M}=\text{CR}_2$ .

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

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