C(sp³)–H Insertions with Donor Rhodium Carbenoids

**Synthesis of donor rhodium carbenoids and their use in C(sp³)–H insertions**

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\begin{align*}
\text{X} = \text{CH}_2, \text{O} &; \text{Y} = \text{OR, Alk, Ar} \\
n = 0, 1
\end{align*}
\]

1. Ac₂O, DMAP, CH₂Cl₂, r.t.  
2. O₃/O₂, CH₂Cl₂, –78 °C then Ph₃P, –78 °C to r.t.

**Significance:** The functionalization of unactivated C(sp³)–H bonds by insertion of transition-metal carbenoids is an attractive method of forming C–C bonds. However, while acceptor-substituted rhodium(II) carbenoids have been investigated, little is known on the reactivity of donor-substituted rhodium(II) carbenoids in C(sp³)–H insertions, due to the difficulty in handling the unstabilized diazo precursors. The authors report the facile generation of donor-substituted rhodium(II) carbenoids by ring opening of 3,3-dimethylcyclopropenylcarbene, and their use in intramolecular C(sp³)–H insertions, which occur with high yield and diastereoselectivity.

**Comment:** Donor-substituted rhodium carbenoids were found to trigger 1,5- and 1,6-C–H insertions with high diastereoselectivity to generate a variety of functionalized carbocycles and oxygen heterocycles, which can be subsequently ozonolyzed to the corresponding ketones. Deuterium-labelling studies suggest that the reaction involves a stereospecific process at the carbenoid carbon atom, and occurs in a concerted fashion with a late transition state. Furthermore, the C–H insertion process is selective for only one of two diastereotopic methylene groups, which the authors exploited to access various bicyclic compounds.