

**Rh-catalyzed Diastereoselective [3+2+1] Carbocyclization of
Alkenylenecyclopropane with CO:
A Density Functional Study**

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Transition metal-catalyzed [m+n+o] carbocyclization reactions represent an important class of reactions due to their ability to obtain fused polycyclic systems which are useful synthons for biologically active natural products. In order to design a new strategy for the construction of six-membered fused bicyclic fragment with high diastereocontrol, we represent a mechanistic study of Rh(I)-catalyzed [3+2+1] cycloaddition of an alkenylenecyclopropane with CO in presence of phosphite P(OR)₃. We find that ring opening of cyclopropane involves an interesting Rh-trimethylenemethane (Rh-TMM) intermediate where TMM moiety demonstrates tri-coordinate facial binding to Rh. The rate-determining diastereoselective event is only 25 kcal/mol, hence we propose the cycloaddition should be very feasible under mild condition.