Supporting Information

Mechanism of Rhodium-Catalyzed Carbene Formation from Diazo Compounds

Freeman M. Wong[†], Jianbo Wang[#], Alvan Hengge[‡]*, Weiming Wu[†]*

[†]*Department of Chemistry and Biochemistry, San Francisco State University, San Francisco, California 94132* [‡]*Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322*
[#]*Key Laboratory of Bioorganic Chemistry and Molecular Engineering of the Ministry of Education, College of Chemistry, Peking University, Beijing, China.*

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General Experimental Procedure for Rhodium-Catalyzed Carbene Formation and Reaction: Methyl α-diazophenylacetate[1] (176 mg, 1.0 mmol) was dissolved in anhydrous CH_2Cl_2 (20 mL) under nitrogen. The solution was cooled to 0 °C and triethylsilane (128 mg, 1.1 mmol) and $Rh_2(OAc)_4$ (0.01 mg, 0.01 mol%) were added. The reaction mixture was stirred for 5 min at 0 °C under nitrogen. Upon removal of solvent by rotary evaporation, the residue was immediately subjected to column chromatography in basic alumina with hexane/EtOAc (9:1) as eluent to isolate the unreacted starting material. Fraction of the reaction was calculated by comparing the mass of starting material initially used and recovered.

Axial coordination to the dirhodium catalyst is known to affect the reactions of Rh(II) carbene. However, dichloromethane is a very weakly coordinating solvent for transition metal complexes, so it should only weakly coordinate to the Rh(II) carbene, and thus have a negligible effect on the reaction (see reference 6d of the manuscript). The axial ligands are not shown in Scheme 1 of the manuscript for simplicity in presentation, as customary in previous works (see references 6d, 7, 8, 9 in the manuscript)

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1. Qu, Z.; Shi, W.; Wang, J. *J. Org. Chem.* **2001**, *66*, 8139-8144.

Kinetic Isotope Effect Data: Isotope Ratio data for the reactant and for the remaining starting material after partial reaction are below. Four trials were run, and two samples of the remaining starting material from each trial were subjected to isotope ratio mass spectrometry to obtain R_S, the $^{15}N/^{14}N$ ratio relative to the standard, which is the natural abundance of ^{15}N. Such isotope ratios are commonly expressed as delta values, where delta = [(isotope ratio in sample)/(isotope ratio in standard) –1]x1000. Delta values are converted into isotope ratios for calculation of the isotope effect. Six samples of the reactant were subjected to isotope ratio mass spectrometry, and the results averaged to give R_O. The kinetic isotope effects were calculated using the equation shown (equation 1 in the manuscript), where f is the fraction of reaction.

$$^{15}k_{obs} = \log(1 - f) / \log[(1 - f)(R_s / R_o)]$$

	Reactant delta values	R_O
	-14.494	
	-14.388	
	-13.363	
	-13.907	
	-13.91	
	-13.917	
Average:	-13.9965	0.9860035

Trial#	R_S Delta	Rs	f	KIE
1	16.100	1.01610	0.73	1.023503
1	16.722	1.01672	0.73	1.023993
2	2.244	1.00224	0.36	1.037997
2	5.961	1.00596	0.36	1.047012
3	0.322	1.00032	0.35	1.034627
3	0.938	1.00094	0.35	1.036159
4	9.690	1.00969	0.48	1.037669
4	9.420	1.00942	0.48	1.037229
			Mean	1.034774
			SD	0.007744
			SE	0.002738