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A Kinetic Study on the Pairwise Competition Reaction of α-Diazo Esters with Rhodium(II) Catalysts: Implication for the Mechanism of Rh(II)-Carbene Transfer

Zhaohui Qu, Weifeng Shi, and Jianbo Wang*

Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, Department of Chemical Biology, College of Chemistry, Peking University, Beijing 100871, China

wangjb@pku.edu.cn

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The relative rate constants for the Rh(II)-mediated diazo decomposition of a series of para- or meta-substituted diazophenylacetates were measured through intermolecular competition. The kinetic data were further subjected to Hammett correlation analysis and were found to have better linear correlation with σ^+. Reaction constants for four Rh(II) catalysts have been obtained, $Rh_2(OAc)_4$ ($\rho = -1.29$ with σ^+, $r = -0.99$), $Rh_2(Ooct)_4$ ($\rho = -1.31$ with σ^+, $r = -0.99$), $Rh_2(acam)_4$ ($\rho = -1.18$ with σ^+, $r = -0.99$), $Rh_2(O_2CCF_3)_4$ ($\rho = -1.46$ with σ^+, $r = -0.99$). The mechanistic implications of these data are discussed.

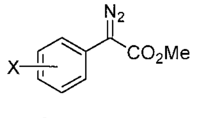
Introduction

Reactions of rhodium(II) complex mediated carbenoids have gained wide application in synthetic organic chemistry in the past decades.[1] Recent advances in asymmetric cyclopropanation, C−H bond insertion, and ylide reactions with chiral Rh(II) complex have reached a high level of enantiocontrol.[1,2] Along with the development in synthesis, the reaction mechanism of the the transformation of these carbenoids, especially the nature of the Rh(II) carbene intermediate, has aroused considerable interest. Previous investigation through intra- and intermolecular competition reactions has shown that Rh(II) carbene is electrophilic in nature,[3] while the ligands of the Rh(II) catalyst and the structure of the diazo compounds can significantly affect the reaction selectivity.[3,4] However, these mechanistic investigations were mainly carried out through the analysis of the final product distribution, which gave only the information on the reaction between metal carbene and the substrate. Little or no information could be obtained concerning the interaction of the diazo substrate with the transition metal catalyst from those studies.

Direct mechanistic investigation on the Rh(II)-catalyzed diazo decomposition process is sparse.[5] Pirrung and Morehead have recently demonstrated the application of saturation kinetics method in the study of diazo decomposition, from which informative kinetic parameters have been obtained.[6] In this paper, we describe our study on the diazo decomposition mechanism based on the linear free energy correlation analysis of the electronic effects of the Rh(II)-catalyzed diazo decomposition process.

Results and Discussion

Our approach is to measure the relative rate constants of the diazo decomposition of a series of para- or meta-substituted diazo phenylacetates **1a**−**g**. These diazo esters are employed in this investigation because the substituent in the phenyl ring can effectively interact with the reaction center through the relatively polarizable aromatic π-electron system. Since steric and conformational factors are minimized, pure electronic effects can be evaluated. The diazo compounds could be easily prepared by conventional diazo transfer reaction with TsN_3 and DBU as base.



1 a. X = *p*-OMe; **b.** X = *p*-Ph; **c.** X = *m*-Me;
d, X = H; **e.** X = *m*-OMe; **f.** X = *p*-Br
g. X = *p*-NO$_2$

In 1952, Yates proposed a mechanism for the diazo decomposition catalyzed by Cu catalyst.[7] For Rh(II)-catalyzed reaction, the previous investigation has shown that the most likely model of the diazo decomposition process involves the initial complexation of the negatively polarized carbon of the diazo compound to the axial site of the Rh(II) catalyst, which is coordinatively unsaturated

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(2) For reviews, see: (a) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911. (b) Davies, H. M. L.; Antoulinakis, E. G. *J. Organomet. Chem.* **2001**, *617−618*, 47. (c) Timmons, D. J.; Doyle, M. P. *J. Organomet. Chem.* **2001**, *617−618*, 98. (d) Hodgson, D. M.; Pierard, F. Y. T. M.; Stupple, P. A. *Chem. Soc. Rev.* **2001**, *30*, 50.

(3) (a) Taber, D. F.; Ruckle, R. E., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 7686. (b) Doyle, M. P.; Westrum, L. J.; Wolthuis, W. N. E.; See, M. M.; Boone, W. P.; Bagheri, V.; Pearson, M. M. *J. Am. Chem. Soc.* **1993**, *115*, 958. (c) Wang, P.; Adams, J. *J. Am. Chem. Soc.* **1994**, *116*, 3296. (d) Pirrung, M. C.; Morehead, A. T., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 8991. (e) Taber, D. F.; Song, Y. *J. Org. Chem.* **1996**, *61*, 6706. (f) Doyle, M. P.; Kalinin, A. V.; Ene, D. G. *J. Am. Chem. Soc.* **1996**, *118*, 8837. (g) Taber, D. F.; You, K. K.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 547. (h) Wang, J.; Chen, B.; Bao, J. *J. Org. Chem.* **1998**, *63*, 1853.

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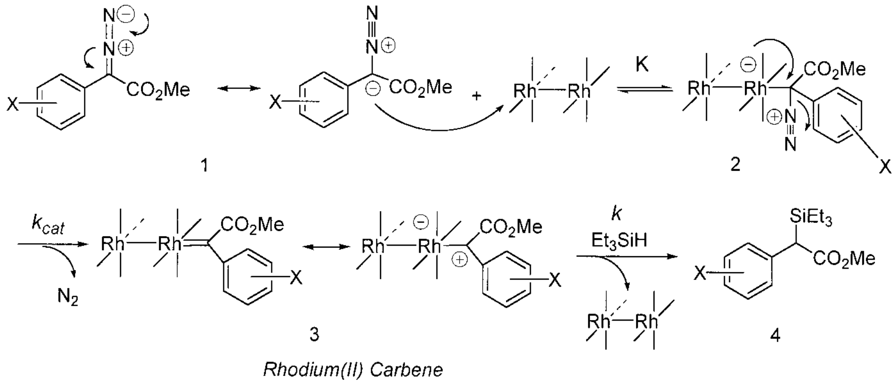
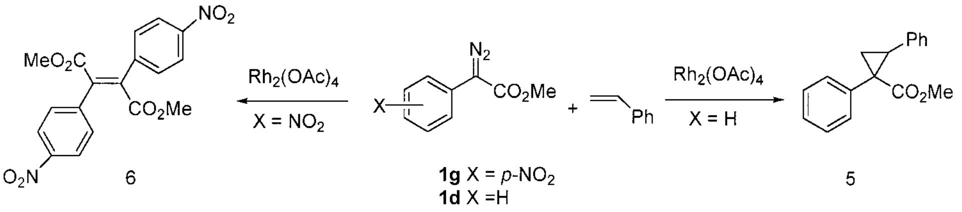
Scheme 1



Scheme 2



(Scheme 1).[6] Subsequent irreversible extrusion of N_2 from the intermediate **2** generates the Rh(II) carbene intermediate **3**. In this model, if the first step is a fast equilibrium and the second step is slow and rate limiting, as suggested by a previous study,[6] then the overall observed rate of the diazo decomposition will be $k_{obs} = Kk_{cat}[Rh(II)]$, where [Rh(II)] is the concentration of the catalyst.[8] In a pairwise intermolecular competition in which a substituted phenyldiazoacetate **1a**−**c**,**e**−**g** and diazo phenylacetate **1d** compete for the Rh(II) catalyst in the same reaction solution, the catalyst concentration is the same for the two diazo substrates and is assumed to keep constant within the period that the kinetic measurement is performed.[9] Thus, the relative rate constant for a substituted diazo phenylacetate to the diazo phenylacetate **1d** can be calculated as follows.[10]

$$k_{rel} = k_{obs(X)}/k_{obs(H)} = (K_X/K_H)[k_{cat(X)}/k_{cat(H)}] \quad (1)$$

The Hammett equation can be expressed in the following way.

$$\log [k_{obs(X)}/k_{obs(H)}] = \log [(K_X/K_H)(k_{cat(X)}/k_{cat(H)})] = \rho_1\sigma + \rho_2\sigma \quad (2)$$

Therefore, the measured electronic effects actually involve both the preequilibrium step and the following rate-limiting step.[11] In the diazo compounds, the carbon bearing the diazo group is negatively polarized, while the same carbon in the resulting Rh(II) carbene is positively polarized. An electron-withdrawing group like NO_2 will stabilize the diazo compound but destabilize the Rh(II) carbene intermediate. An electron-donating group will operate in the opposite manner. Thus, the diazo compounds bearing electron-withdrawing substituents will decompose more slowly than those bearing electron-donating substituents. Consequently, we should be able to observe significant electronic effects.

Since the Rh(II) carbene intermediate is highly reactive and the subsequent reaction is fast, to perform a kinetic measurement it will be necessary to choose a suitable clean carbenoid reaction to complete a catalytic cycle. We initially used styrene to trap the Rh(II) carbene intermediate. However, the diazo decomposition of *p*-nitrophenyldiazoacetate **1g** in the presence of excess styrene gave exclusively coupling product **6** (Scheme 2). Therefore, cyclopropanation is not suitable for our purpose. After several screenings, we were delighted to find Si−H insertion[12] is a highly efficient process and give clean insertion products for all the diazo substrates to be used in the kinetic study.

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[6] Pirrung, M. C.; Morehead, A. T., Jr. *J. Am. Chem. Soc.* **1996**, *118*, 8162.

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[8] A detailed kinetic treatment is submitted as Supporting Information.

[9] Although the Rh(II) catalyst has a very high turnover number when decomposing diazo compounds, the catalyst itself does decompose and lose activity as the reaction proceeds. Our experiment showed that if the reaction is completed within a relatively short period of time (in 60 min) the catalyst does not show a significant lose of activity.

[10] Panek et al. have recently reported an investigation of a competitive Si−H insertion of a series of para-substituted methyl aryldiazoacetates catalyzed by chiral Cu(I) complex. In the Hammett correlation, the k_X/k_H ratio was simply determined by the relative product yields. This situation could only be valid when the reaction is zero-order or pseudo zero-order both to the diazo substrate and to the silane. A reaction constant of −1.12 with σ was obtained. See: Dakin, L. A.; Ong, P. C.; Panek, J. S.; Steples, R. J.; Stavropoulos, P. *Organometallics* **2000**, *19*, 2896.

[11] For an example of Hammett analysis in multistep reactions, see: Miller, L. L.; Watkins, B. F. *J. Am. Chem. Soc.* **1976**, *98*, 1515.

[12] For example of Rh(II) carbene Si−H insertion, see: (a) Bagheri, V.; Doyle, M. P.; Taunton, J.; Claxton, L. E. *J. Org. Chem.* **1988**, *53*, 6158. (b) Landais, Y.; Parra-Rapado, L.; Planchenault, D.; Weber, V. *Tetrahedron Lett.* **1997**, *38*, 229.

Table 1. Relative Rate Constants of Diazo Decomposition[a]

		k_{rel}[b]			
entry	X	$Rh_2(OAc)_4$	$Rh_2(Ooct)_4$	$Rh_2(acam)_4$	$Rh_2(tfa)_4$
1	*p*-MeO	10.5	12.3	7.58	16.4
2	*p*-Ph	1.35	1.73	1.65	1.32
3	*m*-Me	1.20	1.19	1.25	1.54
4	H	1.00	1.00	1.00	1.00
5	*m*-MeO	1.00	0.62	1.12	0.98
6	*p*-Br	0.84	0.90	0.74	0.65
7	*p*-NO_2	0.084	0.102	0.099	0.072

[a] Experiments were preformed in CH_2Cl_2 at 0 °C, except when $Rh_2(acam)_4$ was the catalyst, in which case the reaction was run at room temperature. [b] Error limits are less than 5% with average deviation of two runs.

The pairwise competition kinetic measurement was performed by following the decrease of the diazo substrate concentration with HPLC.[13] Thus, a substituted diazo compound (**1**, X= *p*-NO_2, *p*-Br, *m*-OMe, *p*-Ph, *m*-Me, *p*-OMe) together with the phenyldiazoacetate (**1d**, X = H) was dissolved in CH_2Cl_2 at 0 °C or at room temperature, followed by the addition of a solution of the Rh(II) catalyst dissolved in CH_2Cl_2 or chlorobenzene. Aliquots were removed from the reaction solution at 5 min intervals. To terminate the diazo decomposition before analysis, the catalyst was either removed by a fast silica gel column [for $Rh_2(OAc)_4$] or was blocked by adding pyridine [for $Rh_2(acam)_4$, $Rh_2(Ooct)_4$, $Rh_2(O_2CCF_3)_4$], which can strongly bind to the catalytic sites.[14] The aliquots thus treated were immediately subjected to HPLC analysis to determine the concentration of the diazo substrates.

Kinetic plots of the data have revealed that the rate of the diazo compound consumption does obey the first-order kinetics in the concentration of diazo substrates. This is consistent with the mechanism shown in Scheme 1.

The relative rate constant calculated according to eq 1 is summarized in Table 1. As shown by the kinetic data, the diazo substrates with electron-donating substituents do decompose faster than those with electron-withdrawing substituents. For example, when $Rh_2(O_2CCF_3)_4$ is the catalyst, *p*-methoxyphenyldoazoacetate **1a** decomposes 226 times faster than *p*-nitrophenyldiazoacetate **1g**. Davies and Panaro have recently compared the chemoselectivity of *p*-methoxyphenyldiazoacetate **1a** and phenyldiazoacetate **1d** in Rh(II)-mediated carbenoid reactions. They observed that the diazoacetate with the most electron-donating functionality gave the highest chemoselectivity.[4f] Therefore, we can conclude here that the fastest reaction is actually most selective, because the step to generate the Rh(II) carbene intermediate is the rate-limiting step in overall transformation. The more stable Rh(II) carbene, which is consequently more chemoselective, will form faster.

Although the absolute rate constants are not measured in this study, it is apparent from the experiments that there is a difference in rates between the catalysts. The diazo decomposition is faster with $Rh_2(O_2CCF_3)_4$ than with $Rh_2(OAc)_4$ and then with $Rh_2(acam)_4$. It is known that the carbenoids generated from $Rh_2(O_2CCF_3)_4$ are less stable and more reactive,[3] but they formed faster. A reasonable explanation for this superficial contradiction with the above-mentioned substituent effects is that for $Rh_2(O_2CCF_3)_4$, the complexation constant is larger than that for $Rh_2(OAc)_4$ or $Rh_2(acam)_4$, because trifluoroacetate ligand is more electron-withdrawing. Although the subsequent nitrogen extrusion reaction maybe slower due to the formation of a less stable carbenoid, the overall rate constant of the diazo decomposition is larger.

Table 2. Correlation of log k_{rel} with Substituent Constants[a]

subst constants	ρ (r)[b]			
	$Rh_2(OAc)_4$	$Rh_2(Ooct)_4$	$Rh_2(acam)_4$	$Rh_2(tfa)_4$
σ^+	−1.29 (−0.99)	−1.31 (−0.99)	−1.18 (−0.99)	−1.46 (−0.99)
σ	−1.72 (−0.94)	−1.69 (−0.92)	−1.60 (−0.96)	−1.94 (−0.94)
σ^-	−1.11 (−0.91)	−1.07 (−0.87)	−1.03 (−0.93)	−1.23 (−0.89)

[a] Substituent constants were taken from ref 15. [b] ρ = reaction constant, r = correlation coefficient.

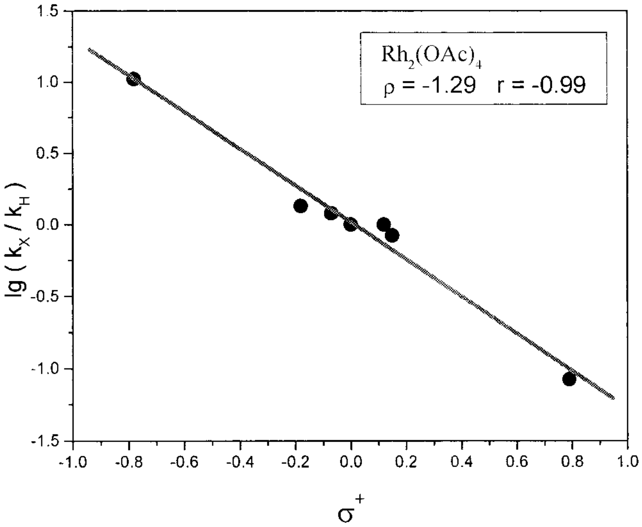

Figure 1. Plot of log k_{rel} against σ^+ for the reaction with $Rh_2(OAc)_4$.

The relative rate constants were further applied to the Hammett equation. The results are summarized in Table 2 and in Hammett plots (Figures1−4, with σ^+ only). In all cases, we found better correlation with σ^+ than with σ or σ^- was obtained. As expected, the Hammett treatment gives the negative value of the reaction constants.

As shown by eq 2, the observed reaction constant ρ is the sum for the two individual steps. In the preequilibrium step, an electron-donating group should push the equilibrium to the right, since the partial negative charge will disappear when the substrate goes to complex with the catalyst. Therefore, ρ_1 should be negative. Because partial negative charge is involved in this equilibrium, ρ_1 may have better correlation with σ^- or σ, rather than with σ^+. In the second step, partial positive charge develops in the transition state, so the electron-donating group should speed up the nitrogen extrusion and ρ_2 is again negative. Although in multistep reactions like this the composition nature of ρ means that it may not give a direct measure of electronic effects on the transition state in the rate-limiting step, the observed overall ρ of

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[13] (a) We initially attempted to follow the reaction by ^1H NMR (400 MHz). However, we found it did not give well reproducible results, probably due to the difficulty in determining the time of precise intervals when collecting the data, and also due to the error of the NMR integration in the spectra. (b) We also tried to measure the absolute rate constants by following the consumption of a single diazo compound. But for some reason that is still unclear, the measurement did not give reproducible data.

[14] The first and second equilibrium constants for binding of pyridine to rhodium(II) butyrate are 1.6×10^8 and 2.4×10^4; see: Drago, R. S.; Long, J. R.; Cosmano, R. *Inorg. Chem.* **1981**, *20*, 2920.

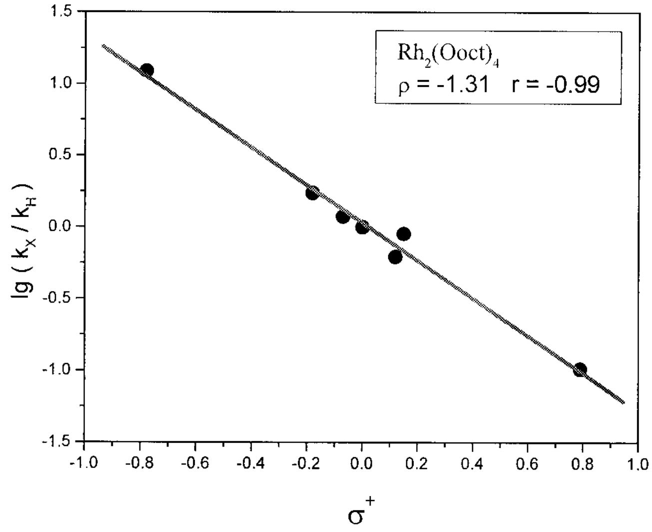

Figure 2. Plot of log k_{rel} against σ^+ for the reaction with Rh$_2$(Ooct)$_4$.

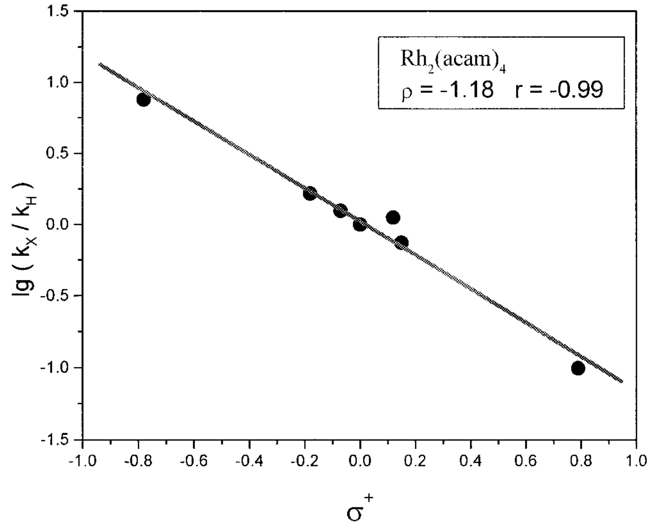

Figure 3. Plot of log k_{rel} against σ^+ for the reaction with Rh$_2$(acam)$_4$.

better correlation with σ^+ may suggest that ρ_2 is dominant. That means there are little electronic effects in the preequilibrium step; the significant electronic effects of the overall reaction may largely due to the second step, which is closely related to the nature of the Rh(II) carbene intermediate.

Better correlation with σ^+ than with σ or σ^- suggests the involvement of positive charge or partial positive charge in the mechanism. Since the polarity of the reaction center is reversed, one might expect larger magnitude of the reaction constants. The moderately large reaction constant values obtained from this study indicate that either the positive charge buildup in the Rh(II) carbene is only moderate, or the nitrogen extrusion step has a relatively earlier transition state.

It has been known that the ligands of the Rh(II) catalysts have remarkable effect on the reaction selectivity.[4] This ligand effect has been explained being due to their electron-donating or -withdrawing ability. The Rh$_2$(O$_2$CCF$_3$)$_4$, which has a strong electron-withdrawing ligand, has been found in many cases behave quite differently with Rh$_2$(OAc)$_4$ or Rh$_2$(acam)$_4$.[4,16] The diazo decomposition with this catalyst gave an appreciably larger magnitude of reaction constant ($\rho = -1.46$ with σ^+, $r = -0.99$), which suggests more positive charge buildup in the Rh(II) carbene intermediate. This is consistent with the argument that electron-withdrawing ligand like trifluoroacetate will have little back-bonding. On the other hand, the Rh$_2$(acam)$_4$, in which the ligand is electron-donating, is just in the opposite ($\rho = -1.18$ with σ^+, $r = -0.99$). Rh$_2$(OAc)$_4$ has a reaction constants in between ($\rho = -1.29$ with σ^+, $r = -0.99$). As expected, rhodium octanoate Rh$_2$(Ooct)$_4$ has a reaction constant close to that of Rh$_2$(OAc)$_4$ ($\rho = -1.31$ with σ^+, $r = -0.99$).

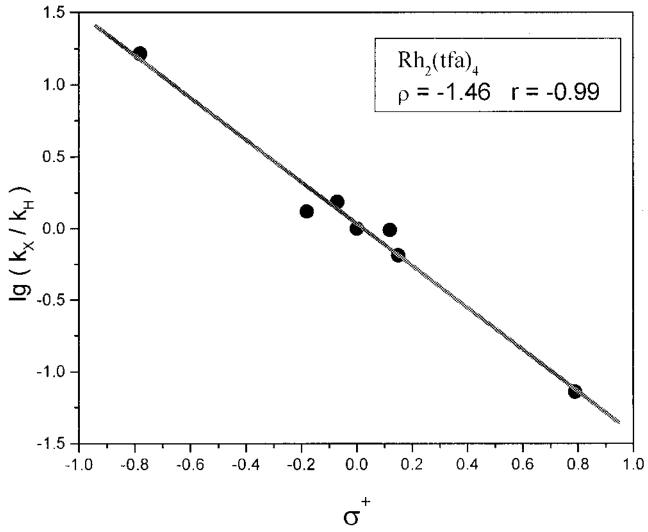

Figure 4. Plot of log k_{rel} against σ^+ for the reaction with Rh$_2$(tfa)$_4$.

There has been considerable controversy concerning the structure of the Rh(II) carbene intermediate. Doyle proposed that the Rh(II) carbene is more likely to be a metal-stabilized cation,[3b] while Pirrung suggests the importance of back-bonding in the Rh(II)−carbon bond.[3d] A theoretical calculation favors neither the structure of Rh(II) carbene nor a metal-stabilized cation, instead a neutral or negatively charged rhodium bond carbon is suggested.[17] However, there has been little direct experimental evidence to clarify the exact nature of the Rh(II) carbene structure.[18] The electronic effect analysis in the present study do provide some experimental evidence favoring the partial positive charge buildup in the Rh(II) carbene.

In conclusion, we have carried out the first Hammett correlation study on the Rh(II) complex catalyzed diazo carbonyl decomposition and obtained quantitative data on the electronic effects. The results provide useful insights into the mechanism of the decomposition process, as well as the nature of the Rh(II) carbene intermediate. The limitation of the current analysis is that the overall electronic effects involve two individual steps. The effort

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(15) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

(16) For a recent example, see: Moniz, G. A.; Wood, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 5095.

(17) Sheehan, S. M.; Padwa, A.; Snyder, J. P. *Tetrahedron Lett.* **1998**, *39*, 949.

(18) White and Hrnciar recently reported an unusual Rh(II) carbenoid reaction, which implies a zwitterionic mechanism; see: White, J. D.; Hrnciar, P. *J. Org. Chem.* **1999**, *64*, 7271. Also see: Clark, J. S.; Dossetter, A. G.; Russell, C. A.; Whitingham, W. G. *J. Org. Chem.* **1997**, *62*, 4910.

to obtain the reaction constants for both steps is currently underway, and the results will be reported in due course.

Experimental Section

General Methods. Melting points were determined with a Yanaco micro melting point apparatus and are uncorrected. All reactions with air- and moisture-sensitive components were performed under a nitrogen atmosphere in a flame-dried reaction flask, and the components were added via syringe. All solvents were distilled prior to use. CH_2Cl_2 and CH_3CN were freshly distilled from CaH_2 before use. For chromatography, 100−200 mesh silica gel (Qindao, China) was employed. ^1H and ^{13}C NMR spectra were recorded at 200 and 50 MHz with a Varian Mercury 200 spectrometer or at 400 and 100.6 MHz with a Bruker ARX400 spectrometer. Chemical shifts are reported in ppm using tetramethylsilane as internal standard. IR spectra were recorded with a Nicolet 5MX-S infrared spectrometer. Mass spectra were obtained on a VG ZAB-HS mass spectrometer. Rhodium(II) acetate, rhodium(II) trifluoroacetate and rhodium(II) octanoate were purchased from Aldrich. Rhodium(II) acetamide was prepared according to the literature procedure.[19] HPLC analysis was performed on an HP 1100 apparatus.

General Procedure for the Synthesis of Methyl Aryldiazoacetate.[20] To a solution of methyl aryl acetate (10 mmol) in anhydrous CH_3CN (20 mL) was added 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) (15 mmol). A solution of *p*-toluenesulfonyl azide (TsN_3) (12 mmol) in anhydrous CH_3CN (10 mL) was added dropwise at room temperature. The solution was stirred at room temperature overnight. Solvent was evaporated, and 5% aqueous KOH solution (~30 mL) was added to the residue. The mixture was extracted with ether (3 × 30 mL) and the combined ethereal layer washed with H_2O, brine, and then dried over anhydrous $MgSO_4$. Column chromatography with silica gel provided the desired diazo compounds **1a**−**g**.

Methyl *p*-phenylphenyldiazoacetate 1b: 89%; mp 96−97 °C; $R_f = 0.19$ (petroleum ether/ethyl acetate = 30:1); ^1H NMR (200 MHz, $CDCl_3$) δ 3.88 (s, 3H), 7.33−7.65 (m, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 52.00, 124.33, 124.38, 126.88, 127.36, 127.60, 128.82, 138.71, 140.35, 165.59; IR 2080, 1700, 1340, 1240, 1150 cm^{-1}; MS (*m*/*z*, relative intensity) 252 (15), 224 (16), 194 (52), 181 (100), 165 (47), 152 (56), 76 (20). Anal. Calcd for $C_{15}H_{12}N_2O_2$: C, 71.42; H, 4.79; N, 11.10. Found: C, 71.40; H, 4.79; N, 11.07.

Methyl *m*-methylphenyldiazoacetate 1c: 73%; $R_f = 0.34$ (petroleum ether/ethyl acetate = 30:1); ^1H NMR (200 MHz, $CDCl_3$) δ 2.35 (s, 3H), 3.85 (s, 3H), 6.94−7.01 (m, 1H), 7.23−7.27 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.43, 51.79, 63.04, 121.09, 124.53, 125.20, 126.64, 128.73, 138.58, 165.54; IR 2080, 1700, 1590, 1430, 1340, 1240, 1140, 1050 cm^{-1}; MS (*m*/*z*, relative intensity) 190 (M^+, 19), 162 (15), 119 (100), 104 (24), 91 (84), 77 (21), 65 (24), 51 (19); HRMS calcd for $C_{10}H_{10}N_2O_2$ 190.0742, found 190.0742.

Methyl *m*-methoxyphenyldiazoacetate 1e: 76%; $R_f =$ 0.22 (petroleum ether/ethyl acetate = 30:1). ^1H NMR (200 MHz, $CDCl_3$) δ 3.79 (s, 3H), 3.83 (s, 3H), 6.69−7.31 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 51.83, 55.14, 63.37, 109.66, 111.44, 115.91, 126.88, 129.76, 160.06, 165.36; IR 2080, 1700, 1600, 1250, 1040 cm^{-1}; MS (*m*/*z*, relative intensity) 206 (M^+, 39), 178 (22), 135 (99), 120 (100), 107 (52), 92 (41), 77 (61); HRMS calcd for $C_{10}H_{10}N_2O_3$ 206.0691, found 206.0682.

General Procedure for $Rh_2(OAc)_4$-Mediated Si−H Insertions. Methyl arydiazoacetate (0.5 mmol) was dissolved in anhydrous CH_2Cl_2 (5 mL). To the solution were added triethylsilane (0.6 mmol) and $Rh_2(OAc)_4$ (0.2 mg, 0.1% mmol). The solution was stirred at room temperature until the diazo compound disappeared according to TLC. Solvent was removed by evaporation, and the residue was subjected to silica gel column chromatography with petroleum ether/EtOAc (30:1) to give pure compounds **4a**−**g** for analysis.

Methyl α-triethylsilyl-*p*-methoxyphenylacetate 4a: 78%; $R_f = 0.37$ (petroleum ether/ethyl acetate = 30:1); ^1H NMR (200 MHz, $CDCl_3$) δ 0.52−0.64 (m, 6H), 0.86−0.94 (m, 9H), 3.46 (s, 1H), 3.66 (s, 3H), 3,78 (s, 3H), 6.82 (d, $J = 8$ Hz, 2H), 7.25 (d, $J = 8$ Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 2.71, 7.02, 41.62, 51.24, 55.17, 113.56, 128.54, 129.42, 157.62, 173.45; IR 2953, 2877, 1723, 1511, 1247, 1148 cm^{-1}; MS (*m*/*z*, relative intensity) 294 (M^+, 12), 148 (100), 120 (16), 87 (25), 59 (21); HRMS calcd for $C_{16}H_{26}O_3Si$ 294.1651, found 294.1639.

Methyl α-triethylsilyl *p*-phenylphenylacetate 4b: 81%; $R_f = 0.31$ (petroleum ether/ethyl acetate = 30:1); ^1H NMR (200 MHz, $CDCl_3$) δ 0.56−0.68 (m, 6H), 0.89−0.96 (m, 9H), 3.57 (s, 1H), 3.69 (s, 3H), 7.24−7.60 (m, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 2.77, 7.04, 42.55, 51.33, 126.77, 126.89, 127.00 128.69, 128.86, 135.75, 138.41, 140.94, 174.6; IR 2952, 2877, 1723, 1487, 1148 cm^{-1}; MS (*m*/*z*, relative intensity) 340 (M^+, 16), 194 (100), 165 (15), 117 (14), 87 (28), 59 (25); HRMS calcd for $C_{21}H_{28}O_2Si$ 340.1858, found 340.1855.

Methyl α-triethylsilyl *m*-methylphenylacetate 4c: 83%; $R_f = 0.40$ (petroleum ether/ethyl acetate = 30:1); ^1H NMR (200 MHz, $CDCl_3$) δ 0.52−0.64 (m, 6H), 0.87−0.94 (m, 9H), 2.32 (s, 3H), 3.48 (s, 1H), 3.66 (s, 3H), 6.95−6.99 (m, 1H), 7.13−7.16 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 2.67, 6.98, 21.46, 41.61, 51.21, 125.52, 126.27, 127.91, 129.12, 136.36, 137.53, 173.64; IR 2953, 2877, 1725, 1605, 1458, 1146 cm^{-1}; MS (*m*/*z*, relative intensity) 278 (M^+, 12), 132 (100), 117 (22), 87 (26), 57 (23); HRMS calcd for $C_{16}H_{26}O_2Si$ 278.1702, found 278.1705.

Methyl α-triethylsilyl phenylacetate 4d: 89%; $R_f = 0.54$ (petroleum ether/ethyl acetate = 30:1); ^1H NMR (200 MHz, $CDCl_3$) δ 0.52−0.65 (m, 6H), 0.86−0.94 (m, 9H), 3.52 (s, 1H), 3.67 (s, 3H), 7.15−7.38 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 2.70, 7.00, 42.80, 51.30, 125.55, 128.10, 128.28, 136.58, 173.64; IR 2953, 2878, 1725, 1496, 1454, 1433, 1147 cm^{-1}; MS (*m*/*z*, relative intensity) 264 (M^+, 18), 118 (100), 117 (41), 87 (56), 59 (42); HRMS calcd for $C_{15}H_{24}O_2Si$ 264.1545, found 264.1537.

Methyl α-triethylsilyl *m*-methoxyphenylacetate 4e: 78%; $R_f = 0.29$ (petroleum ether/ethyl acetate = 30:1); ^1H NMR (200 MHz, $CDCl_3$) δ 0.53−0.66 (m, 6H), 0.87−0.95 (m, 9H), 3.51 (s, 1H), 3.67 (s, 3H), 3,79 (s, 3H) 6.68−7.25 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 2.67, 7.02, 42.78, 51.29, 55.11, 111.00, 114.15, 120.97, 128.97, 138.03, 159.39, 173.49; IR 2953, 2877, 1723, 1611, 1511, 1247, 1148 cm^{-1}; MS (*m*/*z*, relative intensity) 294 (M^+, 14), 148 (100), 117 (18), 87 (28), 59 (21); HRMS calcd for $C_{16}H_{26}O_3Si$ 294.1651, found 294.1639.

Methyl α-triethylsilyl *p*-bromophenylacetate 4f: 82%; $R_f = 0.44$ (petroleum ether/ethyl acetate = 30:1); ^1H NMR (200 MHz, $CDCl_3$) δ 0.51−0.63 (m, 6H), 0.86−0.94 (m, 9H), 3.49 (s, 1H), 3.67 (s, 3H), 7.23 (d, $J = 8$ Hz, 2H), 7.39 (d, $J = 8$ Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 2.63, 8.98, 42.23, 51.40, 119.36, 130.10, 131.14, 135.71, 173.20; IR 2953, 2878, 1724, 1488, 1151 cm^{-1}; MS (*m*/*z*, relative intensity) 342 (M^+, 13), 196 (99), 117 (52), 87 (100), 57 (84); HRMS calcd for $C_{15}H_{23}79BrO_2Si$ 342.0650, found 346.0644.

Methyl α-triethylsilyl *p*-nitrophenylacetate 4g: 83%; $R_f = 0.15$ (petroleum ether/ethyl acetate = 30:1); ^1H NMR (200 MHz, $CDCl_3$) δ 0.53−0.65 (m, 6H), 0.88−0.96 (m, 9H), 3.69 (s, 1H), 3.71 (s, 1H), 7.54 (d, $J = 8$ Hz, 2H), 8.14 (d, $J = 8$ Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 2.47, 6.83, 43.22, 51.55, 123.22, 128.80, 144.82, 145.74, 172.33; IR 2957, 1735, 1602, 1513, 1346, 1173 cm^{-1}; MS (*m*/*z*, relative intensity) 195 (81), 136 (47), 120 (76), 90 (83), 59 (100).

General Procedure for the Kinetic Competition Study. A. With $Rh_2(OAc)_4$ as Catalyst. A three-necked round-bottom flask was flashed with N_2 three times, and then anhydrous CH_2Cl_2 (21.6 mL) was introduced. After the solvent was cooled with an ice bath for 30 min, phenyldiazoacetate **1d** (1 mL, 50 mM solution in CH_2Cl_2) and a meta- or para-substituted phenyldiazoacetate (1 mL, 50 mM solution in CH_2Cl_2), internal standard biphenyl (1 mL, 50 mM solution in CH_2Cl_2), and triethylsilane (0.3 mL) were added. $Rh_2(OAc)_4$ (0.1 mL, 1.0 mM solution in chlorobenzene) was then rapidly introduced, and the time was set as zero. Aliquots of the reaction solution (1.0 mL) were removed from the flask at 5

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min intervals and were immediately subjected to flash silica gel (5 g) column and eluted with ether (25 mL) or CH_2Cl_2 (25 mL) to gave catalyst-free solution. Solvent was removed by evaporation. The residue was dissolved in CH_3CN (HPLC grade, 1.0 mL) and then was analyzed with HPLC.

B. With $Rh_2(Oct)_4$, $Rh_2(acam)_4$, or $Rh_2(O_2CCF_3)_4$ as Catalyst. The reaction system was same as the case when $Rh_2(OAc)_4$ was the catalyst. To remove the catalyst from aliquots, flash column column chromatography was not effective for these catalysts. Therefore, pyridine (1.0 mL, 0.4 mM solution in CH_2Cl_2) was added to each aliquot to block the catalyst. Control experiments showed that no appreciable diazo decomposition was observed for the pyridine-treated aliquots at 0 °C after 5 h. The aliquots were then similarly analyzed with HPLC. For $Rh_2(acam)_4$, the reaction was run at room temperature, because the diazo decomposition at 0 °C with this catalyst was too slow to be practically measured.

HPLC Conditions. The diazo compound was analyzed by HP1100 with a MonoChrom 5 μm C18 column (MetaChem., Inc.) and UV detector at 250 nm. After injection, the column was eluted with MeCN−H_2O (70:30) for 6.5 min, and the MeCN was then increased gradually to 100% within 1.5 min. The elution was continued with 100% MeCN for 6 min, and then MeCN was decreased to 70% within 1.5 min. Elution was continued for 6.5 min with MeCN−H_2O (70:30). The retention time for the diazo compound under these conditions is as follows: **1a**, 5.54 min; **1b**, 10.73 min; **1c**, 7.53 min; **1d**, 5.93 min; **1e**, 5.71 min; **1f**, 8.78 min; **1g**, 5.08 min. Biphenyl has a retention time of 9.74 min. The diazo compound consumption could be accurately quantified against the internal standard biphenyl. The experiment was repeated at least two times until the deviation was within 5%.

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Supporting Information Available: ^1H NMR and ^{13}C NMR spectra for compounds **1b**,**c**,**e**, **4a**−**g**, the kinetic plots, and the Hammett plots with σ and σ^-. This material is available free of charge via the Internet at http://pubs.acs.org.

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