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Substituent Effects on Reactions of $[RhCl(COD)]_2$ with Diazoalkanes

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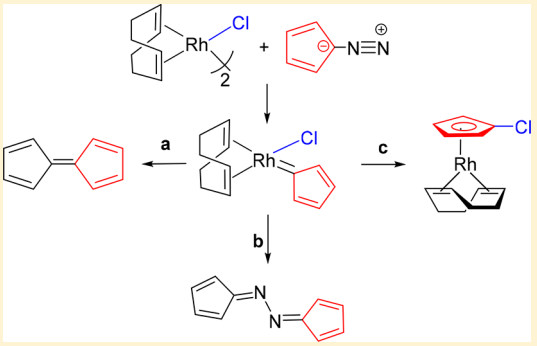
Supporting Information

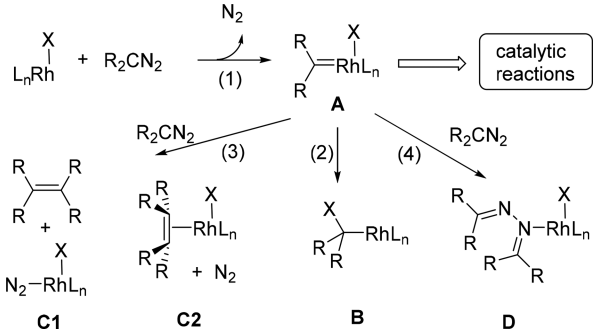
ABSTRACT: The reactions of $[RhCl(COD)]_2$ with a series of diazoalkanes with different substitutents were investigated. The outcomes of the reactions were found to be substituent-dependent via four different pathways. (1) The reactions with diazoindenes produced η^5-cyclopentadienyl complexes. (2) The reaction with diazofluorene produced a mixture of olefin and azine compounds. (3) The reactions with monosubstituted diazoalkanes $RCHN_2$ (R = Ph, MeO_2C) produced olefins RCH═CHR. (4) The reaction with the disubstituted diazoalkane Ph_2CN_2 produced the azine $Ph_2C═N−N═CPh_2$ only. Computational studies have been carried out to understand the interesting substituent effect by comparing the kinetics and thermodynamics of the reaction pathways. It was found that the reactions with diazocyclopentadiene, diazoindene, and Ph_2CN_2 are kinetically controlled, while the reactions with $RCHN_2$ and diazofluorene are both thermodynamically and kinetically controlled.



INTRODUCTION

There has been interest in rhodium-catalyzed carbene transfer reactions using diazoalkanes R_2CN_2 as the carbene source, for example, cyclopropanations, H−X insertions, ylide formations, and cross-couplings.[1,2] It is generally believed that the catalytic reactions proceed by initial formation of carbene intermediates **A** (reaction 1, Scheme 1) followed by the reactions of the carbene intermediates with partner substrates. The efficiency of a catalytic system for carbene transfer reactions could be adversely affected by side-reactions of the carbene intermediates. For example, carbene intermediates **A** may undergo intramolecular migratory insertion reactions to give alkyl complexes $L_nRh−C(X)R_2$ (**B**) (reaction 2). The carbene carbon of **A** could be attacked by the $C(N_2)$ carbon of a diazo molecule to give dinitrogen complexes $L_nRh(N_2)$ (**C1**) or olefin complexes $L_nRh(\eta^2$-olefin) (**C2**) (reaction 3); and attacked by the terminal nitrogen of a diazo molecule to give azine complexes **D** (reaction 4). For carbene transfer reactions to work efficiently, the formation of the reactive carbene species should proceed easily and the side reactions 2−4 of the carbene species should be minimized. Thus, a good understanding of processes for the generation and reactions of carbene intermediates is important for rationalizing the results of catalytic reactions and their further development.

Scheme 1. Generation and Reactions of Rhodium Carbene Complexes



Studies of the reactions of diazoalkanes R_2CN_2 with rhodium complexes can give important information regarding generation and reactivity of carbene intermediates.[3] Previous studies in this direction have led to the isolation of a number of carbene complexes with Rh(I),[4−9] Rh(II)[10,11] and Rh(III)[10,12] centers (reaction 1). Both experimental and computational evidence[7] supports the hypothesis that carbene complexes are formed via η^1-C-diazoalkane complexes $L_nRh−C(N_2)R_2$.

While much is known about the formation of carbene complexes from reactions of diazoalkanes with rhodium complexes, reported examples of reactions of diazoalkanes with rhodium complexes to give complexes **B**, **C1**, **C2**, and **D** via reactions 2−4 are rather limited. The alkyl complex $Cp^*RhCl\{CCl(CO_2Me)(o\text{-}C_6H_4−OMe)\}$ was obtained from the reaction of $[Cp^*RhCl_2]_2$ with $(MeO_2C)(p\text{-}MeOC_6H_4)$-$CN_2$.[10] Cyclopentadienyl complexes of the type $(\eta^5\text{-}C_5R_4X)$-RhL_2 were obtained from the reactions of diazocyclopentadienes $C_5R_4N_2$ (R = H, Ph, and Cl) with $[RhCl(L)_2]_2$ (L = 1/2 COD,[13−17] CO,[18] and $CH_2═CH_2$).[17] Olefin complexes $L_2ClRh(\eta^2$-olefin) were obtained from the reaction of $[RhCl(P^iPr_3)_2]_2$ with CH_2N_2,[19] and the reaction of RhCl-

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$(C_2H_4)(Sb^iPr_3)_2$ with EtO_2CHCN_2.[5] As related reactions, Rh(II) complexes catalyzed dimerization of diazoalkanes to give olefins.[20,21] Dinitrogen complexes $(P^iPr_3)_2XRh(\eta^2\text{-}N_2)$ were obtained from the reactions of $[RhCl(P^iPr_3)_2]_2$ with $(EtO_2C)HCN_2$[19] and $PhCHN_2$,[22] and the reaction of $Rh(O_2CCF_3)(P^iPr_3)_2$ with $PhCHN_2$.[23] Azine derivatives were obtained from the reactions of $CpRh(Sb^iPr_3)(=CPh_2)$ with Ph_2CN_2[8] and from the reaction of $Rh_2(OAc)_4$ with diazofluorene.[24] Factors determining the reactivity of the carbene intermediate species and the tendency for reactions 2−4 to occur are not well systematically investigated, defined, or understood.

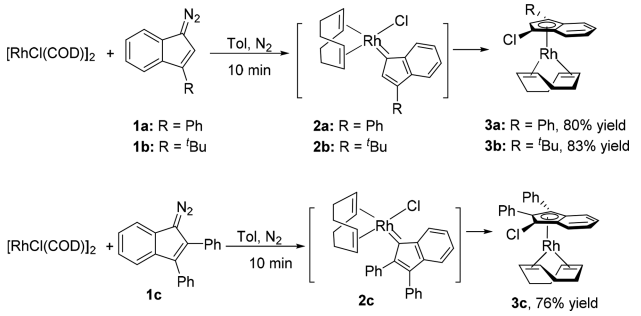
In our effort to address these deficiencies, we have studied the reactions of $[RhCl(COD)]_2$ with a series of diazoalkanes. Experimentally, we have identified the products of the reactions of $[RhCl(COD)]_2$ with various diazoalkanes such as diazoindenes, diazofluorene, Ph_2CN_2, $PhCHN_2$, and $(MeO_2C)CHN_2$. The outcomes of the reactions were found to be substituent-dependent. The reactions with diazoindenes produced η^5-cyclopentadienyl complexes. The reactions with the monosubstituted diazoalkanes $RCHN_2$ (R = Ph, MeO_2C) produced olefins RCH=CHR. The reaction with the disubstituted diazoalkane Ph_2CN_2 produced the azine $Ph_2C{=}N{-}N{=}CPh_2$ only. The reaction with diazofluorene produced a mixture of olefin and azine compounds. We have also carried out computational studies to understand the interesting substituent effect by comparing the kinetics and thermodynamics of the energy profiles of the pathways leading to the formation of complexes analogous to **B**−**D** for each representative diazoalkanes. The findings from these investigations are reported here.

RESULTS AND DISCUSSION

Reactions of $[RhCl(COD)]_2$ with Diazoalkanes. Rh(I)-diene complexes have been actively investigated as catalysts or catalytic precursors for carbene transfer reactions using diazoalkanes as the carbene sources.[25−28] Thus, it is naturally of interest in investigating the stoichiometric reactions of Rh(I)-diene complexes with diazoalkanes. However, reported stoichiometric reactions of Rh(I)-diene complexes with diazoalkanes are rare and limited to the reactions of diazocyclopentadienes $C_5R_4N_2$ (R = H, Ph, and Cl) with $[RhCl(L)_2]_2$ (L = $^1/_2$ COD,[13−17] and $CH_2{=}CH_2$).[17] To systematically investigate the effect of substituents of diazoalkanes on the reactions of Rh(I)-diene complexes with diazoalkanes, we have studied the reactions of $[RhCl(COD)]_2$ with diazoindenes, diazofluorene, and monosubstituted and disubstituted diazoalkanes.

First, the reaction of $[RhCl(COD)]_2$ with diazoindene **1a** was investigated. When 2.2 equiv of diazoindene **1a** was added to a solution of $[RhCl(COD)]_2$ in C_6D_6, gas evolution (presumed to be N_2) was observed. The in situ ^1H NMR spectrum (collected 10 min after mixing the reagents) showed that most of the diazoindene was consumed and the reaction produced a new species displaying a characteristic doublet ^1H signal at 6.41 ppm with J_{H-Rh} = 1.92 Hz. The new complex can be isolated as a yellow powder in 80% yield and was identified to be η^5-indenyl rhodium complex **3a** (Scheme 2).[15] Similarly, the reactions of $[RhCl(COD)]_2$ with the diazoindenes **1b** and **1c** produced η^5-indenyl rhodium complexes **3b** and **3c**, respectively. Thus, the substitutents of diazoindenes have no effect on the pathways leading to the formation of the η^5-indenyl complexes.

Scheme 2. Reactions of $[RhCl(COD)]_2$ with Diazoindenes



Complexes **3** are presumably formed via chlorine migratory insertion reaction of rhodium indenylidene complexes **2**. Similar reactions occurred between diazocyclopentadienes $C_5R_4N_2$ (R = H, Ph, and Cl) and $[RhCl(L)_2]_2$ (L = $^1/_2$ COD,[13−17] and $CH_2{=}CH_2$)[17] to give η^5-chlorocyclopentadienyl complexes.

The structures of the complexes **3a** (Figure 1) and **3c** (Figure 2) have been confirmed by X-ray diffraction. The

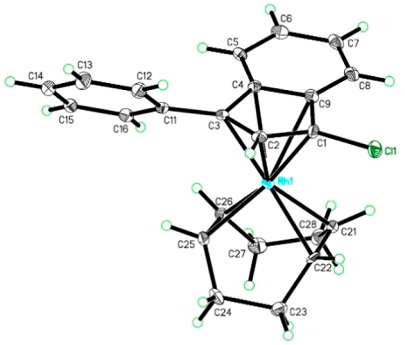


Figure 1. Molecular structure of **3a**. Selected bond distances (Å): Rh(1)−C(1) 2.180(4), Rh(1)−C(2) 2.247(4), Rh(1)−C(3) 2.235(4), Rh(1)−C(4) 2.379(4), Rh(1)−C(9) 2.381(4), Rh(1)−C(21) 2.122(4), Rh(1)−C(22) 2.124(4), Rh(1)−C(25) 2.127(4), Rh(1)−C(26) 2.132(4), Cl(1)−C(1) 1.735(4), C(1)−C(2) 1.424(6), C(1)−C(9) 1.448(6), C(2)−C(3) 1.424(6), C(3)−C(4) 1.457(6), C(4)−C(9) 1.434(6), C(21)−C(22) 1.395(6), C(25)−C(26) 1.398(7).

structural features are similar to those of $(\eta^5\text{-}C_9R_7)Rh(\eta^4\text{-cod})$ (R = H, Me) reported in the literature.[29] The solid-state structures are supported by the solution NMR data. For example, the ^1H NMR spectrum of **3a** displayed the olefinic C*H* signal of COD at 3.69 and 3.54 ppm and the cyclopentadienyl C*H* signal at 6.40 ppm. In the $^{13}C\{^1H\}$ NMR spectrum of **3a**, the olefinic *C*H signals of COD were observed at 75.5 and 74.7 ppm, and the five cyclopentadienyl signals at 112.2, 110.4, 110.4, 93.0, 91.1, and 90.6 ppm.

Next, the reaction of diazofluorene with $[RhCl(COD)]_2$ was investigated. After a mixture of diazofluorene and $[RhCl(COD)]_2$ in a molar ratio of 2:1 in C_6D_6 was kept at room temperature for 10 min, the in situ NMR indicates that $[RhCl(COD)]_2$ remains unchanged, while the diazofluorene was completely converted to a mixture of olefin **4** and azine **5** in a molar ratio of 3:1. The expected rhodium carbene or η^5-fluorenyl complexes were not detectable. The result suggests that $[RhCl(COD)]_2$ catalyzed the homo coupling reactions of diazofluorene. With 2.5 mol % of $[RhCl(COD)]_2$, a

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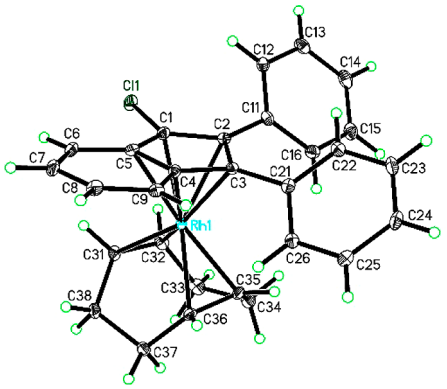
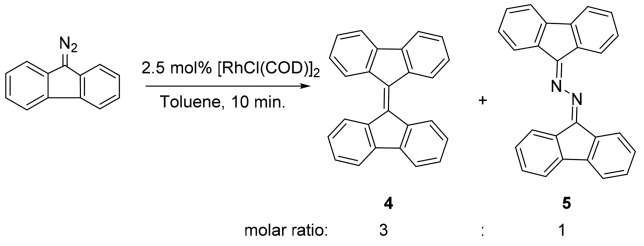


Figure 2. Molecular structure of **3c**. Selected bond distances (Å): Rh(1)−C(1) 2.1670(16), Rh(1)−C(2) 2.2404(17), Rh(1)−C(3) 2.2362(16), Rh(1)−C(4) 2.3977(16), Rh(1)−C(5) 2.3564(15), Rh(1)−C(31) 2.1227(17), Rh(1)−C(32) 2.1267(17), Rh(1)−C(35) 2.1286(16), Rh(1)−C(36) 2.1517(16), Cl(1)−C(1) 1.7319(17), C(1)−C(2) 1.441(2), C(1)−C(5) 1.443(2), C(2)−C(3) 1.440(2), C(3)−C(4) 1.468(2), C(4)−C(5) 1.424(2), C(31)−C(32) 1.410(3), C(35)−C(36) 1.415(2).

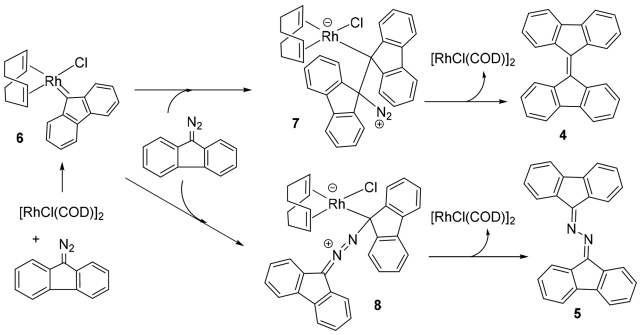
quantitative conversion was achieved within 10 min (Scheme 3).

Scheme 3. Reaction of $[RhCl(COD)]_2$ with Diazofluorene



Scheme 4 shows a plausible mechanism for the formation of the olefin **4** and the azine **5** from the catalytic reaction. The

Scheme 4. Proposed Mechanism for $[RhCl(COD)]_2$-Catalyzed Reactions of Diazofluorene

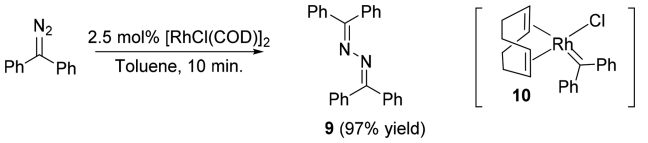


complex $[RhCl(COD)]_2$ initially reacted with diazofluorene to produce the rhodium fluorenylidene **6**. Nucleophilic attack of the carbene carbon by the $C(N_2)$ carbon of diazofluorene would give the intermediate **7**, which then loses N_2 to form olefin **4** and regenerate $[RhCl(COD)]_2$. Nucleophilic attack of the carbene carbon by the terminal nitrogen of diazofluorene would give intermediate **8**, which then evolves to azine **5** and regenerates $[RhCl(COD)]_2$. Similar pathways have been proposed previously for metal-mediated coupling of diazoalkanes to give olefins[20,30] and azines.[31]

It is noted that different products were obtained in previously reported reactions of diazofluorene ($N_2CC_{12}H_8$) with rhodium(I) complexes, including diazo complexes,[19] carbene complexes[5] and azine compounds.[24]

To further study the substituent effect on the outcomes of the reactions of $[RhCl(COD)]_2$ with diazoalkanes, the reactions with Ph_2CN_2, $PhHCN_2$ and $(MeO_2C)HCN_2$ were carried out. After a toluene solution of the disubstituted diazoalkane Ph_2CN_2 was stirred at room temperature for 10 min in the presence of 2.5 mol % of $[RhCl(COD)]_2$, the in situ NMR indicates that the $[RhCl(COD)]_2$ remains unchanged, and all Ph_2CN_2 was converted to the azine $Ph_2C{=}N{-}N{=}CPh_2$ (**9**), which can be isolated in 97% yield. Azine **9** is presumably formed by nucleophilic attack on the carbene carbon of intermediate **10** by the terminal nitrogen of Ph_2CN_2 (Scheme 5).

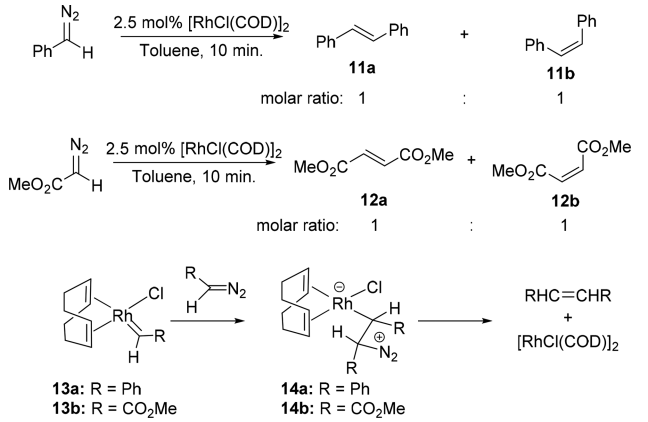
Scheme 5. Reaction of $[RhCl(COD)]_2$ with Ph_2CN_2



In a closely related reaction, the carbene complex CpRh-(Sb^iPr_3)(=CPh_2) reacted with Ar_2CN_2 (Ar = Ph, *p*-tolyl) to give $Ph_2C{=}N{-}N{=}CAr_2$.[8] It is noted that products other than azines were obtained in reported reactions of Ph_2CN_2 with Rh(I) complexes, such as carbene complexes,[5,6] diazo complexes,[19,23,32,33] and dinitrogen complex.[32]

Under conditions similar to those for the reaction with the disubstituted diazoalkane Ph_2CN_2, $[RhCl(COD)]_2$ reacted with the monosubstituted diazoalkane $PhHCN_2$ completely to give a mixture of *trans*-stilbene (**11a**) and *cis*-stilbene (**11b**) in a molar ratio of 1:1, while $[RhCl(COD)]_2$ remains unchanged (Scheme 6). A similar catalytic reaction occurred for $(MeO_2C)HCN_2$, giving a mixture of dimethyl fumarate (**12a**) and dimethyl maleate (**12b**) in 1:1 molar ratio. Olefins **11** and **12** are presumably formed via the reaction of the carbene intermediates **13** with the diazoalkanes to give intermediates **14** followed by elimination of N_2 and dissociation of the olefins from the metal center (Scheme 6).

Scheme 6. Reactions of $[RhCl(COD)]_2$ with Phenyl Diazomethane and Methyl Diazoacetate



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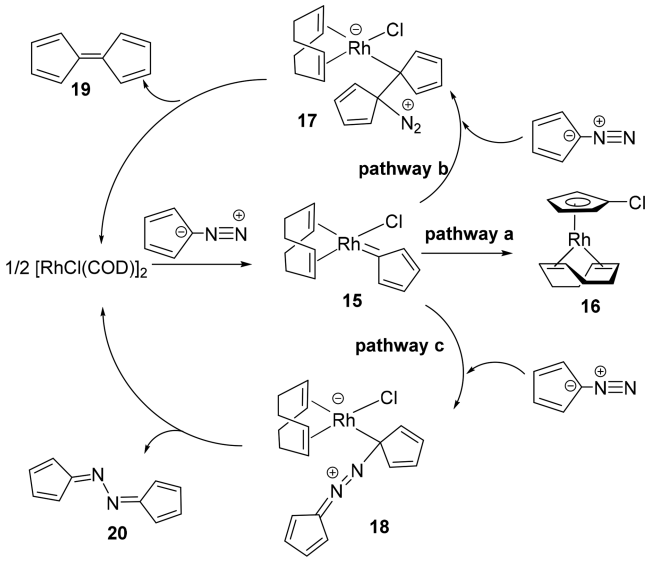
The reactions with $RCHN_2$ (R = Ph, MeO_2C) to give **11** and **12** are interesting as they represent rare examples of homodimerization of diazoalkanes to give olefins catalyzed by Rh(I) complexes, although similar reactions catalyzed by Rh(II) complexes are now well-documented.[20] Several types of products have been isolated from the reactions of Rh(I) complexes with monosubstituted diazoalkanes $RCHN_2$, such as carbene complexes,[7,9] diazoalkane complexes,[6,19,23,34] olefin complexes,[5] and dinitrogen complexes.[22,23]

Computational Studies. We have shown that three possible products are experimentally produced in the reactions of $[RhCl(COD)]_2$ with diazoalkanes, depending on the substituents of the diazoalkanes. Taking the reaction with diazocyclopentadiene ($C_5H_4N_2$) as an example, the plausible pathways for the formation of these products are summarized in Scheme 7. The dimeric complex $[RhCl(COD)]_2$ could react with $C_5H_4N_2$ to give initially active Rh-carbene species **15**.

Scheme 7. Plausible Mechanisms for the Formation of Three Side Products



There exist three competing pathways starting from Rh-carbene species **15**: (a) chloride migratory-insertion to give chlorocyclopentadienyl complex **16**; (b) nucleophilic attacking of the diazo carbon ($C(N_2)$) on the carbene carbon to give intermediate **17** which evolves to homocoupling olefin product **19**; and (c) nucleophilic attacking of the terminal N of the diazo reagent on the carbene carbon to generate intermediate **18** which evolves to azine **20**.

The experimental results described above indicate that the thermodynamics and kinetics of the competing reaction pathways are influenced by the substituents of the diazoalkanes or carbene intermediates. To understand the effect of substituents of diazoalkanes on the reaction pathways, we have calculated the energy profiles for the reactions of $[RhCl(COD)]_2$ with four representative diazoalkanes, namely, diazocyclopentadiene, 3-*tert*-butyl-diazoindene, diazofluorene, and $PhCHN_2$.

In the following discussion of the computational results, species evolving from the reaction with diazocyclopentadiene are named with the suffix **DC**, those evolving from the reaction with diazoindene are named with the suffix with **ID**, those evolving from the reaction with diazofluorene are named with the suffix **FD**, and those evolving from the reaction with phenyl diazomethane are named with the suffix **PM**.

Carbene Formation. In all the reactions described above, the formation of carbene species is the initial step. Therefore, we have first calculated the energy profiles for the formation of carbene complexes. The results are presented in Figure 3.

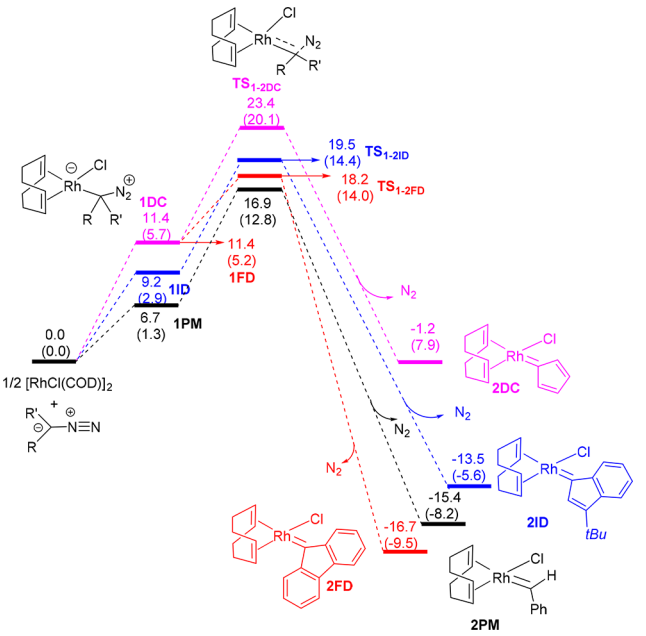


Figure 3. Calculated energy profiles for the formation of carbene complexes from chloro-rhodium dimer complex $[RhCl(COD)]_2$ with diazocyclopentadiene ($C_5H_4N_2$) (pink line), 3-*tert*-butyl-diazoindene (blue line), diazofluorene ($C_{13}H_8N_2$) (red line), and phenyl diazomethane ($C_7H_6N_2$) (black line). The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

It is generally accepted that reactions of diazoalkanes with transition metal compounds to give carbene complexes proceed through η^1-*C*-coordinated diazoalkane intermediates.[9] Reaction of $[RhCl(COD)]_2$ with neutral ligands L to give RhCl(COD)L is very common. As shown in Figure 3, the reaction of $[RhCl(COD)]_2$ with diazocyclopentadiene ($C_5H_4N_2$) to give η^1-*C*-coordinated diazoalkane complex **1DC** is thermodynamically unfavored by 11.4 kcal/mol. The dissociation of N_2 from diazoalkane complex **1DC** to give Rh-carbene intermediate **2DC** is thermodynamically favored by 12.6 kcal/mol with a kinetic barrier of 12.0 kcal/mol. The overall reaction of $[RhCl(COD)]_2$ with $C_5H_4N_2$ to give Rh-carbene species **2DC** is thermodynamically favored by 1.2 kcal/mol with a kinetic barrier of 23.4 kcal/mol. The reaction of $[RhCl(COD)]_2$ with $C_5H_4N_2$ could also give other initial products $RhCl(COD)(\eta^1\text{-}N\text{-}C_5H_4N_2)$, $RhCl(COD)(\eta^2\text{-}CC\text{-}C_5H_4N_2)$, and $RhCl(COD)(\eta^2\text{-}NC\text{-}C_5H_4N_2)$. However, our computational work suggests that these species are unlikely to be involved in the formation of carbene complex **2DC** (see the Supporting Information for details).

To study the substituent effect on carbene formation, the energy profiles for the reactions of $[RhCl(COD)]_2$ with 3-*tert*-butyl-diazoindene, diazofluorene and $PhCHN_2$ were also carried out. The profiles were found to be similar to that of the reaction with diazocyclopentadiene. Compared with the reaction with diazocyclopentadiene, the formation of indenylidene complex **2ID** from the reaction of $[RhCl(COD)]_2$ with

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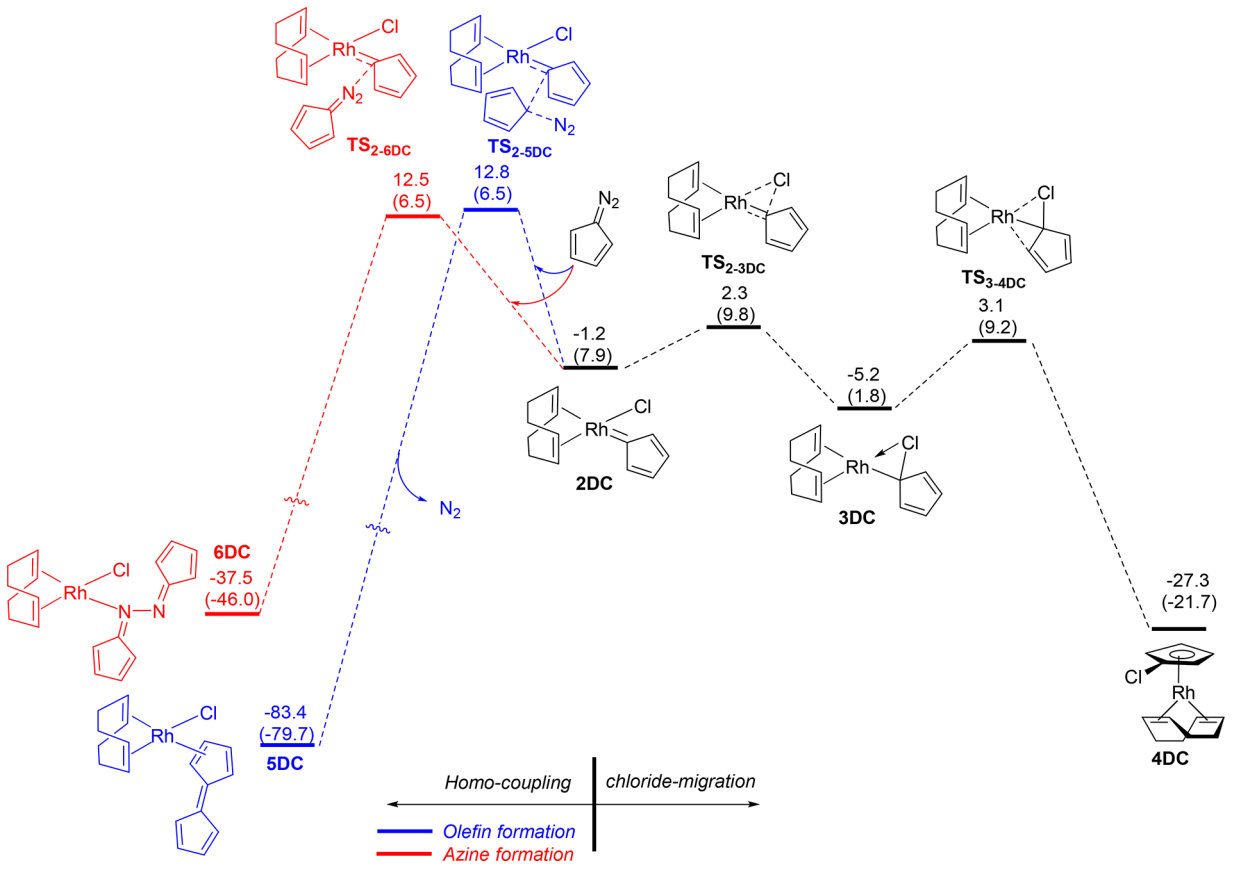

Figure 4. Calculated energy profiles for the possible reaction pathways of chloro-rhodium cyclopentadienylidene intermediate (**2DC**). The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

2-*tert*-butyl-diazoindene is both thermodynamically and kinetically more favorable. The reaction is thermodynamically favored by 13.5 kcal/mol with an appreciably low barrier of 19.5 kcal/mol. Following the trend, the formation of fluorenylidene complex **2FD** from the reaction of $[RhCl(COD)]_2$ with diazofluorene is even more favorable both thermodynamically and kinetically. The reaction is thermodynamically favored by 16.7 kcal/mol with a barrier of 18.2 kcal/mol. The reaction of $PhCHN_2$ with $[RhCl(COD)]_2$ to give carbene complex **2PM** should be kinetically most favorable with an overall barrier of 16.9 kcal/mol. Interestingly, carbene (**2PM**) formation was found to be thermodynamically slightly less favorable (the free energy change is −15.4 kcal/mol) than that from the reaction with diazofluorene (the free energy change is −16.7 kcal/mol).

Except in the case of diazofluorene, the overall carbene formation barriers for reactions with diazoalkanes seem to be related to the stability of the η^1-*C*-diazoalkane complexes. The overall carbene formation barrier is higher if the formation of the η^1-*C*-diazoalkane complex is thermodynamically less favorable. As can be seen from Figure 3, while the overall barriers (from $[RhCl(COD)]_2$) vary from 16.9 to 23.4 kcal/mol, the barriers from the η^1-*C*-diazoalkane complexes **1PM**, **1ID**, and **2DC** are within a small range of 10.2−12.0 kcal/mol.

In related works, energy profiles for the formation of rhodium carbene complexes from reactions of Rh(I) complexes with diazoalkanes have been previously described for the reactions of the pincer complexes $Rh(N_2)(RPCP)$ (RPCP = 2,6-$(R_2PCH_2)_2C_6H_3$ (R = H, ^{i}Pr) with $PhCHN_2$[9] and the reactions of RhCl(2,5-Ph_2-NBD) with $(MeO_2C)RCN_2$ (R = Ph, CH_2Ph).[26,35] The energy profiles for the reactions of $Rh(RPCP)(N_2)$ with $PhCHN_2$ resemble those shown in Figure 3. For example, the complex $Rh(N_2)(^iPrPCP)$ reacts with $PhCHN_2$ to give the diazoalkane complex $Rh(\eta^1$-*C*-$PhCHN_2)(^iPrPCP)$ in an endothermic process (by 18.1 kcal/mol). The intermediate $Rh(\eta^1$-*C*-$PhCHN_2)(^iPrPCP)$ evolves to the carbene complex $Rh(=CHPh)(^iPrPCP)$ exothermically with a kinetic barrier of 11.0 kcal/mol, which is similar to those (10.2−12.0 kcal/mol) calculated for the transformation of **1PM**, **1ID**, and **2DC** to the corresponding carbene complexes.

Reactions of Carbene Complexes. The experimentally observed variation in the preference of the reaction pathways is likely caused by the difference in the kinetics and thermodynamics of reactions of carbene intermediates as a result of the effect of the substituents of the carbene intermediates and diazoalkanes. To study the effect, we calculated the energy profiles for the three possible reaction pathways shown in Scheme 7 for the reactions of Rh-carbene species **2DC**, **2ID**, **2FD**, and **2PM**.

The calculated energy profiles for the reactions of rhodium cyclopentadienylidene complex **2DC** are shown in Figure 4. The formation of chlorocyclopentadienyl complex **4DC** from **2DC** involves migratory-insertion and rearrangement steps. The migratory-insertion to give the η^2-CCl-coordinated complex **3DC** is thermodynamically favored by 4.0 kcal/mol with a small barrier of 3.5 kcal/mol. The rearrangement of **3DC** to **4DC** is thermodynamically favored by 22.1 kcal/mol with a barrier of 8.3 kcal/mol. Overall, the formation of η^5-chlorocyclopentadienyl complex **4DC** from Rh-carbene species **2DC** is thermodynamically favored by 26.1 kcal/mol.

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Cyclopentadienylidene complex **2DC** evolves to olefin complex **5DC** by nucleophilic attack on the carbene carbon by the $C(N_2)$ carbon of diazocyclopentadiene via transition state $\mathbf{TS_{2-5DC}}$.[20,30] The process is thermodynamically favored by 82.2 kcal/mol with a barrier of 14.0 kcal/mol ($\mathbf{TS_{2-5DC}}$). For comparison, the reaction of $Rh_2(O_2CH)_4(=CPh(CO_2Me)$ with $(MeO_2C)CHN_2$ to give the olefin $(MeO_2C)CH=CPh(CO_2Me)$ was reported to have a barrier of ca. 18 kcal/mol.[20]

Cyclopentadienylidene complex **2DC** evolves to azine complex **6DC** by nucleophilic attack on the carbene carbon by the terminal nitrogen of diazocyclopentadiene via transition state $\mathbf{TS_{2-6DC}}$.[31] The process is also thermodynamically favored (by 36.3 kcal/mol) with a barrier (13.7 kcal/mol) similar to that (14.0 kcal/mol) for the formation of olefin complex **5DC**.

As can be seen from the profiles, all three pathways are thermodynamically favored, with the formation of olefin complex **5DC** being most favorable and that of chlorocyclopentadienyl complex **4DC** being least favorable. Kinetically, the pathway leading to the formation of cyclopentadienyl complex **4DC** is mostly favored, consistent with the experimental isolation of η^5-cyclopentadienyl complex **16**.

Figure 5a shows the energy profiles calculated for the reactions of rhodium indenylidene **2ID**. Overall, the calculated energy profiles are similar to those calculated for the reaction of rhodium cyclopentadienylidene **2DC**. Like those from the reactions of **2DC**, the formations of η^5-indenyl complex **4ID**, olefin complex **5ID**, and azine complex **6ID** from the reactions of **2ID** are all thermodynamically favored, with the formation of the olefin complex being most favored and that of the chloroindenyl complex being least favored. The overall barriers for the formations of **4ID**, **5ID**, and **6ID** are 11.5, 16.0, and 16.2 kcal/mol, respectively. Thus, the formation of η^5-indenyl complex **4ID** is the most kinetically favored, consistent with our observation that η^5-indenyl complexes (**3a**, **3b**, and **3c**) were isolated experimentally.

The calculated energy profiles for the conversions of the rhodium fluorenylidene intermediate (**2FD**) are shown in Figure 5b. Different from the cases of **2DC** and **2ID**, the chlorine migratory insertion reaction of **2FD** to give η^5-fluorenyl complex **4FD** was found to be thermodynamically unfavorable (by 2.4 kcal/mol), indicating that this process is unlikely. Like the cases from the reactions of **2DC** and **2ID**, the homocoupling pathways to give the olefin (**5FD**) and azine (**6FD**) complexes are both thermodynamically favorable (by 57.5 and 28.5 kcal, respectively). The barrier for the formation of olefin complex **5FD** (14.7 kcal/mol) is similar to (or slightly lower than) that for the formation of azine complex **6FD** (17.7 kcal/mol), consistent with the experimental observation that a mixture of olefin (**4**) and azine (**5**) were produced.

Figure 5c shows the energy profiles calculated for the reactions of rhodium phenylcarbene **2PM**. The energy profiles clearly indicate that chloride migration reaction should not occur because the reaction will produce thermodynamically unfavorable products (**3PM** or **4PM**). In contrast, the formation of olefin complex **5PM** and azine complex **6PM** are both thermodynamically and kinetically feasible, with the formation of the olefin complex being appreciably more favorable (by 6.7 kcal/mol). The results are therefore consistent with the experimental observation that $[RhCl(COD)]_2$ catalyzes the coupling reaction of $PhHCN_2$ to give PhHC=CHPh.

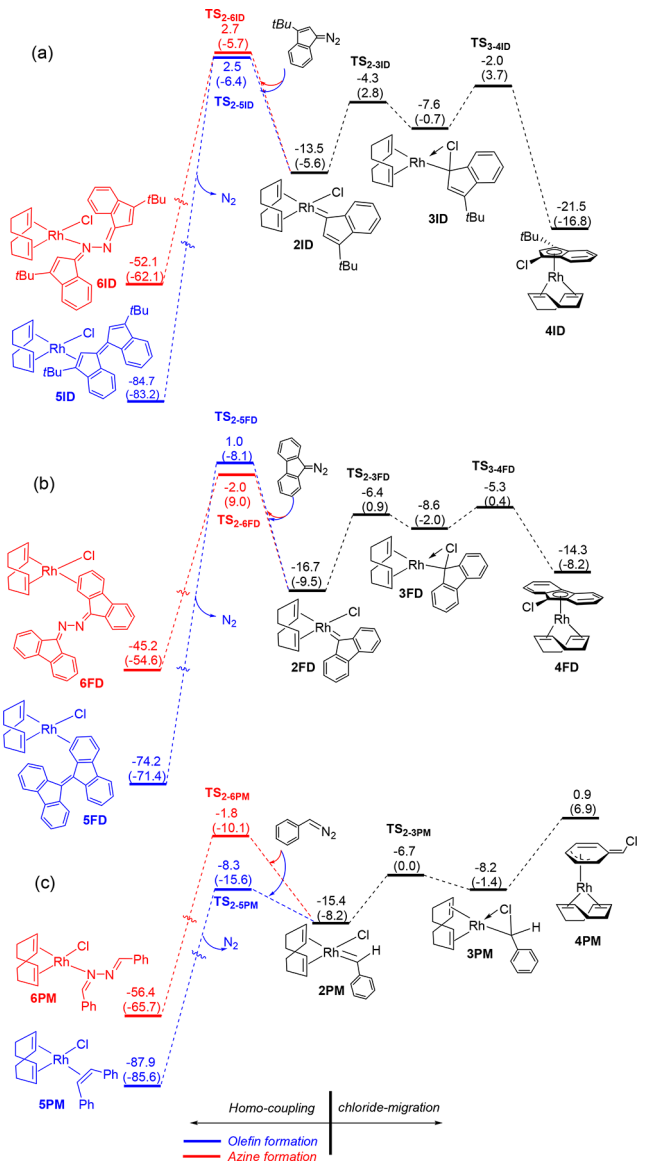

Figure 5. Calculated energy profiles for the conversions of chlororhodium indenylidene (**2ID**), fluorenylidene intermediate (**2FD**), and phenylcarbene (**2PM**). The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

Comments on the Reactions of Carbene Complexes.

General Comments. The computational work described above represents the first study systematically comparing the kinetics and thermodynamics of the reaction types of diazoalkanes with rhodium complexes to give complexes **B**, **C1**, **C2**, and **D** via the reactions 2−4 shown in Scheme 1. Several interesting observations were noted from the computational results. Among the three reaction pathways of the carbene intermediates, the chlorine migratory insertion to give η^5-pentadienyl complexes is thermodynamically least favored, while nucleophilic attacking of the diazo carbon ($C(N_2)$) on the carbene carbon to give olefin complexes is thermodynamically most favored. However, the relative kinetic barriers for the three pathways can vary with the substituents of the diazoalkanes affecting the observed product.

Chlorine Migratory Insertion Reactions. The initial chlorine migratory insertion reactions of the carbene species to give the corresponding η^2-CCl complexes are kinetically

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feasible as indicated by the low reaction barriers (being 3.5, 9.2, 10.3, and 8.7 kcal/mol calculated for **2DC**, **2ID**, **2FD**, and **2PM**, respectively). However, these processes, with the exception of the reaction of **2DC**, are in general thermodynamically unfavorable. The free energy changes for the migratory reactions of **2DC**, **2ID**, **2FD**, and **2PM** are −4.0, 5.9, 8.1, and 7.2 kcal/mol, respectively.

The thermodynamics of the chlorine migratory insertion reactions of the carbene species could be altered if the initially formed η^2-CCl complexes can rearrange to more stable species. Our computational work confirms that η^2-CCl complexes **3DC**, **3ID**, and **3FD** can rearrange to the corresponding thermodynamically more stable η^5-pentadienyl complexes with a low kinetic barrier. As a result, both **2DC** and **2ID** can rearrange to η^5-pentadienyl complexes in a thermodynamically favorable process. In the case of **2FD**, the stabilization effect is not enough, such that the formation of η^5-pentadienyl complex **4FD** from **2FD** is still not favorable. The trend in the relative stability of cyclopentadienylidene, indenylidene, and fluorenylidene complexes with respect to the formation of the corresponding η^5-chlorocyclopentdienyl complexes can be related to the strength of the Rh-η^5-pentadienyl interactions in the η^5-pentadienyl complexes. The average Rh−C(ring) distances of the η^5-pentadienyl complexes are in the order of cyclopentadienyl complex **4DC** (2.31 Å) < indenyl complex **4ID** (2.34 Å) < fluorenyl complex **4FD** (2.38 Å), suggesting that the Rh-(η^5-chlorocyclopentadienyl) bond is the strongest and the Rh-(η^5-chlorofluorenyl) bond is the weakest. Thus, the formation of chlorocyclopentadienyl complex **4DC** is most favored, and the formation of the chlorofluorenyl complex **4FD** is least favored. Interestingly, rearrangement of η^2-C−Cl complex **3PM** (derived from phenyl carbene complex **2PM**) to give η^3-cyclohexadienyl complex **4PM** is thermodynamically unfavored, probably because the delocalization of electrons in the aromatic ring of **3PM** is disrupted in the formation of η^3-cyclohexadienyl complex **4PM**.

Dimerization Reactions. The reactions of the carbene species with diazoalkanes to give olefin or azine complexes are all thermodynamically favored, with the formation of the olefin complexes being significantly more favorable.

Interestingly, the barriers for reactions of carbene species **2DC**, **2ID**, **2FD**, and **2PM** to form the corresponding azine complexes are similar to each other (being 13.7, 16.2, 14.7, and 13.6 kcal/mol, respectively). In contrast, the barriers for reactions of carbene species **2DC**, **2ID**, **2FD**, and **2PM** to form the corresponding olefin complexes vary appreciably and are in the order of **2PM** (7.1 kcal/mol) < **2DC** (14.0 kcal/mol) < **2ID** (16.0 kcal/mol) < **2FD** (17.7 kcal/mol). The trend in the barriers appears to be related to the steric effect. Especially, the barrier for the reaction of **2PM** with the monosubstituted diazoalkane $PhCHN_2$ is appreciably lower than those of the reactions of **2DC**, **2ID**, and **2FD** as $PhCHN_2$ is a monosubstituted diazoalkane, while the others are disubstituted diazoalkanes.

Our computational results suggest that the barriers for metal-mediated coupling reactions of disubstituted diazoalkanes to give olefins are similar to, or even higher than those to give diazines. In contrast, the barriers for metal-mediated coupling reactions of monosubstituted diazoalkanes to give olefins are lower than those to give diazines. Supporting these trend predicted from the computational results, we found in the literature that the reactions of *trans*-$RhCl(CH_2{=}CH_2)(Sb^iPr_3)_2$ with $RR'CN_2$ [RR′ = Ph_2, $Ph(C_6H_4Me)_2$, $Ph(CF_3)$, $C_{12}H_8$) and EtO_2CCHN_2 have been shown to produce *trans*-$RhCl(=CRR)(Sb^iPr_3)_2$ and *trans*-$RhCl\{(E)\text{-}(EtO_2CCH{=}CH(CO_2Et)\}(Sb^iPr_3)_2$, respectively.[5]

Interestingly, reported Rh-catalyzed carbene transfer reactions usually involve disubstituted diazoalkanes with at least one electron-withdrawing group. We suspect that such diazoalkanes are less likely to undergo transition metal mediated homocoupling reactions. In supporting our hypothesis and findings, in the presence of 1 mol % $Rh_2(OPiv)_4$ (Piv = pivaloyl) catalyst, an equimolar mixture of $Ph(MeO_2C)CN_2$ and EtO_2CCHN_2 rapidly afforded the cross-coupling product $Ph(MeO_2C)C{=}CH(CO_2Et)$ and the homocoupling product $(EtO_2C)HC{=}CH(CO_2Et)$, but the homocoupling product $Ph(MeO_2C)C{=}C(CO_2Me)Ph$ was not produced in the catalytic reaction.[20]

CONCLUSIONS

In summary, we have investigated the reactions of $[RhCl(COD)]_2$ with a series of diazoalkanes containing different substitutents. The outcomes of the reactions were found to be substituent-dependent. The reactions with diazocyclopentadiene and diazoindenes produced η^5-cyclopentadienyl complexes. The complex $[RhCl(COD)]_2$ catalyzed dimerization of $RCHN_2$ (R = Ph, MeO_2C) to give olefins RCH=CHR, dimerization of diazofluorene to give a mixture of olefin and azine compounds, and dimerization of Ph_2CN_2 to give the azine $Ph_2C{=}N{-}N{=}CPh_2$. Computational studies suggest that the reactions of diazocyclopentadiene, diazoindenes, and Ph_2CN_2 are kinetically controlled, while the reactions of $RCHN_2$ and diazofluorene are both thermodynamically and kinetically controlled.

The results have the following implications: (1) Reactions of monosubstituted diazoalkanes with Rh(I) complexes to give carbene complexes are kinetically more favorable than those of disubstituted diazoalkanes. (2) Reactions of diazocyclopentadienes and diazoindenes with Rh(I)-halo complexes can easily produce η^5-pentadienyl complexes due to facile halogen migratory inserion reactions of the halo-rhodium carbene complexes. (3) The barriers for metal-mediated coupling reactions of diazoalkanes to give olefins are sensitive to steric effect. Coupling reactions of sterically less bulky monosubstituted diazoalkanes to give olefins can be kinetically and thermodynamically very favorable. (4) Bulky diazoalkanes tend to react with Rh(I) complexes to give azines, because the competing reactions to give olefins can be kinetically retarded.

EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (hexane), sodium (toluene), or CaH_2 (dichloromethane (DCM)). Methanol was bubbled with N_2 before use. The starting materials $[RhCl(COD)]_2$,[36] $C_5H_4N_2PPh_3$,[37] diazofluorene,[38] diphenyl diazomethane,[39] phenyl diazomethane,[40] and methyl diazoacetate[40] were prepared following the procedure described in the literatures. Diazoindenes **1a−c** were synthesized by the routes described in the Supporting Information. All other reagents were purchased from commercial suppliers and used without further purification. Microanalyses were performed by M−H-W Laboratories (Phoenix, AZ). ^1H and $^{13}C\{^1H\}$ NMR spectra were collected on a Bruker-400 spectrometer (400 MHz). ^1H and ^{13}C NMR shifts are relative to TMS.

Caution! *Diazo compounds are explosive and assumed to be toxic. All operations involving with diazo compounds should be carried out with*

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care. A safety shield should be used during heating or distillation of diazo compounds.

Preparation of Rh(η^5-C_5H_5Cl)(COD) (16). This complex has been previously prepared by Shaver et al.[16,17] by reacting $[RhCl(COD)]_2$ with $C_5H_4N_2$. Herein, we used an alternative synthetic route by reacting $[RhCl(COD)]_2$ with $C_5H_4N_2PPh_3$, a safer precursor to $C_5H_4N_2$. A mixture of $C_5H_4N_2PPh_3$ (72 mg, 0.20 mmol) and $[RhCl(COD)]_2$ (100 mg, 0.20 mmol) in toluene (6 mL) was stirred overnight at room temperature. After removing volatiles under vacuum, the mixture was purified by flashing silica gel column chromatography with hexane/DCM (v/v 10:1) as the eluent to afford the air stable yellow solid of **16**. Yield: 43 mg (68%). The NMR data are consistent with the literature[17] reported ones.

Preparation of Rh{η^5-C_9H_5(Ph)Cl}(COD) (3a). To a solution of $[RhCl(COD)]_2$ (87 mg, 0.18 mmol) in toluene (5 mL) was added a DCM solution of **1a** (2 mL, 0.2 M, ca. 87 mg, 0.4 mmol) dropwise at room temperature. After stirring for 10 min, the solvents were removed under vacuum. The orange residue was washed with hexane (3 mL × 3) and methanol (3 mL × 3) and dried under vacuum to give a yellow powder. Yield: 121 mg (80%). Anal. Calcd for $C_{23}H_{22}ClRh$: C, 63.25; H, 5.08. Found: C, 63.49; H, 5.03. ^1H NMR (400 MHz, C_6D_6): δ 7.46−7.44 (m, 2H), 7.36−7.34 (m, 2H), 7.20−7.16 (m, 2H), 7.14−7.04 (m, 3H), 6.41 (d, J_{H-Rh} = 1.92 Hz, 1H), 3.72−3.67 (m, 2H), 3.56−3.51 (m, 2H), 1.93−1.78 (m, 4H), 1.74−1.70 (m, 2H), 1.62−1.56 (m, 2H). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 293 K): δ 135.2, 129.1, 126.9, 124.3, 123.7, 118.2, 117.7, 112.2, 110.4, 110.4, 93.0 (d, J_{C-Rh} = 5.2 Hz), 91.1 (d, J_{C-Rh} = 4.1 Hz), 90.6 (d, J_{C-Rh} = 5.2 Hz), 75.5 (d, 2C, J_{C-Rh} = 13.3 Hz), 74.7 (d, 2C, J_{C-Rh} = 13.5 Hz), 32.19, 30.82.

Preparation of Rh{η^5-C_9H_5(^{t}Bu)Cl}(COD) (3b). This complex was prepared as described for **3a**, starting from **1b** (3.2 mL 0.2 M solution in DCM, ca. 127 mg, 0.64 mmol) and $[RhCl(COD)]_2$ (150 mg, 0.30 mmol) in toluene (6 mL). Yield: 221 mg (83%). Anal. Calcd for $C_{21}H_{26}ClRh$: C, 60.52; H, 6.29. Found: C, 60.42; H, 6.43. ^1H NMR (400 MHz, C_6D_6): δ 7.37 (t, J_{H-H} = 7.6 Hz, 2H), 7.09 (t, J_{H-H} = 7.6 Hz, 1H), 7.04−7.00 (m, 1H), 6.08 (d, J_{H-Rh} = 1.96 Hz, 1H), 4.09−4.05 (m, 2H), 3.79−3.74 (m, 2H), 1.94−1.78 (m, 4H), 1.67−1.64 (m, 2H), 1.17 (s, 9H). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 293 K): δ 123.5, 123.4, 119.6, 117.8, 112.1, 111.6, 102.8 (d, J_{C-Rh} = 4.2 Hz), 92.7 (d, J_{C-Rh} = 4.5 Hz), 89.1 (d, J_{C-Rh} = 5.4 Hz), 74.7 (d, 2C, J_{C-Rh} = 13.7 Hz), 71.0 (d, 2C, J_{C-Rh} = 13.8 Hz), 33.0, 32.1, 30.9, 30.7.

Preparation of Rh{η^5-$C_9H_4(Ph)_2Cl$}(COD) (3c). This complex was prepared as described for **3a**, starting from **1c** (130 mg, 0.44 mmol) and $[RhCl(COD)]_2$ (99 mg, 0.20 mmol) in toluene (5 mL). Yield: 156 mg (76%). Anal. Calcd for $C_{29}H_{26}ClRh$: C, 67.91; H, 5.11. Found: C, 68.11; H, 5.31. ^1H NMR (400 MHz, C_6D_6): δ 7.68−7.66 (m, 2H), 7.51 (s,, J_{H-H} = 8.1 Hz, 1H), 7.39 (s, J_{H-H} = 8.2 Hz, 1H), 7.23−7.20 (m, 2H), 7.18−7.14 (m, 5H), 7.10−7.04 (m, 4H), 7.01−6.98 (m, 1H), 3.87−3.75 (m, 4H), 2.00−1.82 (m, 4H), 1.75−1.59 (m, 4H). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 293 K): δ 134.1, 133.9, 132.0, 130.4, 128.6, 128.2, 127.6, 126.9, 124.6, 123.9, 118.1, 117.7, 112.6 (d, J_{C-Rh} = 5.5 Hz), 111.2, 110.5, 91.5 (d, J_{C-Rh} = 3.9 Hz), 91.3 (d, J_{C-Rh} = 4.3 Hz), 75.7 (d, 2C, J_{C-Rh} = 12.7 Hz), 75.6 (d, 2C, J_{C-Rh} = 12.3 Hz), 31.6, 31.1.

Reaction of $[RhCl(COD)]_2$ with Diazofluorene. To a solution of $[RhCl(COD)]_2$ (2.5 mg, 5 × 10^{-3} mmol) in toluene (2 mL) was added a toluene solution of diazofluorene (2 mL, 0.1 M, ca. 38 mg 0.2 mmol) dropwise at room temperature. After stirring for 10 min, the solvents were removed under vacuum. The residues were totally dissolved with $CDCl_3$ for in situ NMR analysis. The diazofluorene was consumed completely to give **4** and **5**. The molar ratio of olefin **4** to azine **5** determined by integrals of ^1H NMR is 3:1.

Reaction of $[RhCl(COD)]_2$ with Diphenyl Diazomethane. To a solution of $[RhCl(COD)]_2$ (2.5 mg, 5 × 10^{-3} mmol) in toluene (2 mL) was added a toluene solution of diphenyl diazomethane (2 mL, 0.1 M, ca. 39 mg, 0.2 mmol) dropwise at room temperature. After stirring for 10 min, the solvents were removed under vacuum. The residues were purified by silica gel column chromatography with hexane/EtOAC (v/v 10:1) to afford a pale yellow solid. Yield: 35 mg (97%). The product was confirmed to be benzophenone azine. The NMR data are consistent with the literature[41] reported ones.

Reaction of $[RhCl(COD)]_2$ with Phenyl Diazomethane. To a solution of $[RhCl(COD)]_2$ (2.5 mg, 5 × 10^{-3} mmol) in toluene (2 mL) was added a toluene solution of phenyl diazomethane (3.2 mL, 0.062 M, ca. 24 mg, 0.2 mmol) dropwise at room temperature. After stirring for 10 min, the solvents were removed under vacuum. The residues were dissolved with $CDCl_3$ for in situ NMR analysis. The phenyl diazomethane was consumed completely and only olefin products were observed. The molar ratio of trans isomer **11a** to cis isomer **11b** determined by integrals of ^1H NMR is 1:1.

Reaction of $[RhCl(COD)]_2$ with Methyl Diazoacetate. To a solution of $[RhCl(COD)]_2$ (2.5 mg, 5 × 10^{-3} mmol) in C_6D_6 (2 mL) in a degassed NMR tube was added methyl diazoacetate (17 μL, ca. 20 mg, 0.2 mmol) at room temperature. An in situ ^1H NMR spectrum was collected after standing the mixture for 10 min. The methyl diazoacetate was consumed completely and only olefin products were observed. The molar ratio of dimethyl fumarate (**12a**) to dimethyl maleate (**12b**) determined by integrals of ^1H NMR is 1:1.

X-ray Crystallography. Single crystals of **3a** and **3c** suitable for X-ray diffraction were grown from a saturated hexane solution in −20 °C fridge. A suitable specimen was selected and mounted in Cryoloop in Paratone, and intensity data were collected at 100 K on a Rigaku Oxford-Diffraction SuperNova diffractometer (Cu Kα). Using Olex2 GUI[42] the structure was solved with the ShelXS[43] structure solution program using Direct Methods and refined with the ShelXL[44] refinement package. Further crystallographic details are summarized in Tables S1 and S2. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1871356 (complex **3a**) and CCDC 1871359 (complex **3c**). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Detail. All of the structures presented in the energy profiles are optimized at DFT level using the M06 functionals.[45] The solvation effect was considered using the polarizable continuum model (PCM),[46] and the solvent was assigned as toluene corresponding to the experiment. The Rh atom is described by the effective core potentials of lanl2dz[47] with one set of polarization functions (ζ_f = 1.350).[48] The 6-311+G(d) basis set was used for the Cl atom. Other atoms, including H, C, and N, were described by 6-31G(d) standard basis set. Vibrational frequency calculations were carried out to confirm the nature of stationary points, as transition states (only one imaginary frequency) or the local minima (no imaginary frequency). Intrinsic reaction coordinate (IRC) calculations[49] were also employed to further demonstrate the transition states connect the relevant local minima. On the basis of the optimized structures obtained in the aforementioned calculation, the single-point energies calculations were performed using DFT-D3[50]mpirical dispersion correction and larger basis set, that is 6-311G(d,p) for the H, C, and N atoms. All of the DFT calculations were carried out using Gaussian 09 packages.[51]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00889.

Additional experimental and computational details, NMR spectra and crystallographic data (PDF)

Cartesian coordinates of all the calculated structures (XYZ)

Accession Codes

CCDC 1871356 and 1871359 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The

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Notes

The authors declare no competing financial interest.

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