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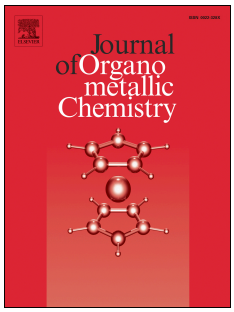

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Insertion of carbenoids into X-H bonds catalyzed by the cyclobutadiene rhodium complexes

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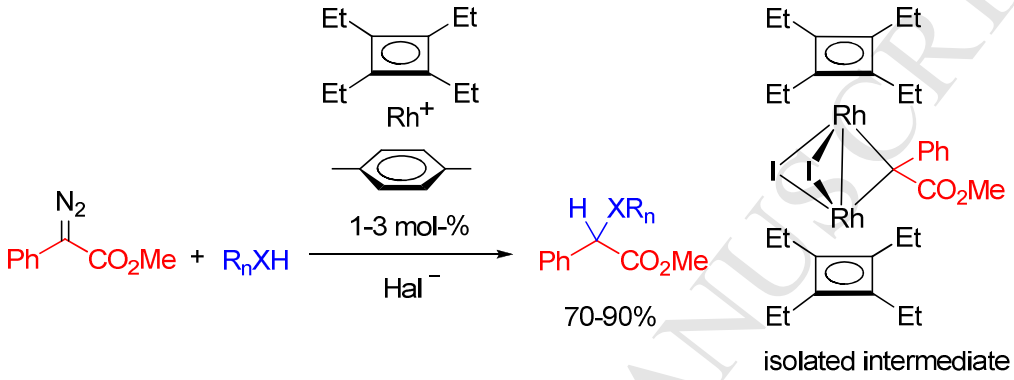
Dedicated to Academician I. P. Beletskaya in recognition of her fundamental contribution to the development of organometallic chemistry and catalysis

Graphical Abstract



Graphical Abstract Synopsis

Cyclobutadiene rhodium complexes catalyze the formation of carbenoid species from diazo acetates and subsequent insertion of carbenoids into X-H bonds (X = B, N, O, Si). The isolated intermediate complex unexpectedly has a binuclear structure with a bridging carbene ligand.

Abstract

The cyclobutadiene rhodium complex $[(C_4Et_4)RhCl]_2$ (generated from $[(C_4Et_4)Rh(p\text{-xylene})]PF_6$ and $BnNEt_3Cl$) catalyzes reaction of methyl α-diazophenylacetate with R_nX-H compounds to give the insertion products methyl 2-R_nX-2-phenylacetates in 70–90% yields (R_nX-H = methanol, *tert*-butylamine, 2,6-diisopropylaniline, morpholine, diallylamine, triethylsilane, triethylamine-borane). The stoichiometric reaction of $[(C_4Et_4)RhI]_2$ with methyl α-diazophenylacetate gives the intermediate complex $(C_4Et_4)_2Rh_2(\mu\text{-}I)_2$(μ-1-carboxymethyl-1-phenylmethylene), which has a binuclear structure with bridging iodide and carbene ligands. This result indicates that catalytically active carbene species may have more complex structures than the commonly assumed $L_nM{=}CR_2$.

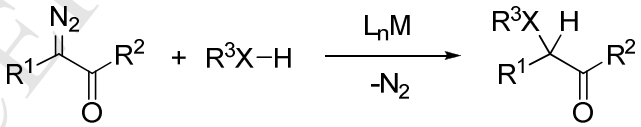
Keywords: diazo compound, carbene, rhodium, cyclobutadiene, catalysis, pi-complex

1. Introduction

Diazo compounds are widely used as a source of carbenoids in organic synthesis [1]. They typically undergo insertion [2], cyclopropanation [3], or cyclization [4] reactions, which lead to the formation of the new carbon-carbon bonds. The insertion of carbenoids into X–H bonds (X = heteroatom) has been less studied, although it is a useful method for the formation of the carbon-heteroatom bonds [5] (Scheme 1). In particular, insertion into X–H bonds has been successfully used in the synthesis of bioactive molecules and modifications of natural compounds, where mild conditions and functional group tolerance are required [6]. For example, a key step in the total synthesis of Maoecrystal V was an intramolecular Rh-catalyzed insertion of carbenoid into O-H bond [7]. Insertion of carbenoids into N-H bonds of indole rings was used for selective labelling of tryptophan residues in proteins [8,9].

A typical catalyst for the reactions of diazo compounds is rhodium(II) acetate $Rh_2(OAc)_4$ or its derivatives [2a]. However, it has been recently found that the diene rhodium(I) complexes $[(diene)RhCl]_2$ can also promote such process (see examples of catalytic cyclopropanation of alkenes [10], insertion into N-H [11], Si-H bonds [12], and B-H bonds [13]).

Two years ago, we have developed a general approach to the cyclobutadiene rhodium(I) complexes [14]. It has been expected that these complexes would have more robust catalytic activity than their diene congeners, because cyclobutadiene ligand provides better stabilization for the active metal center. Indeed, we have found that the cyclobutadiene complex $[(C_4Et_4)Rh(p\text{-xylene})]PF_6$ (**1**) is one of the best catalyst for the selective reductive amination of carbonyl compounds in the presence of the carbon monoxide [15]. Herein we report the application of the cyclobutadiene complexes as a catalysts for insertion of carbenoids into X–H bonds.

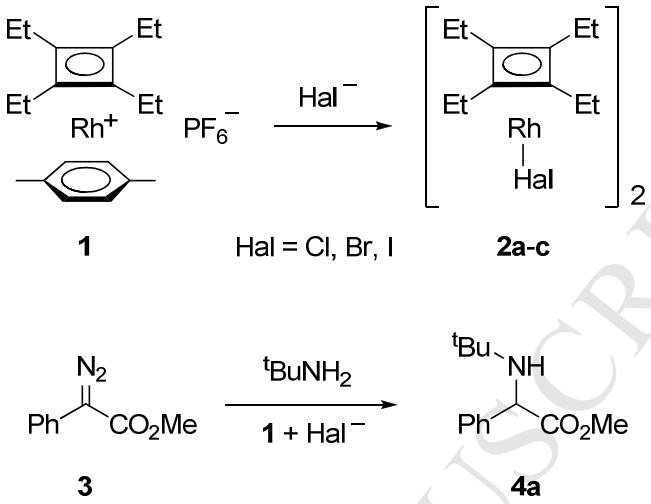


Scheme 1. Insertion of carbenoids into X-H bonds (X = heteroatom; ML_n = metal catalyst).

2. Results and discussions

At the outset of this investigation, we examined the catalytic activity of the cyclobutadiene complexes in a model reaction of methyl α-diazophenylacetate (**3**) with *tert*-butylamine (Scheme 2). It was found that the sandwich complex **1** is completely inactive in this process, apparently because it has no vacant sites for coordination of the reactants. Addition of halide anions to the complex **1** leads to replacement of the labile p-xylene ligand and formation of the more active half-sandwich species

$[(C_4Et_4)RhHal]_2$ (**2a-c**) [14]. It was found that the rate of this reaction increases in the order I < Br ≈ Cl. At the same time, the catalytic activity of **2a**–**c** in the model reaction of α-diazophenylacetate increases in the opposite order: Cl ≈ Br < I (Table 1). For further investigation, we selected the chloride complex **2a**, which we generated *in situ* from **1**.



Scheme 2. Generation of catalysts **2a**–**c** and the model reaction of α-diazophenylacetate (**3**).

Table 1. The catalytic activity of **2a**–**c** in the model reaction, depending on the time of the catalyst generation.

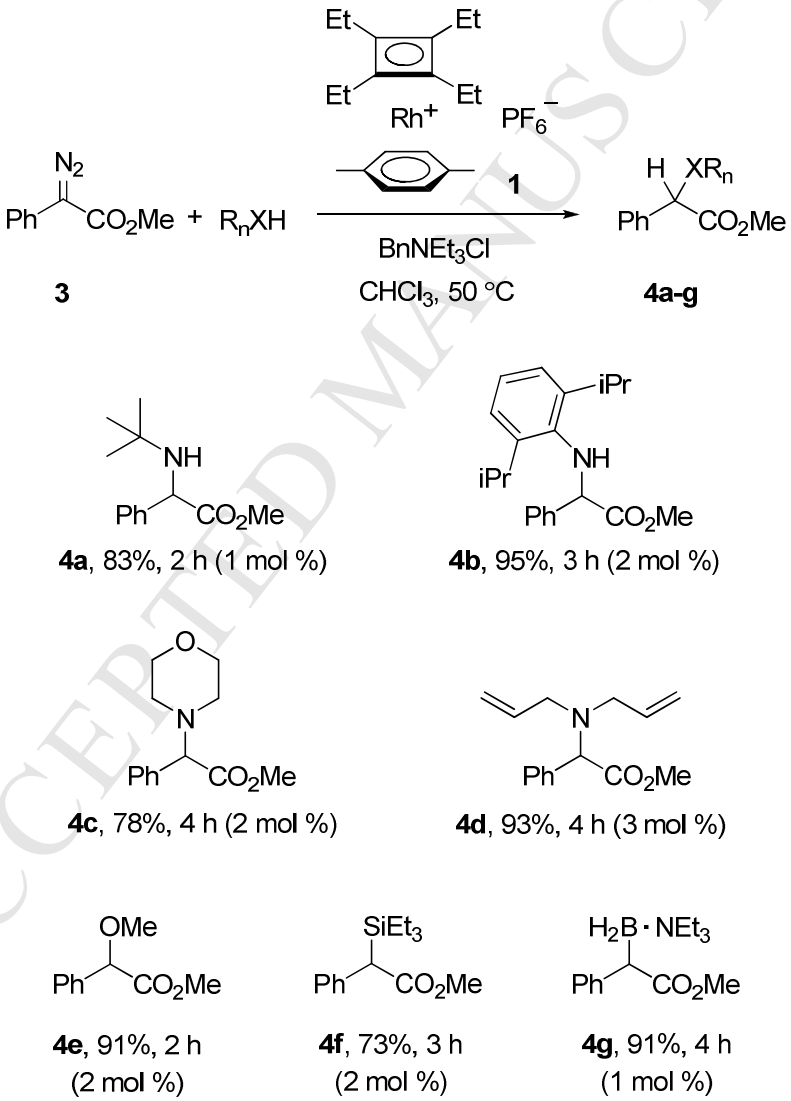
Catalyst loading	Time of the catalyst generation (**1** + Hal^-)	NMR yield[a] of the product **4a** after 30 min		
		Cl^-	Br^-	I^-
2 mol-%	5 min[b]	87%	75%	17%
1 mol-%	20 hours[c]	23%	17%	44%

[a] All conversions were determined by ^1H NMR. Catalysts **2a-c** were generated *in situ* from precatalyst **1** and halide salts $BnNEt_3Cl$, Bu_4NBr, and NEt_4I, respectively. [b] The reaction was performed with **1** (2 mol-%), Hal^- source (2 mol-%), **3** (0.057 mmol), and $^tBuNH_2$ (0.113 mmol) in 0.5 ml of $CDCl_3$ at room temperature. [c] The reaction was performed with **1** (1 mol-%), Hal^- source (1 mol-%), **3** (0.111 mmol), and $^tBuNH_2$ (0.222 mmol) in 0.5 ml of $CDCl_3$ at room temperature.

Next, we evaluated the diversity of amines that can react with α-diazophenylacetate **3** in the presence of our catalyst (Scheme 3). The insertion of carbenoid into *tert*-butyl amine proceeded smoothly to give the product **4a** in 83% isolated yield. Similar reaction with hindered and less nucleophilic 2,6-diisopropylaniline still led to the formation of the amine **4b** in excellent 95% yield. The reactions with secondary amines morpholine and diallylamine gave products **4c** and **4d** in 78% and 93%

yields. Note, that no cyclopropanation was observed in the case of diallylamine. Depending on the steric and electronic effects of the amines, the insertion reactions typically required 1–3 mol-% catalyst loadings for complete conversion of the diazoacetate **3**.

Substrates with other X-H bonds also reacted with the diazo compound **3**. For example, methanol produced the ether **4e** (91%), while triethylsilane gave the silane **4f** (73%). A carbon-boron bond was formed by reaction of **3** with triethylamine-borane, which produced the stable adduct **4g** in 91% yield. The first example of such transformation has been reported only several years ago [16], in particular with the use of the related diene rhodium complexes $[(diene)RhCl]_2$ as catalysts [13]. This method is an attractive way to prepare functionalized organoboranes from the commercially available amine-borane adducts.



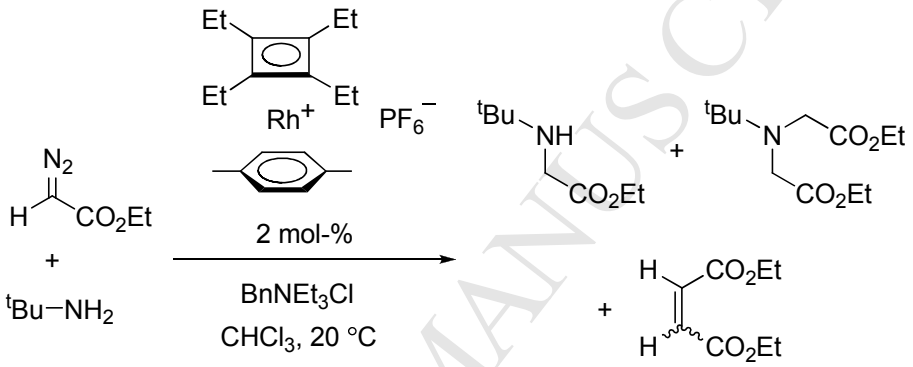
Scheme 3. Substrate scope of X-H insertion reactions. Isolated yields are given.

The reaction times are indicated, the catalyst loadings are put in parentheses.

It should be mentioned that reactions of the diazoacetate **3** with alkenes and alkynes in the presence of the rhodium catalyst **2a** were slow and non-selective. Fortunately, the unsaturated bonds

do not interfere with the insertion of carbenoids into X-H bonds (e.g. product **4d**). At the same time, thiols completely inhibited the catalysis and no reaction was observed when 4-aminobenzenethiol was used as X-H reagent.

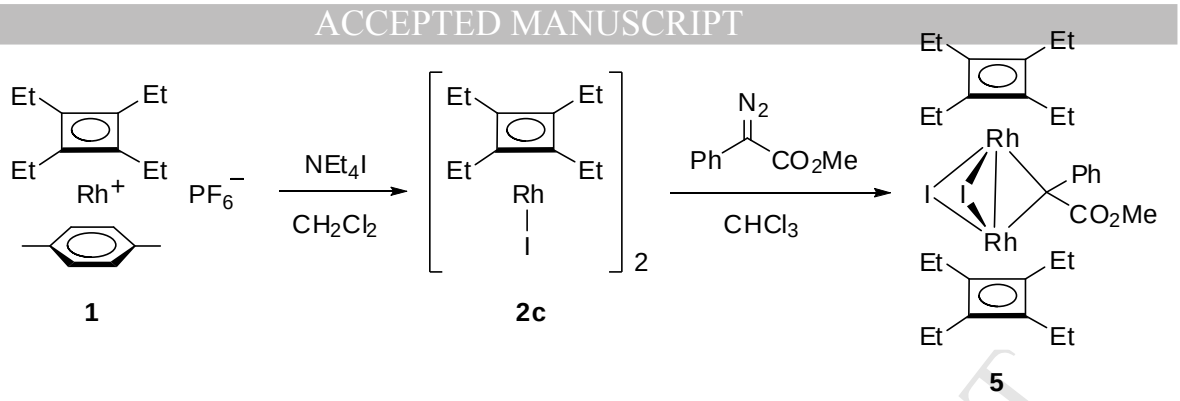
We also evaluated similar insertion reactions of ethyl diazoacetate, but found that they proceeded too fast and non-selective. This can be exemplified by the reaction of ethyl diazoacetate with *tert*-butylamine in the presence of the generated catalyst **2a**, which produced the products of single and double insertions as well as the product of homocoupling of the diazo compound (Scheme 4). Attempts to improve the selectivity by the slow addition of the diazo compound or lowering the reaction temperature were not sufficiently successful. It should be noted, that some known catalysts provide the sole product of mono insertion without undesired dimerization of ethyl diazoacetate [17].



Scheme 4. Non-selective reaction of ethyl diazoacetate with *tert*-butylamine.

In order to get some insight into the nature of the carbenoid rhodium species we have carried out the reaction of the iodide complex **2c** with the stoichiometric amount of diazoacetate **3** (Scheme 5). Surprisingly, the bright-green complex **5** was formed as a sole organometallic product according to ^{1}H NMR. This green color was also typically observed in the catalytic reactions, which suggested the intermediate formation of **5**. Furthermore, the test reaction of **5** with *tert*-butylamine in 10 min gave the expected insertion product **4a** and the starting iodide complex **2c** in almost quantitative yields.

Complex **5** was somewhat unstable in air and was isolated by the column chromatography under argon and subsequent crystallization in 72% yield. The ^{1}H NMR spectra of **5** indicated the hindered rotation of the phenyl substituent at room temperature. At −30 °C it was so slow that the protons of the phenyl ring appeared as four separated resolved multiplets (see supporting information). At the same time, the rotation of the cyclobutadiene ligands remained fast on ^{1}H NMR time scale even at −30 °C. However, the signals of CH_2 groups of the substituted cyclobutadiene appeared as two doublets of quadruplets indicating that the corresponding protons are diastereotopic. The ^{13}C NMR of **5** shows characteristic doublet at 94.74 ($J_{Rh\text{-}C}$ = 9.5 Hz), which corresponds to the cyclobutadiene ligand, but no clear signal of the carbene atom. The latter is not surprising as this signal is presumably broad, because of the dynamic behavior of the complex and the spin coupling interaction with two rhodium atoms.



Scheme 5. Synthesis of the reaction intermediate **5** from the precatalyst **1**.

Finally, the unusual binuclear structure of the complex **5** was revealed by the X-ray diffraction analysis (Figure 1). The cyclobutadiene ligands are non-symmetrically coordinated to the rhodium atoms because of the different trans-effects of iodide and carbene ligands. In particular, the Rh−$C_{cyclobutadiene}$ distances in **5** vary in 2.11−2.17 Å range. For comparison, these distances in more symmetrical sandwich cation **1** are in 2.10−2.12 Å range [14]. The distance between two rhodium atoms of 2.6280(3) Å is consistent with the presence of a single covalent bond, which is required by 18 electron rule.

The bridging carbene ligand is symmetrically coordinated to both rhodium atoms with 2.124(3) Å average Rh−C25 distance. Interestingly, the carbene center has no significant conjugation with the phenyl ring, which is indicated by the rather long C25-C26 bond of 1.481(5) Å (compare with 1.41−1.43 Å in the mononuclear carbene rhodium complexes [18]). The carbene atom C25 is well hidden in the molecular environment (Figure 2), so it seems that 'opening of the bridge' with the cleavage of one of the Rh−C25 bond is required for its reaction with the X-H bonds. In order to access such possibility we carried out the DFT calculations (Scheme 6). It was found that formation of the opened structure **6** from **5** requires only 14.3 kcal mol^{-1} and therefore is quite feasible at room temperature.

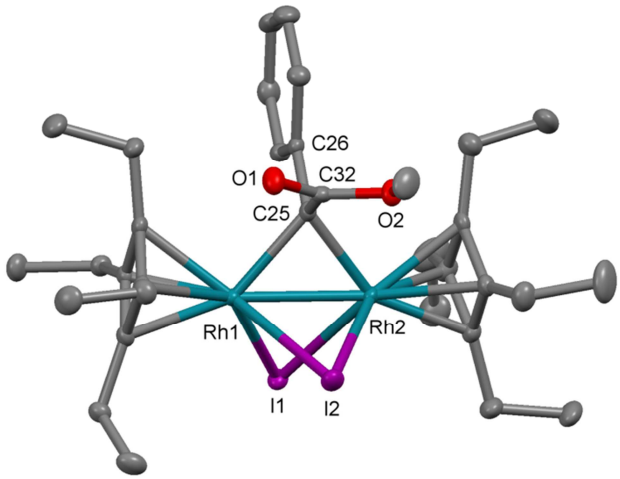


Figure 1. The crystal structure of the complex **5** in 50% thermal ellipsoids. The disordered part of one of ethyl groups and all hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Rh1—

Rh2 2.6280(3), Rh1—I1 2.7173(3), Rh1—I2 2.9081(3), Rh1—C25 2.122(3), Rh2—I1 2.7438(3), Rh2—I2 2.8493(3), Rh2—C25 2.126(3), C25—C26 1.482(4), C25—C32 1.507(4).

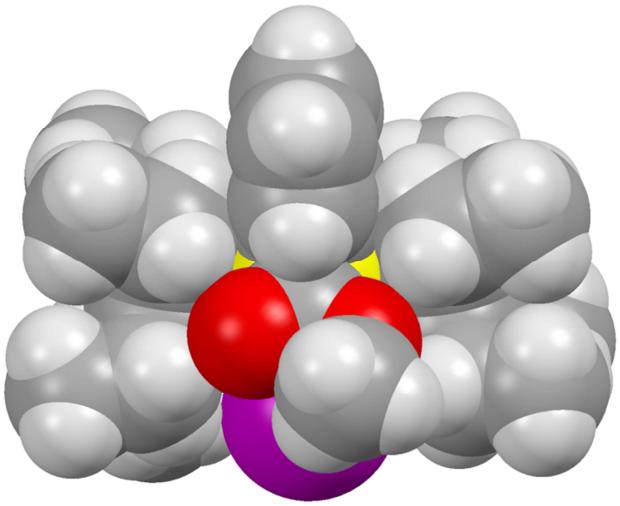
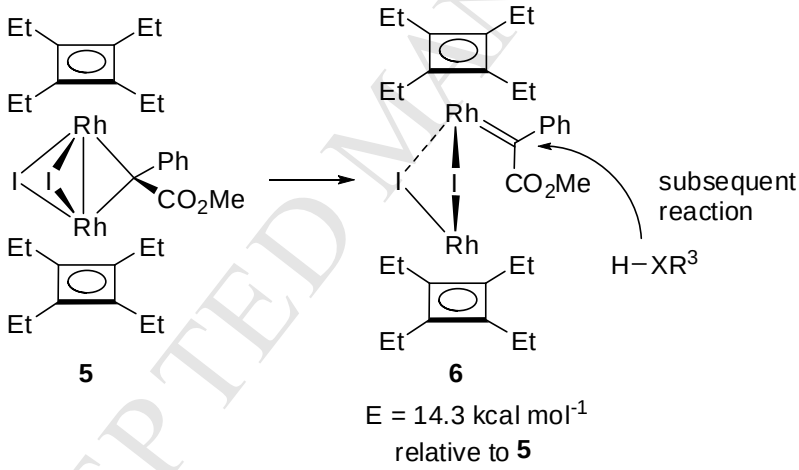


Figure 2. The crystal structure of the complex **5** with atoms represented as spheres with van der Waals radii. The carbene atom is in the center, shown in yellow (in black in printed version).



Scheme 6. Proposed opening of the bridged structure of the intermediate **5** according to DFT calculations.

3. Conclusions

To conclude, the cyclobutadiene rhodium complexes $[(C_4Et_4)RhHal]_2$ catalyze decomposition of diazoacetates and subsequent insertion of carbenoids into various X-H bonds with formation of the new C–B, C–N, C–O, and C–Si bonds. The intermediate of this reaction has an unusual binuclear structure with a bridging carbene ligand. Catalytically active carbenoid complexes of transition metals are typically assumed to be monomeric [18,19]. Our results show that it may not always be the case.

4. Experimental section

4.1. General

All reactions were carried out under argon in anhydrous solvents, while the products were isolated in air, unless stated otherwise. Chloroform was deacidified over calcium hydride, degassed by bubbling of argon for 15 minutes, and stored over molecular sieves (5 Å) in the dark. Anhydrous 1,2-dichloroethane was obtained by distillation under argon from calcium hydride. Column chromatography was performed with standard Macherey-Nagel silica gel 60 (0.04–0.063 mm particle size). The progress of the catalytic reactions were monitored by NMR or TLC using PE/ether = 10/1 as an eluent and starting methyl α-diazophenylacetate (**3**) as a reference compound (R_f = 0.3). ^{1}H, ^{13}C, ^{11}B NMR spectra were recorded on a Bruker Avance 400 spectrometer at 20°C in $CDCl_3$. Data were reported as chemical shifts in ppm relative to the residual signals of the solvent $CDCl_3$ (7.26 ppm for ^{1}H, 77.2 ppm for ^{13}C). The abbreviations used for explaining the multiplicities were as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Mass spectra were measured on high-resolution time-of-flight Bruker micrOTOF instrument using electrospray ionization (ESI-MS) [20]. Measurements were performed in positive ion mode, interface capillary voltage at 4.5 kV, effective scan range at m/z 100 – 3000, external calibration ESI-L Low Concentration Tuning Mix, Agilent Technologies, direct syringe injection at flow rate of 3 μL/min, nitrogen as dry gas at 4 L/min, interface temperature at 180°C. The spectra were processed using Bruker Data Analysis 4.0 software package. Methyl α-diazophenylacetate (**3**) [21] and complex $[(C_4Et_4)Rh(p\text{-xylene})]^{+}PF_6^{-}$ (**1**) [14] were synthesized according to the published procedures. All other reagents were purchased from Acros or Aldrich and used as received.

*4.2. Methyl 2-(tert-butylamino)-2-phenylacetate (**4a**).*

A 10 ml Schlenk flask was charged with complex **1** (1 mol-%) and $BnNEt_3Cl$ (1 mol-%) and 0.5 ml of 1,2-dichloroethane was added. The solution was stirred for 10 minutes, then the diazo compound (67 mg, 0.38 mmol) was added, followed by *tert*-butylamine (48 ml, 0.45 mmol). Additional 2.5 ml of 1,2-dichloroethane was added and the mixture was heated at 50°C for 2 hours. After the completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography using dichloromethane (with 1% of triethylamine) as an eluent to give analytically pure product **4a** (69 mg, 83%). This compound was previously synthesized using ruthenium [22] and iridium catalysts [23]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10 (s, 9H, *tert*-butyl), 2.07 (br, 1H, NH), 3.67 (s, 3H, ester), 4.48 (s, 1H, CH), 7.30 (m, 1H, Ph), 7.34 (m, 2H, Ph), 7.40 (d, J = 7.16 Hz, 2H, Ph).

*4.3. Methyl 2-(2,6-diisopropylphenylamino)-2-phenylacetate (**4b**).*

A 10 ml Schlenk flask was charged with a complex **1** (2.0 mg, 2 mol-%) and $BnNEt_3Cl$ (0.9 mg, 2 mol-%) and 0.5 ml of $CHCl_3$ was added. The solution was stirred for 10 minutes, then the diazo compound (36 mg, 0.20 mmol) was added, followed by 2,6-diisopropylaniline (42 μl, 39.4 mg, 0.22 mmol). Additional

2.5 ml of $CHCl_3$ was added and the mixture was heated at 50°C for 3 hours. After the completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography using petroleum ether – diethyl ether mixture (20:1) as eluent to give analytically pure product **4b** (62 mg, 95%). The ethyl ester analogue of **4b** was synthesized previously using copper catalysts [24]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.09 (d, J = 6.8 Hz, 6H, *iso*-propyl), 1.17 (d, J = 6.8 Hz, 6H, *iso*-propyl), 3.17 (septet, J = 6.8 Hz, 2H, *iso*-propyl), 3.69 (s, 3H, ester), 4.32 (d, J = 9.9 Hz, 1H, NH), 4.68 (d, J = 9.9 Hz, 1H, CH), 7.06 (m, 3H, C_6H_3), 7.33-7.38 (m, 5H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.30, 24.55, 27.92, 52.63, 67.09, 123.89, 127.21, 128.34, 128.91, 138.76, 141.48, 142.19, 174.00. ESI-MS: calculated for $C_{21}H_{28}NO_2$ (M+H) 326.2115, recorded 326.2105.

*4.4. Methyl 2-morpholino-2-phenylacetate (**4c**).*

A 10 ml Schlenk flask was charged with a complex **1** (2.0 mg, 2 mol-%) and $BnNEt_3Cl$ (0.9 mg, 2 mol-%) and 0.5 ml of $CHCl_3$ was added. The solution was stirred for 10 minutes, then the diazo compound (36 mg, 0.20 mmol) was added, followed by morpholine (34 µl, 34.2 mg, 0.39 mmol). Additional 2.5 ml of $CHCl_3$ was added and the mixture was heated at 50°C for 4 hours. After the completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography using petroleum ether – ethyl acetate mixture (5:1) as eluent to give product **4c** (37 mg, 78%). The compound **4c** was previously synthesized previously by the methods that do not involve diazo compounds [25, 26, 27]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.46 (d, 2.13 Hz, 4H, -$(CH_2)_2$O), 3.69 (m, 3H, ester), 3.74 (m, 4H, –$(CH_2)_2$N-), 3.99 (s, 1H, CH), 7.34 (m, 3H, Ph), 7.44 (m, 2H, Ph).

*4.5. Methyl 2-(diallylamino)-2-phenylacetate (**4d**).*

A 10 ml Schlenk flask was charged with a complex **1** (3.1 mg, 3 mol %) and $BnNEt_3Cl$ (1.4 mg, 3 mol %) and 0.5 ml of $CHCl_3$ was added. The solution was stirred for 10 minutes, then the diazo compound (36 mg, 0.20 mmol) was added, followed by diallylamine (49 µl, 38.6 mg, 0.40 mmol). Additional 2.5 ml of $CHCl_3$ was added and the mixture was heated at 50°C for 4 hours. After the completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography using petroleum ether – diethyl ether mixture (7:1) as eluent to give analytically pure product **4d** (46 mg, 93%). The compound **4d** was synthesized previously by the methods that do not involve diazo compounds [25, 28]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.24 (br, 4H, 2CH_2), 3.73 (s, 3H, COOMe), 4.64 (s, 1H, CH), 5.20 (m, 4H, 2=CH_2), 5.84 (m, 2H, 2=CH), 7.30-7.40 (m, 5H, Ph).

*4.6. Methyl 2-methoxy-2-phenylacetate (**4e**).*

A 10 ml Schlenk flask was charged with a complex **1** (2.0 mg, 2 mol-%) and $BnNEt_3Cl$ (0.9 mg, 2 mol-%) and 0.5 ml of $CHCl_3$ was added. The solution was stirred for 10 minutes, then the diazo compound (36 mg, 0.20 mmol) was added, followed by methanol (40 µl, 31.7 mg, 0.99 mmol). Additional 2.5 ml of $CHCl_3$ was added and the mixture was heated at 50°C for 2 hours. After the completion of the reaction,

the solvent was evaporated under reduced pressure and the residue was purified by column chromatography using petroleum ether – diethyl ether mixture (10:1) with 1% of triethylamine as an eluent to give analytically pure product **4e** (33 mg, 91%). The compound **4e** was previously synthesized using rhodium [29], iron [30], and copper catalysts [31]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.39 (s, 3H, OMe), 3.71 (s, 3H, COOMe), 4.77 (s, 1H, CH), 7.34-7.42 (m, 5H, Ph).

*4.7. Methyl 2-phenyl-2-(triethylsilyl)acetate (**4f**).*

A 10 ml Schlenk flask was charged with a complex **1** (2.0 mg, 2 mol-%) and $BnNEt_3Cl$ (0.9 mg, 2 mol-%) and 0.5 ml of $CHCl_3$ was added. The solution was stirred for 10 minutes, then the diazo compound (36 mg, 0.20 mmol) was added, followed by triethylsilane (64 µl, 46.6 mg, 0.40 mmol). Additional 2.5 ml of $CHCl_3$ was added and the mixture was heated at 50°C for 3 hours. After the completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography using petroleum ether – ethyl acetate (3:1) with 1% of triethylamine as an eluent to give product **4f** (39 mg, 73%). The compound **4f** was previously synthesized using rhodium [32, 33], iridium [34], and copper catalysts [35]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.57 (m, 6H, $3CH_2$), 0.90 (m, 9H, $3CH_3$), 3.52 (s, 1H, CH), 3.67 (s, 3H, ester), 7.17 (m, 1H, Ph), 7.28 (m, 2H, Ph), 7.37 (m, 2H, Ph).

*4.8. Methyl 2-phenyl-2-(triethylamine-dihydridoboron)acetate (**4g**).*

A 10 ml Schlenk flask was charged with a complex **1** (1.0 mg, 1 mol-%) and $BnNEt_3Cl$ (0.5 mg, 1 mol-%) and 0.5 ml of $CHCl_3$ was added. The solution was stirred for 10 minutes, then the diazo compound (42.2 mg, 0.24 mmol) was added, followed by borane triethylamine complex $BH_3{\cdot}NEt_3$ (36 µl, 27.8 mg, 0.24 mmol). Additional 2.5 ml of $CHCl_3$ was added and the mixture was heated at 50°C for 4 hours. After the completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography using petroleum ether – ethyl acetate (3:1) with 1% of triethylamine as an eluent to give product **4g** (58 mg, 91%). The compound **4g** was previously synthesized by rhodium catalysis [13]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (t, J = 7.2 Hz, 9H, $3CH_3$), 1.50-2.45 (br+d, J = 99.6 Hz, 2H, BH_2), 2.70 (qd, J = 7.6 Hz and J = 3.2 Hz, 6H, $3CH_2$), 3.13 (br t, J = 3.83 Hz, 1H, CH), 3.60 (s, 3H, ester), 7.08 (t, J = 7.33 Hz, 1H, Ph), 7.22 (t, J = 7.62 Hz, 2H, Ph), 7.44 (d, J = 6.8 Hz, 2H, Ph). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ = −6.25 (s, 1B).

*4.9. $[(C_4Et_4)RhI]_2$ (**2c**).*

Synthesis and isolation of this complex was conducted under argon atmosphere. A Schlenk flask was charged with complex **1** (31 mg, 0.06 mmol) and NEt_4I (17 mg, 0.065 mmol) and 2 ml of dichloromethane was added. The pale yellow solution quickly became reddish, but was stirred overnight to ensure complete conversion. The solvent was evaporated and the residue was extracted with hexane (3×2 ml). The hexane solution was evaporated and the residue was dried to give the analytically pure dark red complex **2c** (22 mg, 93%). The complex is stable in air in the solid state for several minutes.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 (t, J = 7.5 Hz, 24H, CH_3), 1.74 (q, J = 7.5 Hz, 16H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.35 (CH_3), 20.26 (CH_2), 85.64 (d, J = 12 Hz, C_4). ESI-MS: calculated for $C_{24}H_{40}I_2Rh_2$ (M): 787.9324, recorded: 787.9329.

*4.10. (C_4Et_4)$_2$Rh$_2$(μ-I)$_2$(μ-1-carboxymethyl-1-phenylmethylene) (**5**).*

Synthesis and isolation of this complex was conducted under argon atmosphere. To a solution of complex [(C_4Et_4)RhI]$_2$ **2c** (37 mg, 0.047 mmol) in 1 ml of $CDCl_3$ methyl α-diazophenylacetate (17 mg, 0.94 mmol) was added and the reaction mixture was stirred overnight. The solvent was evaporated and the residue was purified by column chromatography using gradient eluent (petroleum ether, then petroleum ether – ethyl acetate (20:1), then petroleum ether – ethyl acetate (10:1)). The green fraction was collected and evaporated. The residue was dissolved in hexane and slow evaporation of the solvent gave the crystals, which were suitable for the X-ray analysis (32 mg, 72%). The complex is stable in air in the solid state for several minutes. ^{1}H NMR (600 MHz, 20 °C, $CDCl_3$): δ = 1.05 (t, J = 7.6 Hz, 24H, CH_3), 1.74 (dq, J = 15.0, 7.6 Hz, 8H, 8CH), 1.96 (dq, J = 15.0, 7.6 Hz, 8H, 8CH), 3.73 (s, 3H, COOMe), 7.07 (br s, 2H, Ph), 7.17 (br s, 1H, Ph), 7.38 (t, J = 9.6 Hz, 1H, Ph), 8.43 (br s, 1H, Ph). The integral intensity of broad signals is somewhat lower than expected. ^{13}C NMR (150 MHz, 20 °C, $CDCl_3$): δ = 13.64 (CH_3), 19.71 (CH_2), 50.80 (COO*C*H$_3$), 94.74 (d, J_{Rh-C} = 9.5, *C*$_4$Et$_4$), 128.31, 159.44, 184.32. Elemental analysis for $C_{33}H_{48}I_2O_2Rh_2$ calcd: C 42.33, H 5.17; found: C 41.39, H 5.01. The results of elemental analysis somewhat deviated from the calculated values presumably because of the partial decomposition of the complex in air. ESI-MS: calculated for $C_{33}H_{48}IO_2Rh_2$ (M−I): 809.0804, recorded: 809.0801; calculated for $C_{24}H_{40}I_2Rh_2$ (M−C(Ph)COOMe): 787.9324, recorded: 787.9323.

4.11. Reaction of ethyl diazo acetate with tert-butylamine.

NMR-tube with a small stirring bar was charged with solutions of *tert*-butylamine (15 μl, 11 mg, 0.14 mmol) in $CDCl_3$ (200 μl), complex **1** (1.5 mg, 2 mol-%) in $CDCl_3$ (100 μl), and $BnNEt_3Cl$ (0.7 mg, 2 mol-%) in $CDCl_3$ (100 μl). Upon the addition of ethyl diazo acetate (15 μl, 16.3 mg, 0.14 mmol), vigorous gas evolution was observed. According to ^{1}H NMR the resulting mixture contained *t*-BuNHCH$_2$CO$_2$Et 67%, *t*-BuN(CH$_2$CO$_2$Et)$_2$ 22%, diethyl maleate 8%, diethyl fumarate 3%, and an excess of unreacted *t*-BuNH$_2$.

4.12. DFT calculations.

Geometry optimizations were performed without constraints using PBE exchange-correlation functional [36], the scalar-relativistic Hamiltonian, atomic basis sets of generally contracted Gaussian functions, and a density-fitting technique as implemented in Priroda 6 code [37]. The all-electron double-ζ basis set L1 augmented by one polarization function was used [38]. Frequency calculations were performed to confirm that the structures correspond to the minima. The molecular visualization was done by ChemCraft software (http://www.chemcraftprog.com). Cartesian coordinates of the optimized structures are available as supplementary data.

4.13. X-ray diffraction analysis.

Crystals of **5** ($C_{33}H_{48}I_2O_2Rh_2$, M = 936.33) are monoclinic, space group $P2_1/n$, at 120 K: a = 11.9250(7), b = 21.6274(13), c = 13.9321(9) Å, β = 102.5260(10)°, V = 3507.7(4) $Å^3$, Z = 4 (Z' = 1), d_{calc} = 1.773 gcm^{-3}, μ(MoKα) = 27.27 cm^{-1}, F(000) = 1832. Intensities of 36087 reflections were measured with a Bruker APEX2 CCD diffractometer [λ(MoKα) = 0.71072Å, ω-scans, 2θ<54°], and 7658 independent reflections [R_{int} = 0.0424] were used in a further refinement. The structure was solved by the direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. Positions of hydrogen atoms were calculated, and they were refined in the isotropic approximation in the riding model. The refinement converged to wR2 = 0.0580 and GOF = 1.050 for all the independent reflections (R1 = 0.0256 was calculated against F for 6596 observed reflections with I>2σ(I)). All calculations were performed using SHELXTL PLUS 5.0 [39].

Appendix A. Supplementary data

NMR spectra of the complexes **2c** and **5**. Cartesian coordinates for calculated structures.

Appendix B. Supplementary data

CCDC 1562824 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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Highlights

Cyclobutadiene rhodium complexes catalyze decomposition of diazo compounds.

Rhodium carbenoids react with X-H bonds but do not add to C=C double bonds.

In contrast to general assumption carbenoid complexes can have a binuclear structure.