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Cyclopentadienyl rhodium(III) complexes as catalysts for the insertion of phenyldiazoacetate into E−H bonds

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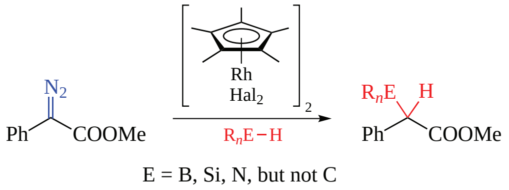
Rhodium(III) complexes catalyze the insertion of carbenoids generated from diazo compounds into E−H bonds (E = B, Si, N, but not C), although less efficiently than classical rhodium(II) carboxylates, despite formally higher oxidation state of the metal.



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The insertion of carbenoids generated from diazo compounds[1] into various heteroatom–hydrogen bonds (Figure 1) represents a unique approach to many types of substances as highlighted by the recent reviews[2,3] and numerous synthetic reports, including those of the Russian scientists.[4–12] Most commonly, such reactions are catalyzed by rhodium(II) carboxylates $Rh_2(OCOR)_4$.[13] However, these carboxylates form a rather narrow class of compounds with limited possibility for variation of ligands. Therefore, the more diverse Rh^I catalysts such as $[(diene)RhCl]_2$ have recently attracted a considerable attention. In accordance with lower oxidation state of rhodium, these catalysts form less electrophilic carbenoid intermediates which can undergo insertion into the reactive E−H bonds (E = B, Si, N, O), but are less efficient for C−H insertion reactions. Noteworthy, the enantioselective insertion into B−H,[14,15] Si−H,[15,16] and even some C−H bonds[17,18] has been achieved using Rh^I catalysts with chiral diene ligands.

On the other hand, the catalytic activity of Rh^{III} complexes in similar reactions of diazo compounds remains almost unexplored, except for the mechanistically distinct insertion of carbenes into aromatic compound containing directing groups.[19,20] Due to the higher oxidation state of rhodium, the corresponding carbenoid intermediates are expected to be more electrophilic that their Rh^I and Rh^{II} analogues. Fürstner *et al.*[21,22] have found that the reaction of the iodide complex $[(C_5Me_5)RhI_2]_2$ with aryldiazoacetate leads to highly active rhodium carbenoid $(C_5Me_5)RhI_2{=}C(Ar)COOMe$. Interestingly, similar reaction of the chloride complex $[(C_5Me_5)RhCl_2]_2$ is accompanied by the migration of chloride to the electrophilic carbene atom giving the α-chloro enolate complex $(C_5Me_5)RhCl{-}CCl(Ar)COOMe$. In accordance with the different structures of the intermediates, $[(C_5Me_5)RhI_2]_2$ appeared to be more efficient catalyst than $[(C_5Me_5)RhCl_2]_2$ in several reactions of diazo compounds.

Following this work, we investigated the catalytic activity of various $[Cp'MHal_2]_2$ complexes in the model insertion of phenyldiazoacetate **1** into E−H bonds of triethylamine-borane, triethylsilane, morpholine, and benzamide (Scheme 1). The employed catalysts (Figure 2) were analyzed in three general groups. The first group includes $[(C_5Me_5)MHal_2]_2$ complexes with different metal atoms M = Co (**C1**), Rh (**C2**), Ir (**C3**). The second group includes rhodium complexes $[(C_5Me_5)RhHal_2]_2$ with different halide ligands Hal = Cl (**C2**) *vs*. I (**C5**). The third one includes rhodium complexes $[Cp'RhI_2]_2$ with different cyclopentadienyl ligands $Cp' = C_5H_5$ (**C4**), C_5Me_5 (**C5**), $C_5H_2Bu^t_2CH_2Bu^t$ (**C6**).[23,24]

The comparison within the first group of catalysts showed that rhodium complex $[(C_5Me_5)RhCl_2]_2$ was generally more

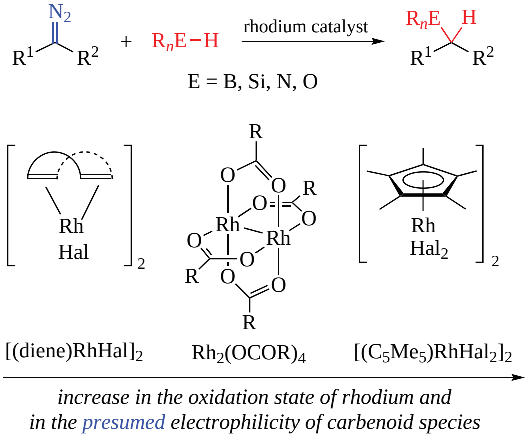
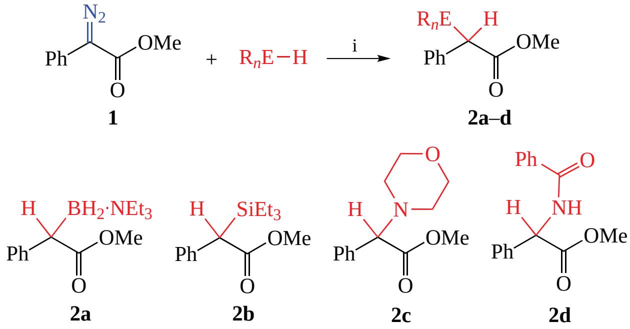


Figure 1 Catalytic insertion of diazo compounds into E−H bonds.



Scheme 1 *Reagents and conditions*: i, catalyst **C1**–**C6** (2 mol%), $CDCl_3$, 20–60 °C, 4–24 h.

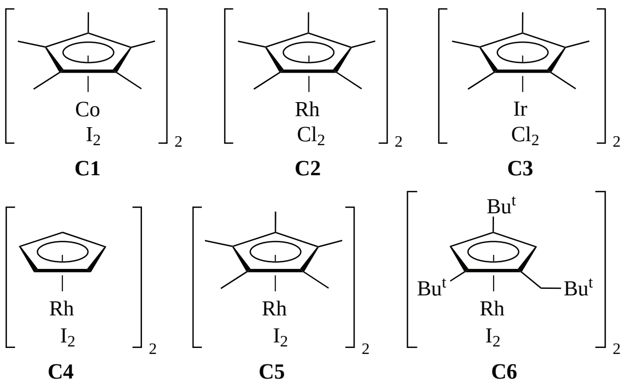


Figure 2 The structures of catalysts used in this work.

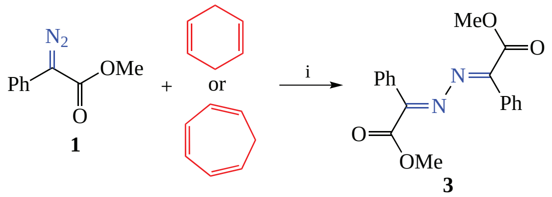
efficient than its cobalt and iridium analogues and gave three insertion products **2a–c** in *ca*. 50% yield (Table 1). The iridium complex $[(C_5Me_5)IrCl_2]_2$ was surprisingly inefficient for the insertion of triethylamine-borane, presumably because of its fast conversion into iridium hydride species.[25,26] Noteworthy, benzamide did not react in the presence of any of these three catalysts **C1**−**C3**. The comparison of chloride $[(C_5Me_5)RhCl_2]_2$ **C2** and the iodide $[(C_5Me_5)RhI_2]_2$ **C5** clearly showed higher efficiency of the latter in accordance with findings of Fürstner *et al*.[21] However, the difference in the catalytic activity was not so pronounced as the difference in the structures of the carbenoid intermediates might suggest. Most notably, only the iodide complex **C5** was capable of catalyzing the insertion of **1** into N−H bond of benzamide. The comparison within the third group of catalysts showed that the unsubstituted complex[27] $[(C_5H_5)RhI_2]_2$ (**C4**) usually gave lower yields than similar complexes with C_5Me_5 (**C5**) and $C_5H_2Bu^t_2CH_2Bu^t$ (**C6**) ligands. This may be attributed to the higher activity of $[(C_5H_5)RhI_2]_2$, which led the lower selectivity of the insertion process. In particular, the formation of methyl phenylacetate as a side product was noted in the reactions of **1** with triethylamine-borane and triethylsilane. On the other hand, catalyst **C6** with the bulky planar-chiral cyclopentadienyl ligand had only slightly lower activity than **C5**.

Encouraged by the high catalytic activity of the iodide catalysts **C5** and **C6** we attempted to use them for the insertion of phenyldiazoacetate **1** into rather reactive C−H bonds of 1,4-cyclohexadiene and cycloheptatriene (Scheme 2). However, even in neat olefins (used as solvents) these reactions did not proceed but rather azine **3**, a dimerization product of the starting diazo compound, was formed. In contrast, the desired C−H insertion was cleanly achieved using Rh^{II} or even Rh^{I} complexes.[18,28] Apparently, despite high formal oxidation state, Rh^{III} carbenoids are less active than their Rh^{II} analogues. Lower electrophilicity of such carbenoids may be explained by the electron donation from the anionic cyclopentadienyl and iodide ligands.

Table 1 The NMR yields of the insertion products **2a**–**d** depending on the catalyst.

Catalyst		Product yield (%)			
Code	Formula	**2a**	**2b**	**2c**	**2d**
C1	$[(C_5Me_5)CoI_2]_2$	25	44	0^a	0^a
C2	$[(C_5Me_5)RhCl_2]_2$	56	53	47	0^a
C3	$[(C_5Me_5)IrCl_2]_2$	0^a	47	85	0^a
C4	$[(C_5H_5)RhI_2]_2$	52	50	42	78
C5	$[(C_5Me_5)RhI_2]_2$	46	83	70	89
C6	$[(C_5H_2Bu^t_2CH_2Bu^t)RhI_2]_2$	28	82	64	69

[a] Zero per cent yields correspond to <5% conversions of the starting diazo compound **1**.



Scheme 2 *Reagents and conditions*: i, catalyst **C5** or **C6** (2 mol%), $CDCl_3$, 20 °C, 12 h.

To conclude, complex $[(C_5Me_5)RhI_2]_2$ can serve as a competent catalyst for insertion of phenyldiazoacetate into Si−H and N−H bonds, but not into B−H and C−H bonds. The iodide complex is notably more active that the more common chloride $[(C_5Me_5)RhCl_2]_2$. So far, Rh^{III} complexes appear to be less efficient catalysts for transformation of diazo compounds than Rh^{II} and Rh^{I} congeners.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.07.017.

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