Rhodacarboranes as catalysts for oxidative coupling of benzoic acid with diphenylacetylene*

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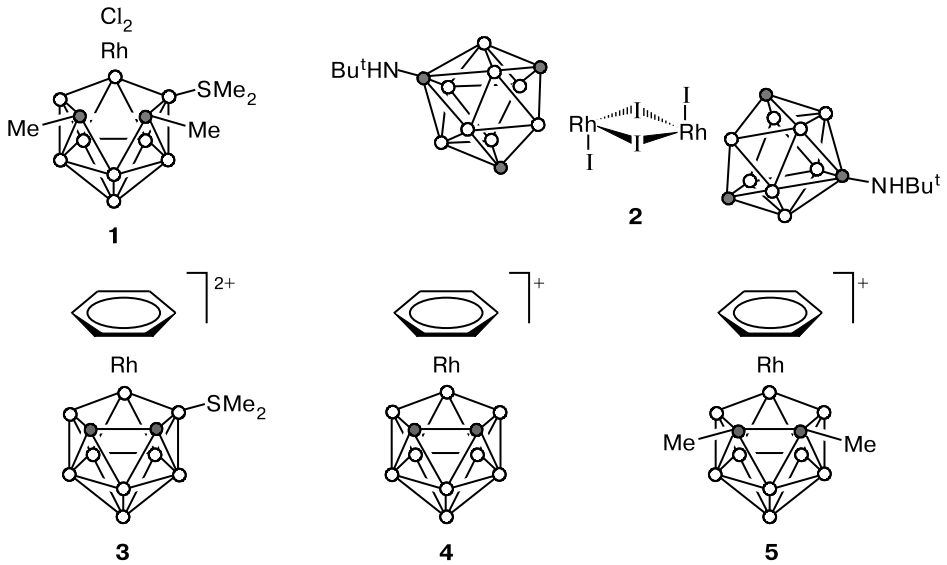
Rhodacarboranes $[(9\text{-}SMe_2\text{-}7,8\text{-}Me_2\text{-}C_2B_9H_8)RhCl_2]_2$, $[(1\text{-}Bu^tNH\text{-}1,7,9\text{-}C_3B_8H_{10})RhI_2]_2$, $[(9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Rh(C_6H_6)]^{2+}$, and $[(7,8\text{-}R_2\text{-}C_2B_9H_9)Rh(C_6H_6)]^+$ (R = H, Me) catalyze, in the presence of $Cu(OAc)_2$, the oxidative coupling of benzoic acid with diphenylacetylene giving 1,2,3,4-tetraphenylnaphthalene in 25—60% yields. The reactions catalyzed by $RhCl_3$ and $[CpRhI_2]_2$ afford the product in 40 and 90% yields, respectively. The decarboxylation of benzoic acid was analyzed by DFT calculations.

Key words: homogeneous catalysis, metallacarboranes, oxidative coupling, rhodium.

Pentamethylcyclopentadienyl complexes of rhodium and iridium $[Cp^*MCl_2]_2$ are efficient catalysts for the oxidative coupling of benzoic acids with alkynes.[1,2] The nature of the metal has a considerable effect on the selectivity of the reaction. In particular, the reactions in the presence of the rhodium derivative $[Cp^*RhCl_2]_2$ afford isocoumarins as the major products (80%). By contrast, the reactions catalyzed by the iridium complex $[Cp^*IrCl_2]_2$ produce naphthalenes (80%). In the present work, we studied the reactions catalyzed by rhodium complexes and showed that the nature of the ligands at the metal atom also has a substantial effect on the selectivity of the oxidative coupling of benzoic acid with alkynes.

Results and Discussion

Recently, we have synthesized the rhodium halide complexes with carborane ligands, $(9\text{-}SMe_2\text{-}7,8\text{–}Me_2\text{-}C_2B_9H_8)RhCl_2$ (**1**)[3] and $[(1\text{-}Bu^tNH\text{-}1,7,9\text{-}C_3B_8H_{10})RhI_2]_2$ (**2**),[4] as well as the benzene derivatives $[(9\text{-}SMe_2\text{-}7,8\text{–}C_2B_9H_{10})Rh(C_6H_6)]^{2+}$ (**3**)[5] and $[(7,8\text{-}R_2\text{-}C_2B_9H_9)Rh(C_6H_6)]^+$ (**4**: R = H; **5**: R = Me).[6] These rhodacarbo-



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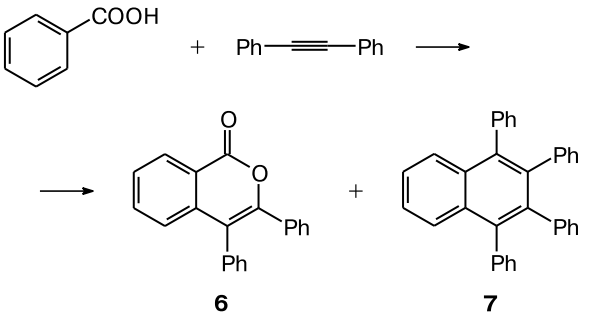
ranes are analogs of the cyclopentadienyl complexes $[Cp^*RhCl_2]_2$ and $[Cp^*Rh(C_6H_6)]^{2+}$.

We examined rhodacarboranes **1**—**5** as catalysts for the oxidative coupling of benzoic acid with diphenylacetylene in refluxing *o*-xylene (Scheme 1). Copper(II) acetate was used as the cocatalyst (necessary for the regeneration of the catalyst). As can be seen from Table 1, dicarbollide (**1**, **3**—**5**) and tricarbollide (**2**) derivatives used in the present study catalyze the oxidative coupling to give naphthalene (**7**) as the major product, as opposed to the reactions catalyzed by $[Cp^*RhCl_2]_2$, which produce mainly isocoumarin (**6**). The yields of **7** and **6** are comparable (25 and 19%, respectively) only in the reactions with the use of benzene derivative **3**. It should be noted that the nature of the second ligand (halide or benzene) has no substantial effect on the selectivity of the reaction. In particular, we showed that the reaction catalyzed by $[Cp^*Rh(C_6H_6)]^{2+}$, like that in the presence of $[Cp^*RhCl_2]_2$, gives isocoumarin **6**.

Scheme 1



Conditions: [Rh] catalyst (2 mol.%), $Cu(OAc)_2$.

It is interesting that, as in the case of carborane derivatives, the use of the unsubstituted cyclopentadienyl complex $[CpRhI_2]_2$ results in the formation of naphthalene **7**. In the latter reaction, the maximum yield is achieved (91%). In addition, we found that the commercially available $RhCl_3 \cdot 3H_2O$ also exhibits moderate activity and gives **7** in 40% yield.

The experimental data suggest that the steric crowding of the ligand is responsible for the selectivity. Thus, in the case of Cp* containing five methyl groups, the reaction gives isocoumarin, whereas the reactions with the use of sterically unhindered Cl, Cp, and carborane derivatives afford naphthalene as the major product. In order to confirm this suggestion, we carried out DFT calculations for Cp and Cp* complexes.

According to the scheme proposed by Japanese researchers,[1] the oxidative coupling involves the decarboxylation of the intermediate **A** as the key step (Scheme 2). The intermediate **B** that formed reacts with the second diphenylacetylene molecule to give naphthalene **7**. The second possible product (isocoumarin **6**) is generated *via* the reductive elimination of the Rh atom from **A**.

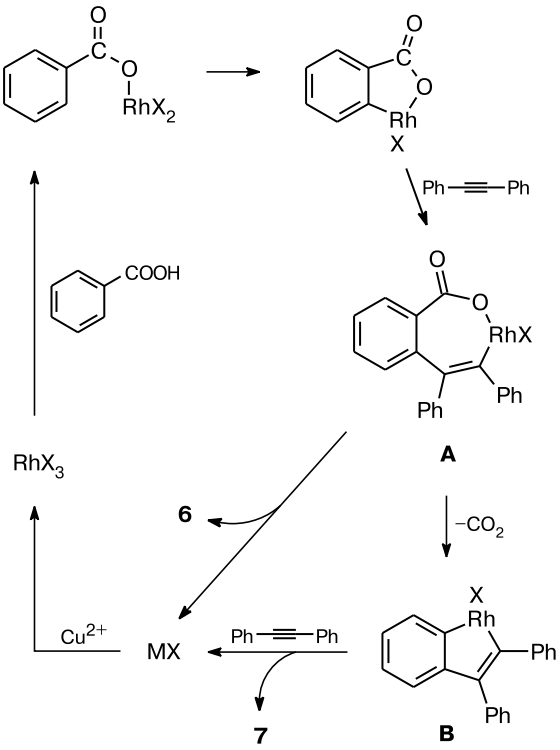
Table 1. Catalytic activity of rhodacarboranes **1**—**5** and their cyclopentadienyl analogs in the oxidative coupling of benzoic acid with diphenylacetylene

Catalyst	Yield (%)	
	6	**7**
$[(9\text{-}SMe_2\text{-}7,8\text{-}Me_2\text{-}C_2B_9H_8)RhCl_2]_2$ (**1**)	—	32
$[(1\text{-}Bu^tNH\text{-}1,7,9\text{-}C_3B_8H_{10})RhI_2]_2$ (**2**)	—	57
$[(9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Rh(C_6H_6)]^{2+}$ (**3**)	19	25
$[(7,8\text{-}C_2B_9H_{11})Rh(C_6H_6)]^{+}$ (**4**)	—	57
$[(7,8\text{-}Me_2\text{-}C_2B_9H_9)Rh(C_6H_6)]^{+}$ (**5**)	9	42
$[Cp^*RhCl_2]_2$[a]	82	12
$[Cp^*Rh(C_6H_6)]^{2+}$	49	11
$[(\eta^5\text{-}C_9H_2Me_5)Rh(C_6H_6)]^{2+}$ [b]	18	57
$[CpRhI_2]_2$	—	91
$[CpRh(C_6H_6)]^{2+}$	13	66
$RhCl_3 \cdot 3H_2O$	—	40

[a] Data from the study.[1]

[b] $C_9H_2Me_5$ is 1,2,3,4,7-pentamethylindenyl.

Scheme 2



The calculations showed that the decarboxylation in the presence of complexes both with Cp and Cp* proceeds *via* two transition states TS1 and TS2 (Figs 1 and 2; exemplified by the reaction with unsubstituted acetylene). In

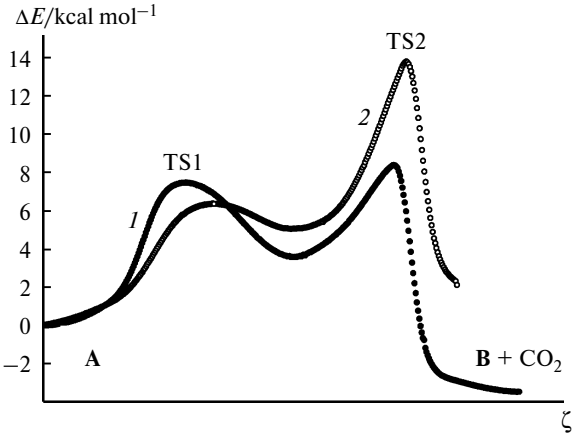


Fig. 1. Intrinsic reaction coordinate of the decarboxylation of the intermediate **A** for the complexes CpRh (*1*) and Cp*Rh (*2*); TS1 and TS2 are the first and second transition states (see Fig. 2), respectively.

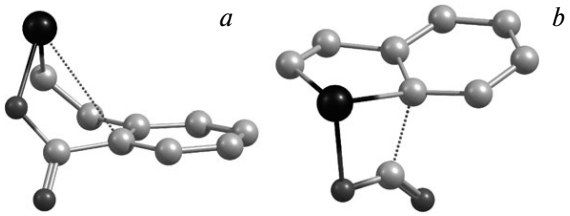


Fig. 2. Calculated structures of TS1 (*a*) and TS2 (*b*) for unsubstituted acetylene. Hydrogen atoms and the Cp ligand are omitted for clarity.

the case of the methylated derivative, the free energy of the activation is 5.1 kcal mol^{-1} higher and the total energy gain (ΔG) is 4.4 kcal mol^{-1} smaller compared to the unsubstituted analog (Table 2). However, such a small energy difference should have no substantial effect on the selectivity of the reaction proceeding at rather high temperature (120 °C). Presumably, the donor effect of five methyl groups of the Cp* ligand reduces the oxidation potential of the intermediate **A**, due to which the reductive elimination of the Rh atom giving isocoumarin **6** becomes more favorable than the decarboxylation.

Therefore, in the present study we showed that dicarbollide and tricarbollide complexes of Rh^{III} exhibit moderate catalytic activity in the oxidative coupling of benzoic acid with diphenylacetylene to give 1,2,3,4-tetraphenylnaphthalene as the major product. Apparently, the selectivity of this reaction is determined mainly by the electronic rather than steric properties of the ligand at the rhodium atom.

Table 2. Free energies (ΔG^{298}/kcal mol^{-1}) of the transition states TS1 and TS2 (ΔG_{TS1} and ΔG_{TS2}) and the reaction (ΔG_r) for the decarboxylation of the intermediate **A** in the presence of CpRh and Cp*Rh complexes (in the case of unsubstituted acetylene)

Ligand	ΔG_{TS1}	ΔG_{TS2}	ΔG_r
Cp	8.29	7.76	11.4
Cp*	7.54	13.43	7.03

Experimental

The reactions were carried out under argon. *o*-Xylene was purified by distillation over Na metal. The products were isolated in air. Complexes **1**,[3] **2**,[4] **3**$(BF_4)_2$,[5] **4**BF_4,[6] **5**BF_4,[7] $[CpRhI_2]_2$,[8] $[CpRh(C_6H_6)](BF_4)_2$,[8] and $[(\eta^5\text{-}C_9H_2Me_5)Rh(C_6H_6)](BF_4)_2$[9] were synthesized according to known procedures. Column chromatography was performed on Merck silica gel (70—230 mesh). The ^{1}H NMR spectra were recorded on a Bruker Avance-400 instrument (400.13 MHz for ^{1}H).

Oxidative coupling of benzoic acid with diphenylacetylene (general procedure). *o*-Xylene (2 mL) was added to a mixture of the catalyst (0.005 mmol), $Cu(OAc)_2$ (182 mg, 1.00 mmol), benzoic acid (31 mg, 0.25 mmol), and diphenylacetylene (89 mg, 0.5 mmol). The reaction mixture was refluxed with vigorous stirring for 6 h. Then the solvent was removed *in vacuo*, and the residue was extracted with diethyl ether. The extract was applied to a 15×1 cm column packed with silica gel. Unreacted diphenylacetylene was washed off with petroleum ether. Then the yellow fraction was collected using diethyl ether as the eluent. After the removal of the solvent *in vacuo*, 1,2,3,4-tetraphenylnaphthalene was obtained as an oily yellow substance. ^{1}H NMR ($CDCl_3$), δ: 6.95—6.97 (m, 10 H); 7.32—7.34 (m, 10 H); 7.47—7.49 (m, 2 H); 7.76—7.78 (m, 2 H) (*cf.* lit data[10]).

DFT calculations. The geometry optimization was carried out without symmetry restrictions using the Priroda 6 program,[11] the PBE functional,[12] the scalar-relativistic Hamiltonian,[13] atomic basis sets composed of Gaussian functions,[14] and the density-fitting scheme.[15] The all electron three-exponent basis set L2 with two polarization functions was used.[16] The frequencies and the intrinsic reaction coordinate (IRC)[17] were calculated at the same level of theory. The molecular modeling and the visualization were carried out using the ChemCraft program.[18]

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