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Supported rhodium-catalysts: new aspects in the formation of trisubstituted olefins from simple alkenes and diazoalkanes

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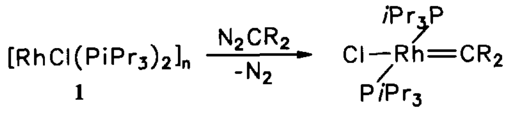
Abstract

During attempts to prepare square-planar rhodium carbene complexes, a new catalytical reaction of C–C bond formation was discovered. Further investigations have shown a catalytic activity of various rhodium(I) complexes in the formation of trisubstituted olefins from simple alkenes and diazoalkanes. The catalytic conditions (toluene solution, 40°C) are very mild and turnover numbers of 250 are possible. Here we report some aspects of the preparation and application of supported rhodium complexes in the catalytic olefin synthesis. In these cases the active species were immobilized on inorganic supports by O- and Cl-metal bridges. The preparation of support materials and the immobilization of rhodium complexes of the type $[RhL(olefin)_2]_n$ ($L = (EtO)_3Si(CH_2)_3C(C(O)CH_3)_2$, Cl and η^3-C_3H_5; $n = 1, 2$) are described.

Key words: Rhodium; Catalysis; Olefin; Supported catalyst

1. Introduction

In the course of our attempts to prepare square-planar rhodium carbene complexes (eqn. (1)) of the type *trans*-$[RhCl(=CR_2)(P^iPr_3)_2]$ a new catalytic reaction forming C–C bonds was discovered. Reaction of $[RhCl(P^iPr_3)_2]_n$ **1** ($n = 1, 2$; here 1)



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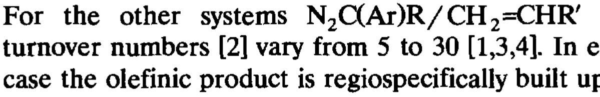
with diazomethane leads, even under very mild conditions, to the ethene complex *trans*-$[RhCl(CH_2{=}CH_2)(P^iPr_3)_2]$ **2** whereas with diphenyldiazomethane the stable complex *trans*-$[RhCl(N_2CPh_2)(P^iPr_3)_2]$ **3** is formed (see Scheme 1).

Upon treatment of a solution of **3** in benzene with ethene at room temperature, an equilibrium between **2** and **3** is reached (Scheme 1). Warming the mixture to 40°C produces 1,1-diphenylpropene [1]. In contrast to this observation, reaction of diphenyldiazomethane and ethene in presence of the known cyclopropanation catalyst $[Rh(OAc)_2]_2$ gives the expected 1,1-diphenylcyclopropane (eqn. (2)).



Until now the most effective homogeneous catalyst for the synthesis of trisubstituted olefins has proved to be $[RhCl(C_2H_4)_2]_2$. With 20 mg of $[RhCl(C_2H_4)_2]_2$ in 15 ml of toluene at 50°C turnover numbers [2] of 100–250 for the system N_2CAr_2/C_2H_4 are observed. For the other systems $N_2C(Ar)R/CH_2{=}CHR'$ the turnover numbers [2] vary from 5 to 30 [1,3,4]. In each case the olefinic product is regiospecifically built up by the formal linking of the :C(Ar)R fragment of the diazoalkane with the carbene isomer :$CHCH_2R'$ of the alkene.

Concerning the mechanism (Scheme 2) of the new olefin synthesis, we assume that in the initial stage of the reaction both substrates, the olefin and the dia-

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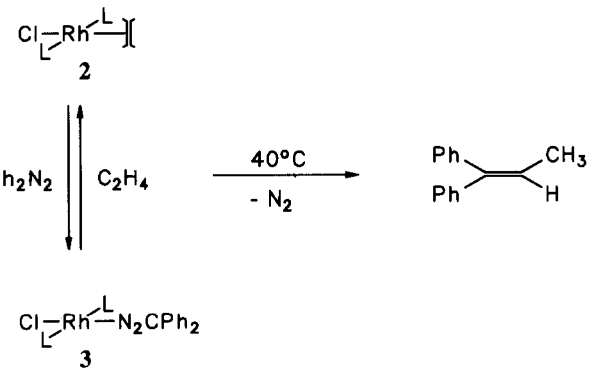
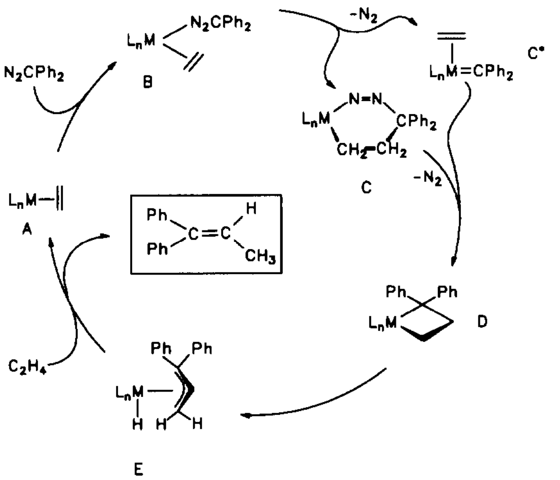


Scheme 1. Catalytical formation of 1,1-diphenylpropene (L = P^iPr_3).

zoalkane, are coordinated to the metal (intermediate **B**) and form alternatively a MN_2C_3 six-membered ring **C** or a carbene complex **C***. Then, a metallacyclobutane derivative **D** may be generated, from which an (η^3-allyl)hydrido intermediate is obtained by a β-H shift. Finally, migration of the hydride ligand to a terminal carbon atom of the allyl group may lead to the product olefin, thus reforming the catalytically active species.

To date homogeneous catalysts have been of somewhat limited use, chiefly because of the difficulty of separation from the reaction products. A good way of combining the advantages of the homogeneous with those of the heterogeneous catalysts is the attachment of soluble and catalytic active metal complexes on suitable materials. To increase the turnover numbers and get a better separation of the olefinic product we have attempted to attach rhodium-complexes to appropriate inorganic support materials.



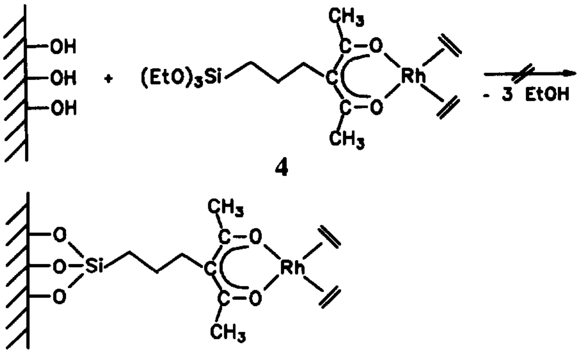
Scheme 2. Proposed mechanism of the catalytic olefin synthesis.

2. Results and discussion

2.1. *Immobilization of complexes containing ligands with anchor groups*

The treatment of inorganic materials (γ-Al_2O_3, SiO_2) with metal complexes containing an anchor group is a common way to generate supported catalysts. Ligands in complexes of this type consist of a "sticky end" ($-Si(OR)_3$, $-SiX_3$; R = alkyl, X = halogen) which can be linked to the support surface, a mono- or bidentate ligating group ($-PR_2$, acac) and a spacer $(-CH_2-)_n$ which connects these two functional units.

Since the immobilization of the complex $(EtO)_3Si(CH_2)_3C(C(O)CH_3)_2Rh(CO)_2$ was known [5], we prepared the analogous complexes with olefinic ligands, $(EtO)_3Si(CH_2)_3C(C(O)CH_3)_2Rh(olefin)_2$ (olefin = C_2H_4 **4**, C_8H_{14} **5**). Only decomposition products and no catalytically active heterogeneous material is obtained after treatment of **4** and **5** with silica (eqn. (3)) in refluxing benzene.



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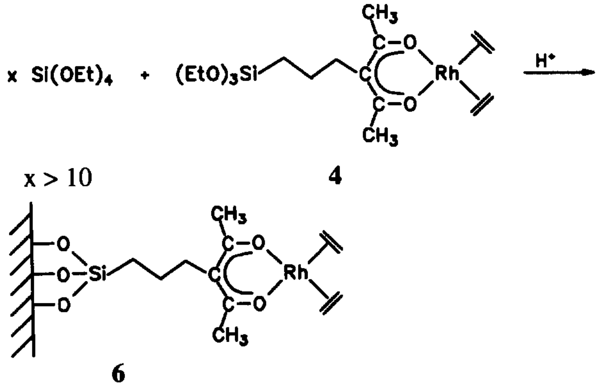
Another way of immobilizing transition metal complexes containing the ligand $(EtO)_3Si(CH_2)_3CH(C(O)CH_3)_2$ is based on the sol–gel-process [6]. After treatment of **4** with tetraethoxysilane in the presence of catalytic amounts of H_3PO_4 (eqn. (4)) we obtained a catalytically active solid.



x > 10 **4**

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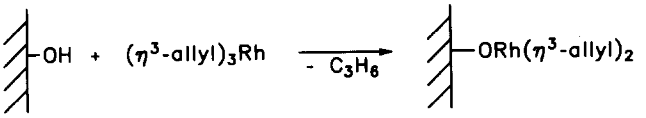
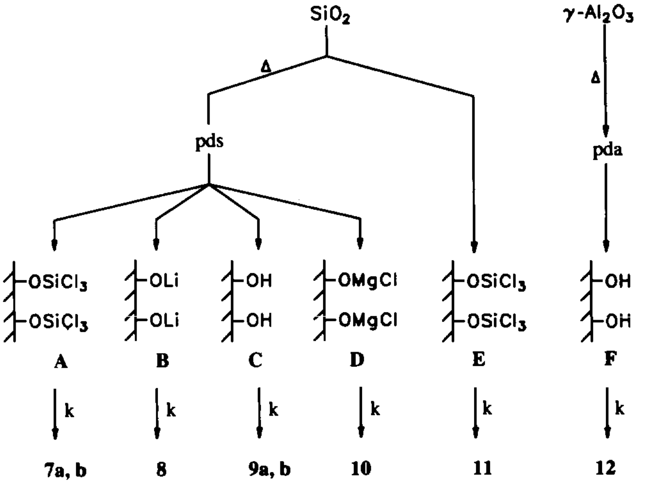
In contrast to the homogeneous catalyst (acac)Rh$(C_2H_4)_2$, which generates only the cyclopropanation product, the reaction of diphenyldiazomethane and ethene in the presence of the supported compound **6** gives a 1 : 1 mixture of 1,1-diphenylpropene and 1,1-diphenylcyclopropane.

2.2. Immobilization of complexes without anchor groups in the ligands

The most efficient catalyst for the homogeneous catalytic system is the complex $[RhCl(C_2H_4)_2]_2$ [1], which can be immobilized on pda (partially dehydroxylated alumina) from a solution of CH_2Cl_2 [7]. For our purposes we have chosen toluene as the solvent for this reaction. The yellow solid **12** obtained is an active catalyst which generates in the catalytic olefin synthesis a mixture of 1,1-diphenylpropene and 1,1-diphenylcyclopropane in low turnover numbers. By the reaction of $[RhCl(C_2H_4)_2]_2$ with pds (partially dehydroxylated silica) instead of pda we obtained a black solid with a low catalytic activity and the amount of 1,1-diphenylcyclopropane in the product mixture of the catalytic reaction increased.

On the other hand, the treatment of allylic rhodium complexes on silica is well understood (eqn. (5)) [8]. We prepared immobilized catalysts from pds and the allylic rhodium complexes $(\eta^3\text{-}C_3H_5)Rh(C_8H_{12})$ and $(\eta^3\text{-}C_3H_5)Rh(P^iPr_3)_2$. The turnover numbers and the product selectivities for **12** were marginally better then those observed for **9b** in the catalytic process.





Scheme 3. Formation of supported catalysts.

TABLE 1. Data of the obtained catalysts in the catalytic process

Catalyst	$k(RhXL_n)_m$	% rhodium	Turnover number [2]	Olefin/cycloprop.
7a	$[RhCl(C_2H_4)_2]_2$	1.60	160	1/0
7b	$[RhCl(C_8H_{14}]_2]_2$	1.08	114	1/0
8	$[RhCl(C_2H_4)_2]_2$	0.96	36	4/1
9a	$[RhCl(C_8H_{14})_2]_2$	0.64	< 1	1/1.75
9b	$(\eta^3\text{-}C_3H_5)Rh(C_8H_{12})$	2.31	7.5	1.3/1
10	$[RhCl(C_2H_4)_2]_2$	0.91	76	1/0
11	$[RhCl(C_2H_4)_2]_2$	1.66	66	1/0
12	$[RhCl(C_2H_4)_2]_2$	1.48	20	1.5/1

However, a higher turnover number is observed for the catalyst **8** in the catalytic reaction. Catalyst **8** was prepared as shown in Scheme 3 by treatment of pds with BuLi and reaction of this support material **B** with $[RhCl(C_2H_4)_2]_2$. For this system a higher amount of 1,1-diphenylpropene was obtained in the product mixture, generated in the catalysis.

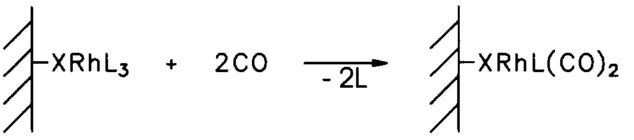
From the reaction of pds with dibutylmagnesium and gaseous HCl we obtained a support material **D**. The immobilization of the dimeric rhodium ethene complex on this supported magnesiumchlorid produced the catalyst **10**. In the catalytic process with **10** (turnover number 76) 1,1-diphenylpropene was the only product obtained. A higher turnover number is observed by using catalyst **7a**. This catalyst was obtained by the reaction of $[RhCl(C_2H_4)_2]_2$ with the support material **A**, which was made from pds with $SiCl_4$. By raising the reaction temperature to 60°C in the catalytic process, turnover numbers of 160 were possible, while no 1,1-diphenylcyclopropane was detected.

To simplify the preparation of **7a** we used untreated silica instead of pds. By an analogous reaction as described for **7**, *i.e.* treatment of the support material **E** with the dimeric rhodium ethene complex, we obtained **11**, which was a less active catalyst.

The data obtained for the supported catalysts in the catalytic process are shown in Table 1. It is remarkable that all catalysts with support materials containing Cl-groups on the surface effect no cyclopropanation. In contrast, the OH-functionalized support materials always produced 1,1-diphenylcyclopropane as the byproduct.

These results show that the decomposition of diazoalkanes by OH-groups on the surface of the support material to nitrogen and organic fragments influences the product selectivity in the catalytic reaction discussed here. An explanation for the formation of 1,1-diphenylcyclopropane is probably the stabilization of organic fragments from the decomposition of the diazoalkane in the coordination sphere of the catalyst and the reaction of these fragments with ethene to the cyclopropanation product. In order to exclude the possibility that the support materials catalyze this reaction by themselves without the transition metal complexes the former were treated with diphenyldiazomethane and ethene under catalytic conditions. We were, however, not able to observe either the olefinic or the cyclization product under these conditions.

When the supported catalysts **7–11** are exposed to carbon monoxide (eqn. (6)), two strong IR bands at 2084 and 2016 cm^{-1} appear for all compounds obtained, consistent with the presence of a rhodium(I)-*cis*-dicarbonyl species, $[Rh(CO)_2]$, on the surface.



This result implies that the catalytically active species is in all cases the same and that the nature of the support material is the reason for the different turnover numbers and selectivities.

3. Experimental details

All reactions were carried out under argon using Schlenk tube techniques. Solvents were dried by standard procedures prior to use. Ethene and gaseous HCl were obtained from commercial suppliers and used without further purification. The starting materials $[RhCl(C_2H_4)_2]_2$ [9], $[RhCl(C_8H_{14})_2]_2$ [10], η^3-C_3H_5-$Rh(C_8H_{12})$ [11] and $(C_2H_5O)_3Si(CH_2)_3CH(C(O)CH_3)_2$ [12] were prepared as described in the literature.

Silica (Merck, Kieselgel 60, 0.2–0.5 mm diameter) and alumina (Merck, γ-Tonerde, Art. 1095) were pretreated at 180°C and 10^{-3} mbar for 14 h. The content of hydroxyl-groups was determined by the method of Zerewitinov with CH_3MgI in anisol in a modified apparatus described in ref. 13. The (Si–OH)-content was found to be 1.8 mmol (OH) g^{-1} (silica) **C** and 2.3 mmol (OH) g^{-1} (alumina) **F** (see Scheme 3).

IR spectra were recorded with a Perkin Elmer 1420 IR-spectrometer and FT-IR spectra with a Bruker IFS 25 spectrometer with Spectrafile^{plus} Software. NMR-spectra were recorded at room temperature on Varian EM 360 L, Bruker AC 200 and Bruker AMX 400 instruments.

3.1. Procedure for the catalytic reaction

A suspension of 100 mg of the immobilized catalyst in 10 ml of toluene was treated dropwise at 40°C with a solution (5 M) of diphenyldiazomethane in toluene while bubbling ethene through the suspension. The catalytic reaction was finished when the violet color of the diazoalkane solution did not disappear upon addition to the reaction mixture. The solvent was removed and the residue dissolved in a small amount of hexane. In order to destroy the excess of diphenyldiazomethane and separate the catalyst, the mixture was filtered through Al_2O_3 (neutral, activity grade III, height of column 3 cm). The eluate gave after evaporation a white solid of 1,1-diphenylpropene or the mixture of 1,1-diphenylpropene and 1,1-diphenylcyclopropane. The ratio of products was determined by integration of characteristic signals in the ^1H-NMR spectra.

3.2. Preparation of $(C_2H_5O)_3Si(CH_2)_3C(C(O)CH_3)_2$-$Rh(C_2H_4)_2$ (4)

To a solution of 245 mg (0.63 mmol) of $[RhCl(C_2H_4)_2]_2$ and 384 mg (1.26 mmol) of $(C_2H_5O)_3Si(CH_2)_3$-$CH(C(O)CH_3)_2$ in 20 ml of ether were added, at 0°C, 141 mg (1.26 mmol) of KO^tBu. The mixture was stirred at room temperature for 4 h. After filtration the solvent was removed *in vacuo*, the residue was dissolved in hexane and the mixture chromatographed on Al_2O_3 (neutral, activity grade V, height of column 5 cm). With hexane as eluent a yellow fraction was obtained which contained 257 mg of **4** (46%) as a yellow oil. (Found: C, 46.68; H, 8.20. $C_{18}H_{35}O_5RhSi$ calc.: C, 46.75; H, 7.63%). IR (hexane): ν(C=O) 1563 cm^{-1}. ^1H-NMR (C_6D_6, 400 MHz): δ 3.75 (q, J(HH) = 7.0 Hz, 6H, O-CH_2), 2.80 (s, br, 8H, C_2H_4), 2.17–2.01 (m, 2H, CH_2C(C(O)-$CH_3)_2$), 1.96 (s, 6H, CH_3C(O)), 1.57–1.48 (m, 2H, CH_2C$H_2$$CH_2$), 1.15 (t, J(HH) = 7.0 Hz, 9H, C$H_3$$CH_2$), 0.66–0.61 (m, 2H, Si-CH_2). ^{13}C-NMR (C_6D_6, 100.6 MHz): δ = 185.62 (s, *C*O), 108.43 (s, *C*(C(O)$CH_3)_2$), 99.80 (d, J(RhC) = 11.1 Hz, C_2H_4), 58.24 (s, CH_3*C*-H_2O), 34.47 (s; *C*H_2C(C(O)$CH_3)_2$), 26.56 (s, *C*H_3C-(O)), 24.59 (s, CH_2*C*$H_2$$CH_2$), 18.56 (s, *C*$H_3$$CH_2$), 11.77 (s, Si*C*$H_2$).

3.3. Preparation of $(C_2H_5O)_3Si(CH_2)_3C(C(O)CH_3)_2$-$Rh(C_8H_{14})_2$ (5)

A suspension of 264 mg (0.37 mmol) of $[RhCl(C_8H_{14})_2]_2$ in a mixture of 15 ml of pentane and 5 ml of ether was treated, at 0°C, with 224 mg (0.74 mmol) of $(C_2H_5O)_3Si(CH_2)_3CH(C(O)CH_3)_2$ and 83 mg (0.74 mmol) of KO^tBu. The mixture was stirred for 3 h at room temperature and then worked up as described for **4**, yielding a yellow oil, 387 mg (61%). (Found: C, 56.86; H, 9.36. $C_{30}H_{55}O_5RhSi$ calc.: C, 57.49; H, 8.85%). IR (hexane): ν(C=O) 1567 cm^{-1}. ^1H-NMR (C_6D_6, 200 MHz): δ 3.76 (q, J(HH) = 7.3Hhz, 6H, CH_3CH_2), 2.46 (s, br, 4H, –C*H*=C*H*–), 2.16–2.00 (m, 2H, CH_2C(C(O)$CH_3)_2$), 1.92 (s, 6H, CH_3C(O)), 1.82–1.26 (m, 26H, CH_2C$H_2$$CH_2$ and CH_2 (C_8H_{14})), 1.14 (t, J(HH) = 7.3 Hz, 6H, C$H_3$$CH_2$), 0.70–0.57 (m, 2H, SiC$H_2$). ^{13}C-NMR (C_6D_6, 50.3 MHz): δ = 184.29 (s, *C*O), 108.56 (s, CH_2*C*(C(O)-$CH_3)_2$), 77.72 (d, J (RhC) = 10.8 Hz, –*C*H= of C_8H_{14}), 58.33 (s, CH_3*C*-

H_2O), 34.18 (s, $CH_2C(C(O)CH_3)_2$), 30.48, 28.32, 26.96 (all s, CH_2 of C_8H_{14}), 26.48 (s, $CH_3C(O)$), 24.48 (s, $CH_2CH_2CH_2$), 18.53 (s, CH_3-CH_2), 11.24 (s, $SiCH_2$).

3.4. Preparation of the support material A

A suspension of 1.19 g of silica (pds) in 10 ml of pentane was treated with 247 μl (2.15 mmol) of $SiCl_4$. The resulting mixture was stirred at room temperature for 2 h (until the formation of gaseous HCl subsided). The solvent was then removed and the residue extracted with portions of 8 ml of pentane until pH neutrality of the washings. The product was brought to dryness *in vacuo* and used without further purification.

3.5. Preparation of the support material B

A suspension of 3.22 g of silica (pds) in 10 ml of hexane was treated with 250 μl of a 2.5 N solution of BuLi in hexane and then stirred for 15 min at room temperature. The solvent was removed and the residue extracted twice with portions of 10 ml of hexane. The resulting mixture was brought to dryness *in vacuo* and used without further purification.

3.6. Preparation of the support material D

A suspension of 1.34 g of silica (pds) in 10 ml of hexane was treated dropwise with 2.41 ml (2.41 mmol) of a 1 N solution of Bu_2Mg in heptane and then stirred for 15 min at room temperature. During 10 min gaseous HCl was bubbled through the mixture at 0°C. The suspension was then stirred for 10 min and subsequently treated with 282 μl of ethanol. After stirring for 15 min the solvent was removed, the residue washed three times with portions of 10 ml of pentane and dried *in vacuo*.

3.7. Preparation of the support material E

A suspension of 2.0 g of silica (without pretreatment) in 20 ml of pentane was treated with 1.6 ml (13.9 mmol) of $SiCl_4$. The mixture was stirred for 3 h at room temperature and worked up as described above for the support material **A**.

3.8. Preparation of the catalyst 6

To a solution of 83.9 mg (0.18 mmol) of **4** and 809 μl (3.62 mmol) of tetraethoxysilane in 10 ml of acetone was added 0.1 ml H_3PO_4 (1 M). The mixture was stirred for 1 h and then stored at room temperature. After 72 h the green-yellow solution and the precipitate were separated. The precipitate was washed twice with portions of 5 ml of pentane and dried *in vacuo*; yield 311 mg of a pale yellow solid (2.65% rhodium). The separated green-yellow solution was evaporated to dryness. The ^{1}H-NMR spectrum of the residue showed only the signals of tetraethoxysilane and unidentified decomposition products.

3.9. Preparation of the catalyst 7a

To a suspension of 753 mg of support material **A** in 6 ml of hexane was added a solution of 53 mg (0.14 mmol) of $[RhCl(C_2H_4)_2]_2$ in 4 ml of toluene under an atmosphere of ethene. The mixture was stirred for 1 h at room temperature. The solvent was removed and the residue then washed with toluene until the washings were clear. The orange solid was subsequently washed twice with portions of 5 ml of pentane and dried *in vacuo* (1.58% rhodium).

3.10. Preparation of the catalyst 7b

To a suspension of 1.04 g of support material **A** in 6 ml of hexane was added a solution of 69 mg (0.096 mmol) of $[RhCl(C_8H_{14})_2]_2$ in 4 ml of toluene under an atmosphere of ethene. The mixture was stirred for 1 h at room temperature and the orange solid was worked up as described for **7a** (1.08% rhodium).

3.11. Preparation of the catalyst 8

Under an atmosphere of ethene a suspension of 3.22 g of support material **B** in 10 ml of toluene was treated with a solution of 112 mg (0.29 mmol) of $[RhCl(C_2H_4)_2]_2$ in 12 ml of toluene. The mixture was stirred for 18 h at room temperature and worked up as described for **7a**. The product was obtained as a yellow solid (0.96% rhodium).

3.12. Preparation of the catalyst 9a

To a suspension of 303 mg of pds **C** in 5 ml of CH_2Cl_2 was added a solution of 103 mg (0.14 mmol) of $[RhCl(C_8H_{14})_2]_2$ in 10 ml of CH_2Cl_2. The mixture was stirred for 3 h at room temperature. The solvent was removed and the black solid then washed twice with portions of 5 ml of CH_2Cl_2. The solid was dried *in vacuo* (0.64% rhodium).

3.13. Preparation of the catalyst 9b

To a suspension of 1.45 g of pds **C** in 15 ml of hexane was added a solution of 90 mg of η^3-$C_3H_5Rh(C_8H_{12})$ in 10 ml of hexane. The mixture was stirred for 15 min at room temperature. The solvent was removed and the residue then washed with 5 ml of pentane. The yellow solid was dried *in vacuo* (2.31% rhodium).

3.14. Preparation of the catalyst 10

To a suspension of 567 mg of support material **D** in 6 ml of hexane was added a solution of 62 mg (0.16 mmol) of $[RhCl(C_2H_4)_2]_2$ in 4 ml of toluene under an atmosphere of ethene. The mixture was stirred for 1 h at room temperature and worked up as described for **7a**. The product was obtained as a pink solid (0.91% rhodium).

3.15. Preparation of the catalyst 11

To a suspension of 2.1 g of support material **E** in 5 ml of toluene was added a solution of 35 mg (0.09 mmol) of $[RhCl(C_2H_4)_2]_2$ in 5 ml of toluene. The mixture was stirred for 30 min at room temperature and worked up as described for **7a**. The catalyst was obtained as an orange solid (1.66% rhodium).

3.16. Preparation of the catalyst 12

To a suspension of 1.4 g of alumina (pda) **F** in 6 ml of hexane was added a solution of 42 mg (0.11 mmol) of $[RhCl(C_2H_4)_2]_2$ in 4 ml of toluene. The mixture was stirred for 30 min at room temperature and worked up as described for **7a**. The catalyst was obtained as a yellow solid (1.48% rhodium).

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