

Supported transition-metal catalysts for the C–C coupling reaction between ethene and diazoalkanes¹

M.E. Schneider, U. Möhring, H. Werner^{*}

Institut für Anorganische Chemie der Universität, Am Hainland, D-97074 Würzburg, Germany

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Abstract

The preparation of a series of immobilized transition-metal catalysts are reported. The catalysts were obtained by chemisorption of either rhodium(I) or iridium(I) complexes $[MX(C_2H_4)_2]_n$ ($M = Rh, Ir$; $X = Cl, OAc, acac, f_3-acac, f_6-acac$) on SiO_2 or MgO supports. The oxides were also activated by $SiCl_4$ or $TiCl_4$ to give support materials in which the acidic nature of the surface is substantially increased. The activity of the immobilized catalysts was tested, particularly in the reaction of ethene with diphenyldiazomethane which yields a mixture of 1,1-diphenylpropene (8) and 1,1-diphenylcyclopropane (9). It was found that the most active and most selective (highest ratio 8:9) catalyst B1 was formed from support material B (SiO_2 activated by $SiCl_4$) and $[RhCl(C_2H_4)_2]_2$ (1) and that both the activity and selectivity of B1 was comparable with that of complex 1 in solution. In contrast, the supported catalysts A2, D2 and A3, D3 obtained from $[Rh(OAc)(C_2H_4)_2]_2$ (2) and $[Rh(acac)(C_2H_4)_2]$ (3) were less active than compounds 2 and 3 in solution. The immobilized catalysts A6, A7, D7 and E7, which were generated from the chloro- and acetatoiridium(I) complexes $[IrCl(C_2H_4)_2]_2$ (6) and $[Ir(OAc)(C_2H_4)_2]_2$ (7), possessed a lower activity than the rhodium counterparts. With diazoalkanes other than Ph_2CN_2 , the activity of the supported catalyst B1 was partly higher and partly lower than that of complex 1 in the homogeneous phase.

Keywords: Rhodium; Iridium; Supported catalyst; C–C coupling; Diazoalkanes; Olefin

1. Introduction

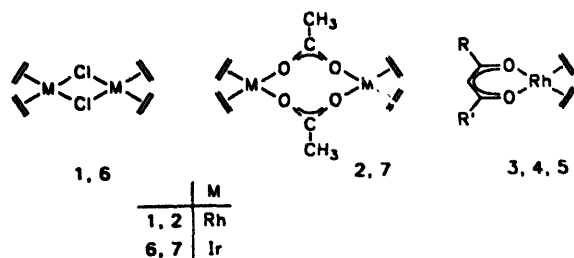
In the course of investigations with the aim of preparing square-planar carbenerhodium(I) complexes of the type *trans*- $[RhCl(=CRR')(P^1Pr_3)_2]$ from $[RhCl(P^1Pr_3)_2]_2$ and diazoalkanes, we recently observed that a rhodium-catalysed reaction between ethene and diphenyldiazomethane occurs which surprisingly yields instead of the expected 1,1-diphenylcyclopropane the isomeric 1,1-diphenylpropene [1,2]. During the continuation of these studies it was found that (1) bis(olefin)rhodium(I) compounds, such as $[RhCl(C_2H_4)_2]_2$ and $[RhCl(C_8H_{14})_2]_2$, are catalytically much more reactive than $[RhCl(P^1Pr_3)_2]_2$ or similar phosphinerhodium derivatives, and (2) in compounds of general composition $[RhX(C_2H_4)_2]_n$ the anionic ligand X^- has a crucial influence on the catalytic activity.

While $[RhCl(C_2H_4)_2]_2$ (1) (see Scheme 1) is quite active and provides turnover numbers of about 250 [3], the related rhodium acetylacetonate $[Rh(acac)(C_2H_4)_2]$ (3) is rather inert. Upon reaction with C_2H_4/Ph_2CN_2 in benzene at 40°C, it does not induce the formation of 1,1-diphenylpropene but instead, and rather slowly, that of 1,1-diphenylcyclopropane (dinuclear rhodium(II) complexes are excellent catalysts for the preparation of cyclopropanes from olefins and diazoalkanes; see Ref. [4]). With the acetato complex $[Rh(\eta^2-O_2CCH_3)(C_2H_4)_2]_2$ (2), in methylcyclohexane at 40°C, turnover numbers of about 80 have been achieved, the dominating coupling product, however, being 1,1-diphenylcyclopropane [5].

Taking these results into consideration, we have now attached compounds 1, 2 and 3, as well as the trifluoro- and hexafluoroacetylacetonato complexes 4 and 5, to appropriate inorganic support materials. In earlier studies [6], we had confirmed that both the chloro complex 1 and the bis(cyclooctene)rhodium(I) counterpart $[RhCl(C_8H_{14})_2]_2$ can be immobilized on SiO_2 or Al_2O_3 to give supported catalysts for the reaction shown in Eq.

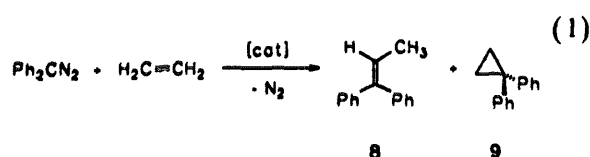
^{*} Corresponding author.

¹ Dedicated to the late Professor Hidemasa Takaya, in recognition of his pioneering contributions to organometallic chemistry and homogeneous catalysis.



Scheme 1. Bis(ethene)rhodium(I) and -iridium(I) complexes used for the preparation of catalysts (3: $R = R' = \text{CH}_3$; 4: $R = \text{CH}_3$, $R' = \text{CF}_3$; 5: $R = R' = \text{CF}_3$).

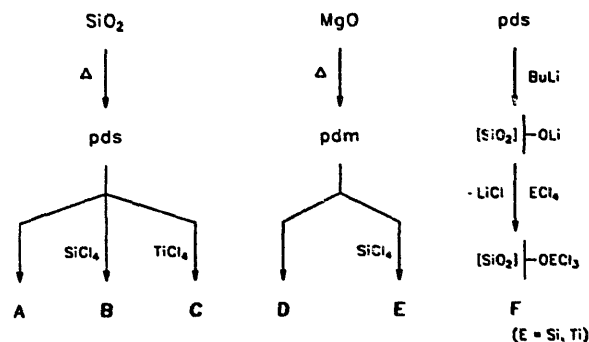
(1). The present work is an extension of these investigations, in particular by including activated oxidic supports and, for comparison, also immobilized iridium(I) complexes $[\text{IrX}(\text{C}_2\text{H}_4)_2]_2$ (6, 7) (Scheme 1). Some preliminary results have already been communicated [7].



2. Results and discussion

2.1. Preparation of the catalysts

Although the treatment of solid oxides (SiO_2 or $\gamma\text{-Al}_2\text{O}_3$) with rhodium complexes containing an an-



Scheme 2. Preparation of support materials A–F.

chor group at one of the ligands is a common way of generating immobilized catalysts [6–8], catalytically more active materials were obtained by chemisorption of compounds such as 1 or 3 on silica or magnesium oxide. Both oxides were pretreated at 180°C and 10^{-3} mbar to form partially dehydroxylated silica (pds) and partially dehydroxylated magnesia (pdm), as shown in Scheme 2. Moreover, these supports were also treated with Lewis acids such as SiCl_4 or TiCl_4 in order to increase the acidic nature of the oxide surface. We assume that during this pretreatment various hydroxy groups on the surface are transformed to $([\text{Ox}]-\text{O})_n\text{ECl}_{4-n}$ units ($n = 1-4$, $\text{E} = \text{Si}, \text{Ti}$); simultaneously n equivalents of gaseous HCl are formed. Support materials (like F in Scheme 2) which are completely covered with $([\text{SiO}_2]-\text{OECln})$ -moieties ($\text{E} = \text{Si}, \text{Ti}$) were obtained by the initial deprotonation of the surface SiOH

Table 1

Preparation of supported rhodium catalysts and data on the activity and the selectivity in the reaction of ethene and diphenyldiazomethane (TON (mmol product/mmol rhodium))

Catalyst preparation			Catalytic reaction			
Catalyst	Rh content (%)	Conversion in the immobilization reaction (%)	40°C		60°C	
			TON	Ratio of 8:9	TON	Ratio of 8:9
A1	0.2	20	< 1	50:50	< 1	40:60
A2	1.0	> 95	8	70:30	10	60:40
A3	1.0	> 95	5	75:25	18	50:50
B1	0.3	33	91	> 99:1	184	97:3
B2	1.0	> 95	13	87:13	7	62:38
B3	1.0	> 95	40	74:26	37	86:14
B4	1.0	> 95	6	81:19	7	89:11
B5	1.0	> 95	6	80:20	7	84:16
C1	1.0	> 95	106	90:10	77	85:15
C2	1.0	> 95	13	93:7	21	84:16
C3	1.0	> 95	33	98:2	49	88:12
C4	1.0	> 95	13	98:2	17	98:2
C5	1.0	> 95	20	97:3	33	97:3
D1	1.0	> 95	13	50:50	30	31:69
D2	1.0	> 95	1	17:83	2	10:90
D3	0.7	69	< 1	—	< 1	12:88
E1	0.8	76	31	93:7	93	78:22
E2	0.7	65	27	95:5	71	83:17
E3	0.4	38	7	94:6	20	81:19

A - E		$\xrightarrow[1 \text{ atm } C_2H_4]{[RhX(C_2H_4)_2]_n}$				immobilized catalysts A1 - E3
support material	X: Cl	OAc	acac	f ₃ -acac	f ₆ -acac	
A	A1	A2	A3			
B	B1	B2	B3	B4	B5	
C	C1	C2	C3	C4	C5	
D	D1	D2	D3			
E	E1	E2	E3			

Scheme 3. Immobilized catalysts prepared from A–E.

groups with ⁿBuLi and subsequent reaction of the lithiated oxide surface with ECl₄.

The preparation of the immobilized rhodium catalysts (Scheme 3) took place by adding a solution of the corresponding complex 1–5 in hexane to a suspension of the support material in the same solvent and shaking the resulting mixture under 1 atm of ethene. Both the nature of the support and the anionic ligand X[−] of the complex determine the rate and degree of chemisorption on the surface. It is generally known that the reaction between an organo-transition metal compound, which contains a basic anionic ligand (which may be protonated) and an oxide support is crucially dependent on the basicity, the number of surface-hydroxy groups and the size of the particles [9–12].

The results summarized in Table 1 illustrate that on treatment of pds (support material A) with 1 only parts (ca. 20%) of the chlororhodium(I) complex are absorbed. A significantly higher amount of 1 (ca. 33%) is bound to the surface of support material B which is formed by pretreatment of pds with SiCl₄. If, however, the related support material E (obtained from pdm and SiCl₄) is used the yield of chemisorbed 1 is increased to 76%.

An even higher percentage of dissolved rhodium can be absorbed at the surface of oxide supports A, B, C or D if, instead of the chloro derivative 1, the corresponding acetato or acetylacetonato complexes 2–5 are employed. From previous work by Schwartz and coworkers [10] and Basset and coworkers [11] it was already known that a quantitative reaction of compounds such as [Rh(η³-C₃H₅)₃] and SiO₂ occurs which is promoted by the facile protonation of an allyl ligand to form propene. In the same way, the complexes 2–5 also react smoothly with A–D to give supported catalysts A2–D2 containing all of the rhodium present in the precursor compound. Only on treatment of D with 3 and of E with 2 or 3, is the rhodium complex not quantitatively absorbed. The inorganic material F, in which all the surface SiOH groups are replaced by SiOEtCl₃ (E = Si, Ti) units, is almost incapable of reacting with one of the rhodium(I) compounds [RhX(C₂H₄)₂]_n; less than 10% of 1, 2 or 3 can be immobilized on this support.

2.2. Catalytic reactions of ethene and diazoalkanes

Following the preparation of materials A1–E3, these species were tested as catalysts for the C–C coupling reaction between ethene and diphenyldiazomethane at 40 and 60°C. As shown in Table 1, in nearly all reactions both of the isomeric products 8 and 9 were generated. We note that although complex 1 up to now is the most efficient and most selective catalyst in solution [1,3], the catalytic activity of the immobilized compounds A1 and D1, which are prepared from 1 and pds or pdm, is the lowest in the series of supported catalysts. These species A1 and D1 are also not selective. With regard to this observation, it is really astonishing that B1, formed by treatment of B with the chloro complex 1, at 60°C is the most active (TON = 184) and at 40°C the most selective catalyst among the immobilized species used in this work.

The catalysts A2 and D2, which were obtained by chemisorption of 2 on the oxide supports, are less active in the reaction of ethene and diphenyldiazomethane than the acetato complex 2 in the homogeneous phase [5]. The same observation has been made with the acetylacetonato-derived species A3 and D3. As far as A3 is concerned, the difference in comparison with the behaviour of compound 3 in solution is, that with A3 at 60°C a 1:1 mixture of 8 and 9 is generated, while in the homogeneous phase only the cyclopropane derivative 9 is formed [13]. It is important to note that the activity of the supported catalysts obtained with complexes 2 and 3 increased if the support material was pretreated with SiCl₄ or TiCl₄. Moreover, it is quite remarkable that the amount of the olefin 8 in the product mixture is higher for C2 (pretreated with TiCl₄) than for B2 (pretreated with SiCl₄) and equally higher for C4 and C5 than for B4 and B5 (see Table 1).

In order to find out whether Lewis-acidic units, which are present on the surface of catalysts B1–B5 or E1–E3, also promote the catalytic activity of bis(ethene)rhodium(I) complexes *in solution*, the reaction of C₂H₄ and Ph₂CN₂ was investigated in toluene at 40°C with complex 1 as the catalyst in the presence of HCl, Me₃SiCl and SiCl₄. The results (see Table 2) reveal, however, that the turnover numbers as well as the ratio of 8:9 decreases if one of the Lewis acids is

Table 2

Data on the activity and selectivity of complex 1 in the presence of Lewis acids in the reaction of ethene and diphenyldiazomethane (TON (mmol product/mmol rhodium))

Lewis acid	Ratio of Rh:acid	TON	Ratio of 8:9
HCl	1:1	10	> 99:1
HCl	1:2	3	89:11
(CH ₃) ₃ SiCl	1:10	19	93:7
SiCl ₄	1:2	10	98:2

Table 3

Comparison of the activity and selectivity of catalyst **B1** in the reaction of ethene with diphenyldiazomethane as a function of temperature (TON (mmol product/mmol rhodium))

Temperature (°C)	40	50	60	70	80
TON	91	160	184	241	194
Ratio of 8:9	> 99:1	> 99:1	97:3	90:10	70:30

added to **1**. The reason for the decreased activity possibly is that from **1** and RX ($R = H, SiMe_3, SiCl_3$) higher coordinated rhodium compounds are formed as intermediates in which the interaction of the olefin and the diazoalkane with the metal centre is inhibited.

The effect of the temperature on the catalytic reaction of C_2H_4 and Ph_2CN_2 is illustrated in Table 3. While *in solution* (methylcyclohexane, toluene, acetone) the largest turnover numbers were found at 40°C [3,5], the highest activity of catalyst **B1** is observed at 70°C. As far as the optimum yield of the olefin **8** is concerned, a lower temperature than 70°C is preferred and, therefore, if combining the two aspects (activity and selectivity) a reaction temperature of 50°C seems to be best. It should be emphasized, however, that although at 50°C the TON value for **B1** is somewhat lower than for complex **1** in solution, the great advantage by using the supported catalyst is the ease of isolation of the olefinic product.

We were also interested in comparing the activity of catalyst **B1** (in heterogeneous phase) and complex **1** (in homogeneous phase) in the reaction of ethene with diazoalkane derivatives other than Ph_2CN_2 . The results, which are shown in Fig. 1, are quite remarkable, and, depending on the substituents R and R' , do not always point in the same direction. In some cases (for $R = Ph$ and $R' = Ph, Me, CH_2Ph$) the activity is higher under heterogeneous conditions while in others (for $R = R' = p-Tol, p-Anis$) the turnover numbers in solution exceed by far those obtained with the supported catalyst.

The immobilization of the iridium(I) complexes

$[IrX(C_2H_4)_2]_2$ (**6**, **7**) (see Scheme 1) occurred similarly to that of the rhodium counterparts **1** and **2**. As inorganic supports, the oxidic materials **A**, **D** and **E** were used which on treatment with **6** and **7** gave the catalysts **A6**, **A7**, **D7** and **E7** respectively. The results which have been obtained with these immobilized catalysts in the reaction of C_2H_4 and Ph_2CN_2 are summarized in Table 4. In general, the conclusion is that the activity of the two iridium(I) complexes cannot be increased by chemisorption on the chosen inorganic supports. As far as the selectivity is concerned, the only difference between the reactions in solution and in the heterogeneous phase is that while the acetato compound **7** in methylcyclohexane at 40°C favours the formation of **9** (ratio 8:9 = 1:9) [5], the olefin **8** is the major product with the supported catalyst **E7**. Under both conditions (homogeneous and heterogeneous), the turnover numbers for **7** and **E7** are about the same.

2.2.1. Concluding remarks

The present study has shown that although the immobilized catalysts containing rhodium or iridium as the active metal have the advantage of ease of product separation and isolation, in the reaction of ethene with diphenyldiazomethane they are less selective than the respective bis(ethene)rhodium(I) and -iridium(I) complexes in the homogeneous phase. The reason for the decreased selectivity probably originates neither in the type of inorganic support nor in the nature of the anion X^- of the precursor compounds $[MX(C_2H_4)_2]_n$ ($M = Rh, Ir$; $X = Cl, OAc, acac, f_1-acac, f_6-acac$) since during the preparation of the catalysts HX is formed and quickly removed from the surface. The question of whether the ratio of olefin:cyclopropane can be increased by further modifying the oxide support is presently difficult to answer. As some preliminary experiments have indicated, however, an increase of activity seems to be possible, in particular by anchoring cationic olefinrhodium and -iridium complexes to the inorganic support.

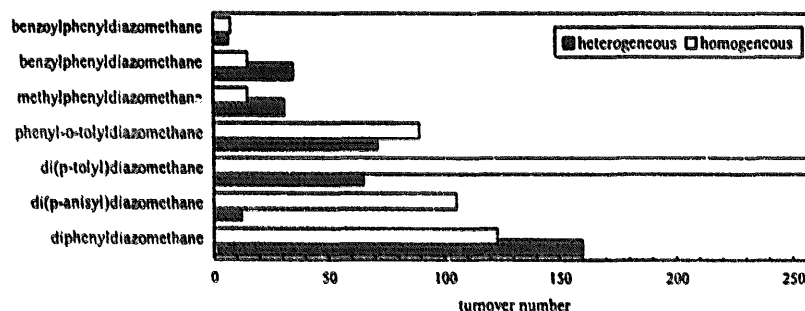


Fig. 1. Comparison of the reactivity of **1** (at 40°C) and supported catalyst **B1** (at 50°C) in the reaction with different diazoalkanes: the turnover number (TON) is equal to mmol product/mmol rhodium.

Table 4

Preparation of supported iridium catalysts and data on the activity and the selectivity in the reaction of ethene and diphenyldiazomethane (TON) (mmol product/mmol iridium)) A, D, E $\xrightarrow[\text{1 atm C}_2\text{H}_4]{\text{[IrX(C}_2\text{H}_4)_2]_2}$ immobilized catalysts A6 – E7

Catalyst preparation					Catalytic olefin synthesis			
Support material	X	Catalyst	Ir content (%)	Conversion in the immobilization reaction (%)	40°C		60°C	
					TON	Ratio of 8:9	TON	Ratio of 8:9
A	Cl	A6	0.3	30			13	15:85
A	OAc	A7	1.0	> 95	3	33:67	5	40:60
D	OAc	D7	1.0	> 95	7	15:85	7	12:88
E	OAc	E7	1.0	> 95	14	68:32	10	71:29

3. Experimental details

All reactions were carried out under argon using Schlenk tube techniques. Solvents were dried by standard procedures prior to use. Ethene was purchased from commercial suppliers and used without further purification. The starting materials $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ (1) [14], $[\text{Rh}(\text{O}_2\text{CCH}_3)(\text{C}_2\text{H}_4)_2]_2$ (2) [5], $[\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2]$ (3) [15], $[\text{Rh}(\text{f}_3\text{-acac})(\text{C}_2\text{H}_4)_2]$ (4) [16] and $[\text{Rh}(\text{f}_6\text{-acac})(\text{C}_2\text{H}_4)_2]$ (5) [17], $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ (6) [18] and $[\text{Ir}(\text{O}_2\text{CCH}_3)(\text{C}_2\text{H}_4)_2]_2$ (7) [5] were prepared as described in the literature.

Silica (Merck, Kieselgel 60, 0.2–0.5 mm diameter) and magnesium oxide (Merck, heavy, powder) 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 anisole in a modified apparatus described in Ref. [19]. The (Si,Mg–OH)-content was found to be 1.8 mmol(OH) g⁻¹ (pds, A) and 2.3 mmol(OH) g⁻¹ (pdm, D) (see Scheme 2).

NMR spectra were recorded at room temperature on Bruker AC 200 instruments. GC–MS analyses were carried out using an HP GCD 1800A system with an electron ionisation (EI) detector.

3.1. Preparation of the support material B

A suspension of 6.65 g of silica A in 15 ml of hexane was treated with 1.45 ml (12.7 mmol) of SiCl_4 . The resulting mixture was shaken at room temperature for 2 h (until the formation of gaseous HCl subsided). The solvent was removed and the residue was extracted with portions of 10 ml of pentane until the washings were pH neutral. The product was dried in vacuo.

3.2. Preparation of the support material C

A suspension of 7.79 g of silica A in 20 ml of hexane was treated with 1.62 ml (14.8 mmol) of TiCl_4 . The resulting mixture was shaken at room temperature for 2 h (until the formation of gaseous HCl subsided). The solvent was removed and the residue was extracted with portions of 10 ml of pentane until the washings were pH neutral. The product was dried in vacuo.

3.3. Preparation of the support material E

A suspension of 1.49 g of magnesium oxide D in 10 ml of hexane was treated with 447 μl (3.90 mmol) of SiCl_4 . The resulting mixture was shaken at room temperature for 2 h (until the formation of gaseous HCl subsided). The solvent was removed and the residue was extracted with portions of 10 ml of pentane until the washings were pH neutral. The product was dried in vacuo.

3.4. Preparation of the support material F

A suspension of 2.10 g of silica A in 10 ml of hexane was treated with 1.51 ml (3.78 mmol) of a 2.5 N solution of $n\text{-BuLi}$ in hexane and shaken for 30 min at room temperature. The solvent was removed and the residue extracted twice with portions of 10 ml of hexane. The resulting solid was suspended in 10 ml of hexane and treated with 430 μl (3.78 mmol) of SiCl_4 . The resulting mixture was shaken at room temperature for 2 h. The solvent was removed and the residue was extracted six times with portions of 10 ml of ether to remove LiCl . The product was dried in vacuo.

3.5. General procedure for the preparation of the catalysts

Under an atmosphere of ethene, a suspension of 2.00 g of support material A–F in 10 ml of hexane was treated with a solution of either 1–5 (0.194 mmol Rh) or 6–7 (0.104 mmol Ir) in 15 ml of hexane. The mixture was shaken at room temperature under a pressure of 1 atm ethene for 2 h. The solvent was removed and the residue washed three times with 20 ml of pentane. The solid was dried in vacuo.

3.6. Procedure for the catalytic reaction of ethene with diphenyldiazomethane with supported catalysts

To a suspension of 150 mg of the immobilized catalyst in 6 ml of methylcyclohexane at either 40 or 60°C (using B1 as catalyst also at 50, 70 and 80°C) a solution

(0.1 M) of diphenyldiazomethane in methylcyclohexane was added dropwise while bubbling ethene through the suspension. The catalytic reaction was finished when the violet colour of the diazoalkane solution did not disappear upon addition to the reaction mixture. The solvent was removed in vacuo and the residue dissolved in a small amount of hexane. In order to destroy the excess of diphenyldiazomethane and separate the reaction products from the catalyst, the mixture was filtered over Al_2O_3 (neutral, activity grade III, height of column 3 cm). The eluate gave after evaporation of the solvent either a white solid (1,1-diphenylpropene) or an oil (mixture of 1,1-diphenylpropene and 1,1-diphenylcyclopropane). The ratio of products was determined by integration of the characteristic signals in the ^1H NMR spectra and by GC analysis.

3.7. Procedure for the catalytic reaction in the presence of HCl , SiCl_4 or $(\text{CH}_3)_3\text{SiCl}$

A solution of 10 mg (0.026 mmol) of **1** in 6 ml of toluene at 40°C was treated either with a solution (0.05 M) of HCl in toluene, SiCl_4 or $(\text{CH}_3)_3\text{SiCl}$ while bubbling ethene through the solution. The following catalytic reaction was done as described in Section 3.6.

3.8. Procedure for the catalytic reaction of ethene with different diazoalkanes

To a suspension of 150 mg of **B1** in 6 ml of toluene at 50°C a solution (0.1 M) of diazoalkane (see Fig. 1) in toluene was added dropwise while bubbling ethene through the suspension. The catalytic reaction was finished when the violet colour of the diazoalkane solution did not disappear upon addition to the reaction mixture. The mixture was worked up as described in Section 3.6. The ratio of cyclopropane to the olefin derivatives was determined by integration of the characteristic signals in the ^1H NMR spectra.

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