Transition metal complexes of diazenes.
Part XXXVII [1]. Heterogeneous Rh(I) catalysis: synthesis of N-anilino-2,3-diphenylindole from azobenzene and diphenylacetylene

S. Westernacher [a], J. Blümel [b], H. Kisch [a, *]

[a] *Institut für Anorganische Chemie, Universität Erlangen–Nürnberg, Egerlandstr. 1, 91058 Erlangen, Germany*
[b] *Anorg.-chem. Institut der Technischen Universität München, Lichtenbergstr. 4, 85747 Garching, Germany*

Abstract

Silica gel supported $RhCl(PPh_3)_3$ and silica gel attached $\{Rh(I)-O-[SiO_2] + PPh_3\}$ are catalysts in the synthesis of N-anilino-2,3-diphenylindole from azobenzene and diphenylacetylene dissolved in toluene. The physisorption of $RhCl(PPh_3)_3$ on the silica gel surface can be described by the model of Freundlich affording an equilibrium constant K_{ad} of 124 1/mol. Loading with 4 wt.% of $RhCl(PPh_3)_3$ affords $SiO_2[4.0]$ which is a better catalyst as compared to samples containing 0.8 and 8.7 wt.%. When the amount of $SiO_2[4.0]$ is increased at constant reaction volume, the reaction rate does not reach a constant value but passes through three maxima. The covalently bound catalyst $\{Rh(I)-O-[SiO_2] + PPh_3\}$ is much less active and induces a maximum reaction rate when PPh_3 is added in a twofold excess.

Keywords: Wilkinson's catalyst; Silica gel; Adsorption; Indole; Supported catalysts; Liquid phase

1. Introduction

In the last two decades supported liquid phase catalysts have become an important field in catalysis [1b–3]. They are easier to remove from the reaction slurry than their homogeneous counterparts although they may retain their high selectivity [4–6]. For immobilization, different support materials like organic polymers and inorganic oxides have been used [7–11]. To the surface of silica gel organometallic catalysts may be attached [12–14] by physi- or chemisorption [2,15–20]. In the latter case this is usually accomplished by covalently bound amine or phosphine ligands [21–24].

Recently we have observed that silica gel improves the catalytic action of $RhCl(PPh_3)_3$, Wilkinson's catalyst, in the addition of diphenylacetylene to azobenzene affording N-anilino-2,3-diphenylindole (**1**). Contrary to that, alumina or zinc sulfide has an inhibiting effect [25]. Here we report on the mechanism of the silica gel supported catalysis with attention to the question whether the catalyst is attached to the support by physi- or chemisorption.

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* Corresponding author.
[1] For number XXXVI, see [1a].

2. Experimental section

Unless otherwise noted all experiments were performed under nitrogen. Toluene and 1-butanol were dried with sodium and K_2CO_3, respectively, and distilled under nitrogen. The silica gel (Merck, 230–400 mesh Astm, 550 m^2/g, water content: 9%) was stored under nitrogen. Azobenzene and diphenylacetylene were dried in vacuo over night. The products were analysed by HPLC (pump: Knauer HPLC pump 64; column: 250 × 8 mm, Spherisorb ODS 2, particle size 5 μm; detector: Knauer UV/VIS filter photometer (filter = 220 nm); integrator: Shimadzu C-R3A Chromatopac; solvent: acetonitrile/H_2O = 5:1). UV–Vis spectra were recorded with a Shimadzu UV-3101 PC instrument. Diffuse reflectance spectra were measured relative to corundum (Hoechst Ceram Tec). ^{31}P CP/MAS NMR spectra were recorded on a Bruker MSL 300 spectrometer, equipped with a 7 mm double bearing MAS probehead (ZrO_2 rotors). Cross polarization (CP) with a contact time of 5 ms, magic angle spinning (MAS) with rotational speeds of 4–4.5 kHz and high power decoupling were used. All spectra were recorded at room temperature (296 K) and referenced with respect to 85% H_3PO_4 (aq.) by setting the ^{31}P NMR peak of solid $NH_4H_2PO_4$ to +0.81 ppm.

2.1. Preparation of RhCl(PPh₃)₃ / SiO₂

1.0 g of silica gel and a defined amount of $RhCl(PPh_3)_3$ [26] were stirred in 10 ml of toluene at room temperature for one hour. After filtering the dark red suspension, the yellow–orange coloured powder was dried in vacuo. The non-adsorbed amount of $RhCl(PPh_3)_3$ remaining in the filtrate was measured by UV–Vis spectroscopy at $\lambda = 288$ nm ($\epsilon = 12742$ 1/(mol · cm)) in toluene. The three catalysts SiO_2[0.8], SiO_2[4.0] and SiO_2[8.7] prepared by this method contained 0.8, 4.0 and 8.7 wt.% of $RhCl(PPh_3)_3$, respectively.

2.2. Preparation of Rh(PPh₃)₂–O–[SiO₂]

The preparation was performed analogous to [27] but using refluxing ethanol as solvent and reducing agent. 13 mg (0.05 mmol) of $RhCl_3$ · $3H_2O$ and 1 g of SiO_2 were heated to reflux in 10 ml of ethanol for one hour. After five minutes the colour of the suspension changed from light red to dark red and dark grey. After filtering, the grey residue, Rh–O–[SiO_2], was washed with diethyl ether and dried in vacuo. This powder was used in toluene as catalyst in the presence of varying amounts (0.05, 0.1, 0.2 and 0.4 mmol) of triphenylphosphine (see Section 2.3, *Catalytic indole synthesis*). The catalytic activity suggests the presence of Rh(I) since Rh(0) and Rh(II)/(III) are known to be inactive [28]. No indole formation was observed when only $RhCl_3$ · $3H_2O$ was employed as catalyst in refluxing 1-butanol or when $RhCl_3/PPh_3/SiO_2$ was used in refluxing toluene (only traces of indole) [25]. $Rh(PPh_3)_2$–O–[SiO_2] was synthesised from 1 g of Rh(I)–O–[SiO_2] prepared as described above and 0.15 mmol of PPh_3 in 10 ml of toluene by refluxing for 1 hour. The solvent was removed, the grey residue was dried in vacuo and characterized by ^{31}P CP/MAS NMR spectroscopy.

2.3. Catalytic indole synthesis

A solution of 364.4 mg (2 mmol) of azobenzene and 356.5 mg (2 mmol) of diphenylacetylene in 15 ml of toluene or 1-butanol or in 13.6 ml of toluene plus 1.4 ml (15 mmol) of 1-butanol, respectively, was added dropwise within 10 min to 10 ml of the refluxing toluene or 1-butanol solution containing the amount of catalyst given in the legends of Figs. 2–5. 250 μl samples were withdrawn, the solvent was removed in vacuo and the residue was dissolved in 5 ml of acetonitrile prior to being analysed by HPLC. The amount of 2,3-diphenylindole was ignored as it was always 5% or less. Initial rates ($R_{(i)}$) and turnover frequencies (TOF$_{(i)}$) were

obtained from the following concentrations of **1** [mmol/l] measured after 6 h:

Reaction in 23.6 ml of toluene + 1.4 ml of 1-butanol: 0.26 g of $SiO_2[4.0]$: traces (1 h), 1 (4 h), 3 (6 h), 8 (24 h). 1 g of $SiO_2[4.0]$: 5 (1 h), 42 (16 h), 44 (18 h), 54 (24 h); $TOF_{(i)} = 1.9$ h^{-1}.

Fig. 2, Curve A (1 g of $SiO_2[0.8]$): 1 (1 h), 4 (4 h), 4 (6 h), 5 (24 h); $TOF_{(i)} = 1.9$ h^{-1}. Curve B (1 g of $SiO_2[8.7]$): 2 (1 h), 18 (4 h), 25 (6 h), 52 (24 h); $TOF_{(i)} = 1.2$ h^{-1}. Curve C (1 g of $SiO_2[4.0]$): 24 (1 h), 62 (4 h), 68 (6 h), 73 (24 h); $R_{(i)} = 11.3$ mmol/l·h; $TOF_{(i)} = 6.3$ h^{-1}.

Fig. 3, 0.26 g of $SiO_2[4.0]$: 8 (1 h), 22 (4 h), 25 (6 h), 50 (24 h). 0.52 g of $SiO_2[4.0]$: 10 (1 h), 22 (4 h), 30 (6 h), 56 (24 h). 0.78 g of $SiO_2[4.0]$: 2 (1 h), 8 (4 h), 10 (6 h), 22 (24 h). 1 g of $SiO_2[4.0]$: see Curve A, Fig. 2. 1.31 g of $SiO_2[4.0]$: 6 (1 h), 12 (4 h), 17 (6 h), 42 (24 h). 1.57 g of $SiO_2[4.0]$): 4 (1 h), 12 (4 h), 15 (6 h), 32 (24 h). 2.08 g of $SiO_2[4.0]$: 39 (1 h), 75 (4 h), 78 (6 h), 75 (24 h); $R_{(i)} = 13.0$ mmol/l·h. 2.6 g of $SiO_2[4.0]$: 18 (1 h), 39 (4 h), 40 (6 h), 70 (24 h).

Fig. 4: Curve A, 0.26 g of $SiO_2[4.0]$ in 1-butanol: traces (1 h), 1 (4 h), 3 (6 h), 10 (24 h). Curve C, 1 g of $SiO_2[4.0]$ in 1-butanol: 2 (1 h), 10 (4 h), 14 (6 h), 30 (24 h); $TOF_{(i)} = 1.3$ h^{-1}. Curves B and D: see Fig. 3. Curves E and F: see [29].

Fig. 5: 0.05 mmol of PPh_3: 0.6 (1 h), 0.9 (4 h), 0.7 (6 h), 2.4 (24 h); $R_{(i)} = 0.12$ mmol/l·h. 0.1 mmol of PPh_3: 0.9 (1 h), 2.1 (4 h), 2.9 (6 h), 6.7 (24 h); $R_{(i)} = 0.48$ mmol/l·h; $TOF_{(i)} = 0.24$ h^{-1}. 0.2 mmol of PPh_3: 0.3 (4 h), 1.6 (6 h), 7.3 (24 h). 0.4 mmol of PPh_3: traces (1 h), 0.7 (4 h), 1.0 (6 h), 4.2 (24 h); $R_{(i)} = 0.17$ mmol/l·h.

2.4. Adsorption experiments

The amount of $RhCl(PPh_3)_3$ adsorbed was determined via UV–Vis spectroscopy (Table 1) after equilibrating the toluene suspension at room temperature for one hour as described in the preparation of $RhCl(PPh_3)_3/SiO_2$. No ad-

Table 1

Equilibrium concentration c_{eq}, amount (n_{ad}) and surface area (A) of adsorbed $RhCl(PPh_3)_3$, and surface coverage Θ at different concentrations (c_0)

c_0 (mol/l)	c_{eq} (mol/l)	n_{ad} (mmol) [a]	A (m^2)	Θ
0.001	0.0001	0.009 (90)	12.7	0.0231
0.005	0.0007	0.043 (86)	61.3	0.1115
0.015	0.00135	0.136 (91)	194.0	0.3527
0.02	0.0028	0.172 (86)	244.5	0.4445

[a] Percentage of complex adsorbed in parentheses.

sorption was observed when toluene was replaced by 1-butanol. Upon withdrawing samples from boiling $SiO_2[4.0]$ and $SiO_2[12.6]$ (12.6 wt.% of $RhCl(PPh_3)_3$ adsorbed; $c_0 = 0.015$ mmol/l) suspensions it was found that 80 and 50% of $RhCl(PPh_3)_3$ were adsorbed in toluene and 1-butanol, respectively; the UV–Vis spectra of the solutions indicated the presence of $RhCl(PPh_3)_3$. When $SiO_2[12.6]$ was washed again with toluene, a pale yellow solution of $RhCl(PPh_3)_3$ was obtained as evidenced by UV–Vis spectroscopy.

3. Results and discussion

3.1. Adsorption of $RhCl(PPh_3)_3$ on silica gel

The amount of complex adsorbed from toluene solution (n_{ad}) was measured by UV–Vis spectroscopy at $\lambda = 288$ nm. At room temperature (Table 1) an average of 90% is adsorbed, whereas it is only 80% at 110°C.

Assuming that a molecule of $RhCl(PPh_3)_3$ has a diameter of $d = 1.7$ nm [30], the cross-sectional area (A) of the adsorbed catalyst is given by $A = r^2 N_L n_{ad}$. Division by the specific surface area of 550 m^2/g affords the surface coverage (Table 1). At the lower concentrations the results can be analysed by the model of Langmuir. However, for the total concentration range a treatment according to Freundlich affords a better agreement with the experimental
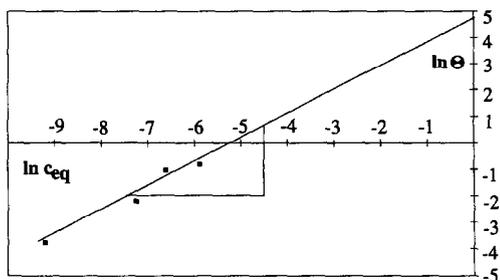
Fig. 1. Plot of $\ln \Theta$ vs. $\ln c_{eq}$ (see Table 1) for the adsorption of $RhCl(PPh_3)_3$ on SiO_2 in toluene.

data [31]. It demands monolayer adsorption and logarithmic dependence of the heat of adsorption on Θ.

$$\ln \Theta = \ln K + (1/m) \ln c_{eq} \qquad (1)$$

A plot of $\ln \Theta$ vs. $\ln c_{eq}$ (equilibrium concentration) according to Eq. 1 afforded a straight line from which the equilibrium constant K and the specific constant m are calculated as $K = 124$ 1/mol and $m = 1.07$ (Fig. 1).

At 293 K the free molar heat of adsorption, ΔG_{ad}, is obtained from $\Delta G_{ad} = -RT \ln K$ as -12 kJ/mol. Since chemisorption usually demands ΔH_{ad} values more negative than -25 kJ/mol [32] and entropic contributions may be small, one can assume that the complex is physisorbed onto the SiO_2 surface. Chemisorption via the SiO–Rh bond formation is unlikely since one would expect a lower percentage of adsorption at higher concentrations of $RhCl(PPh_3)_3$ due to the reaction of Rh(I) and silica gel. However, this percentage did not depend on the concentration (see Table 1). Furthermore desorption of $RhCl(PPh_3)_3$ was observed when the catalyst is treated again with toluene.

Further evidence stems from ^{31}P CP/MAS NMR spectra of adsorbed and free Wilkinson's catalyst. The spectrum of the latter contains a doublet at $\delta = 49$ ppm (P_{trans}) and two doubled doublets at $\delta = 34$ ppm (P_{cis}) and $\delta = 25$ ppm ($P_{cis'}$) [33]. The adsorbed catalyst afforded unresolved signals with the same intensities and chemical shifts at $\delta = 49$, 34 and 25 ppm. The

diffuse reflectance spectra of free and adsorbed Wilkinson's catalyst showed the same habitus, but the absorptions of the adsorbed complex were blue-shifted by 50 nm. At room temperature $RhCl(PPh_3)_3$ on silica gel aged to form $[RhCl(PPh_3)_2]_2$, as indicated by the diffuse reflectance spectrum of a four-day-old sample as compared to an authentic compound. The habitus is similar to that of the free dinuclear complex measured in benzene [34] except that the onset of the plateau-like end-absorption is blue-shifted by about 50 nm.

No adsorption of $RhCl(PPh_3)_3$ onto SiO_2 could be observed from 1-butanol.

3.2. Reaction catalysed by $RhCl(PPh_3)_3 / SiO_2$

3.2.1. Influence of catalyst loading

The three catalysts obtained by loading SiO_2 with 0.8, 4.0 and 8.7 wt.% Rh(I) are abbreviated as $SiO_2[0.8]$, $SiO_2[4.0]$ and $SiO_2[8.7]$, respectively. In this sequence the initial turnover frequencies, $TOF_{(i)}$, were 1.9, 6.3 and 1.2 h^{-1} indicating that $SiO_2[4.0]$ induced the highest catalytic activity (Fig. 2) while catalysis did not occur in absence of $RhCl(PPh_3)_3$ [25]a,b.

When the total amount of $SiO_2[4.0]$ was varied from 10 to 100 g/l (Fig. 3), the reaction rate did not increase to reach a final constant value but passes through three maxima at 16, 41 and 83 g/l. The corresponding initial rates $R_{(i)}$ were 5.3, 11.3 and 13.0 mmol 1/l·h, respectively. This unexpected behavior cannot be ex-
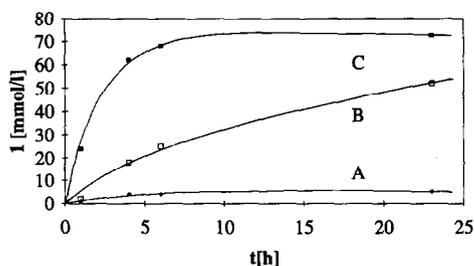

Fig. 2. Product development curves as function of Rh-loading. 1 g of (A) $SiO_2[0.8]$, (B) $SiO_2[8.7]$, (C) $SiO_2[4.0]$ and 2 mmol each of azobenzene and diphenylacetylene in 25 ml of toluene.
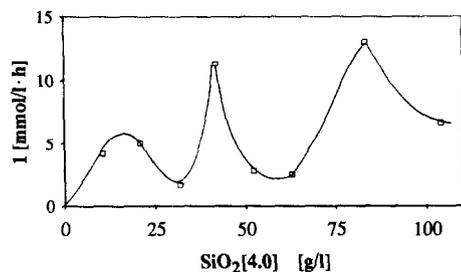
Fig. 3. Variation of initial reaction rate $R_{(i)}$ with total amount of catalyst (see Fig. 2 for experimental conditions).

plained on the basis of the present experimental data [2].

3.2.2. Solvent dependence

When toluene was replaced by 1-butanol as solvent, the reaction was slowed down as indicated by the curves B, A and D, C (Fig. 4) obtained with 10 and 40 g/l of $SiO_2[4.0]$, respectively; under these experimental conditions 20 (toluene) and 50% (1-butanol) of $RhCl(PPh_3)_3$ were desorbed into the solution. Contrary to that, in the homogeneous catalysis 1-butanol induced a 2.6 times faster reaction (curves F and E) [29].

3.3. Reaction catalysed by $Rh(PPh_3)_2$–O–$[SiO_2]$

A covalently bound Rh–O–$[SiO_2]$ complex was synthesised through reduction of $RhCl_3 \cdot 3H_2O$ with boiling ethanol in the presence of silica gel. Assuming a quantitative reaction, the resulting catalyst powder should contain 0.5 wt.% of $Rh(I)$ (0.05 mmol). While no catalytic activity was observed in the absence of PPh_3, a

rate of 0.48 mmol $1/1 \cdot h$ was measured when the phosphine was present in a twofold excess. This corresponds to a $TOF_{(i)}$ value of 0.24 h^{-1} which is only 4% of the activity of 1 g of the physisorbed $SiO_2[4.0]$ catalyst which contains 0.045 mmol of $RhCl(PPh_3)_3$. The same rate decrease should arise when only 4% of the total rhodium amount of Rh–O–$[SiO_2]$ would have been reduced to $Rh(I)$. However, this is very unlikely since the phosphine would then be present in a 50-fold excess and therefore should induce strong inhibition [25]c, [29]. Adding a tenfold excess of PPh_3 to the physisorbed catalyst resulted in a rate decrease of 50% [25]a,b. The presence of a chemisorbed rhodium(I) complex was further corroborated by the ^{31}P CP/MAS NMR spectrum of a sample synthesized by refluxing Rh–O–$[SiO_2]$ and a threefold excess of PPh_3 in toluene solution. A sharp peak at $\delta = -6.9$ ppm arises from the free ligand adsorbed on SiO_2 while the broad signal between $\delta = 30.9$ to 48.2 ppm ($\Delta\nu_{1/2} = 1.3$ kHz), indicates the presence of surface bound $Rh(I)$ species. It is known that in comparable complexes like $Rh(OH)(CO)(PPh_3)_2$ [35a] the phosphorus resonance occurs in the same range (36.5 ppm, in CH_2Cl_2) but at higher field in $Rh(III)$ compounds like $Rh(CO)(PPh_3)_2Cl_3$ (12.9 ppm, in $CDCl_3$ [35b]). Furthermore the grey colour differs significantly from the orange–red observed for $SiO_2[4.0]$.

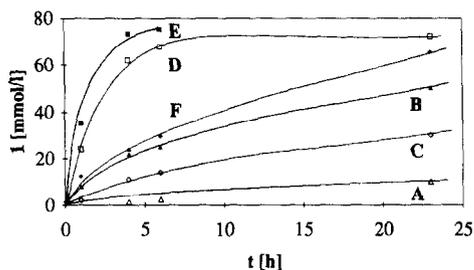

Fig. 4. Solvent influence on product development of the heterogeneous and homogeneous reaction. Curves A and C correspond to 10 and 40 g/l of $SiO_2[4.0]$ in 1-butanol, B and D to 10 and 40 g/l of $SiO_2[4.0]$ in toluene. Curves E and F apply for the homogeneous reaction in 1-butanol and toluene, respectively, in the presence of 0.015 ml of HOAc [29]. Other experimental conditions as described in Fig. 2.

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[2] One possible rationalisation is that the particles ("monomers") conglomerate to three aggregates of increasing size which exhibit maximum activity when their individual agglomeration number is reached. Thus, the rate increase observed upon adding more of the "monomer" would be due to the increase of the catalytic surface until the optimum arrangement is obtained. Upon further addition the "monomer" occupies part of the surface and the activity decreases until the simultaneously built up surface of the next higher aggregate outweighs this negative effect.
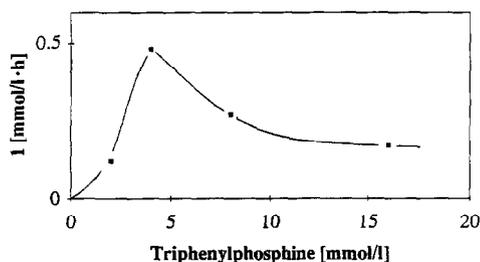
Fig. 5. Dependence of initial rate $R_{(i)}$ on the concentration of triphenylphosphine in the 1 g of Rh–O–[SiO$_2$] corresponding to a total rhodium amount of 2 mmol/l (for experimental conditions see Fig. 2).

The rate decreased to 0.12 and 0.17 mmol 1/1·h when the phosphine concentration was lowered to 2 mmol/l or raised to 16 mmol/l, respectively (Fig. 5). This suggests that the chemisorbed catalyst has the composition Rh(PPh$_3$)$_2$–O–[SiO$_2$].
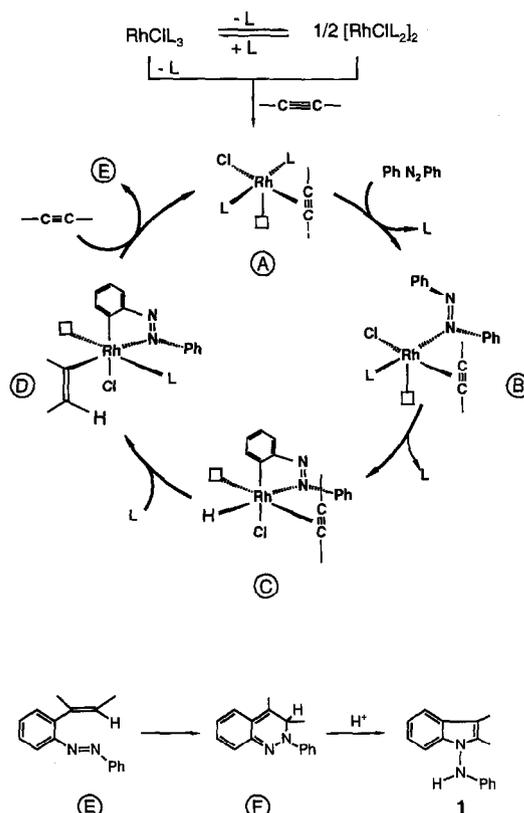
3.3.1. Mechanism

By analogy with the homogeneous system [25,29] the catalytic cycle shown in Scheme 1 is postulated for the heterogeneous reaction catalysed by RhCl(PPh$_3$)$_3$/SiO$_2$ in toluene solution.

The main difference is that all intermediates are assumed to be physisorbed on the SiO$_2$ surface. Furthermore, since SiO$_2$ occupies one coordination site, the 6-coordinated intermediates C–D contain one PPh$_3$ ligand less than their homogeneous counterparts. From D reductive elimination takes place to afford 2-stilbenylazobenzene (E) [36]. It cannot be decided whether the acid catalysed rearrangement [25,29] to 1 takes place on the SiO$_2$ surface or in solution. The possibility that all the product formation catalysed by SiO$_2$[4.0] originates from the 20% of dissolved Wilkinson's catalyst can be excluded since the heterogeneous and homogeneous reactions have different solvent dependencies. While the latter in toluene and 1-butanol gives rise to TOF$_{(i)}$ values of 2.6 and 6.7 h^{-1}, respectively, the corresponding numbers are 6.3 and 1.3 h^{-1} for the SiO$_2$[4.0] catalysed reaction,

respectively. Further evidence that the substrates react with the catalyst in their adsorbed states, is given by the lowering of TOF$_{(i)}$ from 6.3 to 1.9 h^{-1} upon addition of 1.4 ml (15 mmol) of 1-butanol to the SiO$_2$[4.0]/toluene system. Since the amount of 1-butanol is only 10% of the reaction volume the strong influence on the rate indicates successful adsorption of the alcohol [37] onto the SiO$_2$ surface in competition with the substrates. Additional evidence stems from the unsuccessful adsorption experiments with RhCl(PPh$_3$)$_3$ in 1-butanol.

The much lower catalytic activity of the covalently bound catalyst may be due to the presence of the Rh–O–bond and/or to the immobilization of the rhodium complex. No decision can be made on the basis of the available experimental data.

Scheme 1. Postulated mechanism of the heterogeneous reaction.

Acknowledgements

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