Transition Metal Complexes of Diazenes XXXVI [1a]: Formation of Indoles from Azobenzene and Diphenylacetylene through Supported Aqueous Phase Catalysis by Rhodium(I) Complexes

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Summary. A SiO_2 supported Rh(I) catalyst of trisulfonated triphenylphosphine catalyzes the addition of diphenylacetylene to azobenzene in refluxing butanol in the presence of triphenylphosphine to afford N-anilino-2,3-diphenylindole and 2,3-diphenylindole with turnover numbers of 80 and 20, respectively. As compared to the known homogeneous or heterogeneous (SiO_2) catalysis by $RhCl(PPh_3)_3$, the supported aqueous phase system retains a constant turnover frequency throughout the reaction and can be partially recycled.

Keywords. 1,2-Diaryldiazene; Alkynes; Indoles; Heterogeneous catalysis; Supported aqueous phase; Silica gel.

Übergangsmetallkomplexe von Diazenen, 36. Mitt. [1a]: Bildung von Indolen aus Azobenzol und Diphenylacetylen mittels Supported Aqueous Phase-Katalyse durch Rhodium(I)-Komplexe

Zusammenfassung. Ein auf SiO_2 aufgebrachter Rh(I)-Katalysator aus trisulfoniertem Triphenylphosphin katalysiert die Addition von Diphenylacetylen an Azobenzol in siedendem Butanol in Gegenwart von Triphenylphosphin. Es entstehen N-Anilino-2,3-diphenylindol und 2,3-Diphenylindol. Die Umsatzzahlen betragen 80 bzw. 20. Verglichen mit den bekannten Methoden der homogenen oder heterogenen (SiO_2) Katalyse durch $RhCl(PPh_3)_3$ erhält der Katalysator auf Trägermaterial während der gesamten Reaktionsdauer einen konstanten Umsatz aufrecht und kann teilweise wiedergewonnen werden.

Introduction

Supported Aqueous Phase (SAP) catalysts are gaining an important role in industrial catalysis [1b, 2]. They are based on a SiO_2 supported, water soluble complex which reacts with the substrates at the SiO_2/H_2O_{ad}/organic solvent interface [3]. The solubility of organometallic compounds in water is usually accomplished through sulfonated ligands like the trisodium salt of *tris*(*m*-sulfonatophenyl)phosphine (*TPPTS*) [4]. In SAP hydrogenation reactions, a modified *Wilkinson*'s catalyst is used with *TPPTS* instead of triphenylphosphine as a ligand [5, 6].

Recently we have found that $RhCl(PPh_3)_3$ catalyzes the addition of di-phenylacetylene to azobenzene to afford N-anilino-2,3-diphenylindole (**1**, [7,8]). The reaction is observed under homogeneous (toluene or 1-butanol) and hetero-geneous (toluene/SiO_2) conditions. In the following we describe that a SAP-Rh(I) system is an advantageous catalyst for this reaction. To our knowledge, this is the first time that a SAP catalyst was employed in a catalytic organic synthesis other than hydrogenation or hydroformylation [9].

Results and Discussion

TPPTS was prepared by the method of *D. Sinou et al.* [10]. Although the yield became lower, the neutralized reaction slurry was treated several times with methanol to remove all Na_2SO_4. The ^{31}P NMR spectrum showed only one singlet at -5.5 ppm, indicating the absence of mono- or bisulfonated phosphines and of the corresponding phosphine oxides [11]. The silica gel attached water soluble Rh(I)/*TPPTS* complex was synthesized analogously to Ref. [12] *via* direct reduction of Rh(III) to Rh(I) by *TPPTS* in refluxing water within five minutes. Addition of 1 g of silica gel to the reaction slurry and subsequent removal of the solvent afforded an orange coloured powder of Rh(I)/*TPPTS*/SiO_2. Different to the room temperature reaction [12], complete reduction to Rh(I) occurred already within five minutes. This was evidenced by ^{31}P NMR spectroscopy; the peak of *TPPTS* at -5.5 ppm had disappeared, and the singlet of *OTPPTS* could be observed at 33.5 ppm. Simultaneously, doublets at 33.5–37.5 ppm and 50–54.5 ppm appeared which are due to RhCl(*TPPTS*)$_3$, RhCl(*TPPTS*)$_2$, and [RhCl(*TPPTS*)$_2$]$_2$, respectively, as reported in the literature [12].
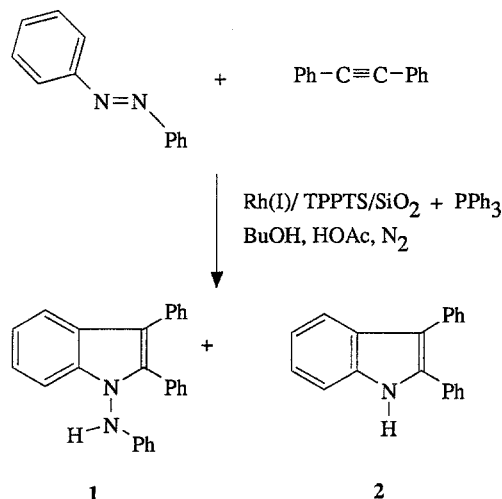
Scheme 1

When a solution of azobenzene and diphenylacetylene in 1-butanol was added dropwise to the boiling suspension of Rh(I)/*TPPTS*/SiO_2 (0.05 g atom of Rh(I)) containing 0.05 mmol of PPh_3 and 15 µl of HOAc, catalytic formation of indoles **1** and **2** was observed (Scheme 1; Fig. 1, curve A). The latter compound, its *TON*
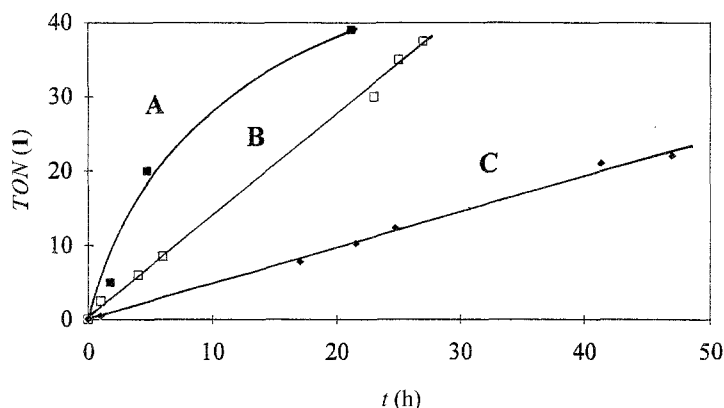
Fig. 1. Variation of turnover number (TON) of **1** with reaction time; 2 mmol of azobenzene and diphenylacetylene, 1.1 g of Rh(I)/$TPPTS$/SiO$_2$ (0.05 mmol of Rh(I)), 0.05 mmol of PPh$_3$, 15 μl of HOAc, 25 ml of 1-butanol; curves A–C correspond to the first, second, and third use of the same catalyst sample (see text), respectively

being less than 5% of that of **1**, is a secondary product formed by reductive N–N cleavage of **1** [8]. When P(OMe)$_3$ instead of PPh$_3$ was employed, the reaction rate was slowed down by 80%, whereas complete inhibition was observed for triethylamine as supporting ligand. Further experiments showed that the Rh(I)/$TPPTS$/SiO$_2$ system is inactive in the absence of triphenylphosphine. This suggests that PPh$_3$ extracts Rh(I) from Rh(I)/$TPPTS$/SiO$_2$ to form solvated RhCl(PPh$_3$)$_3$ and [RhCl(PPh$_3$)$_2$]$_2$ which are known to be catalytically active [7, 8, 13]. Further evidence stems from the isolation of RhCl(CO)(PPh$_3$)$_2$ which is known to be produced when RhCl(PPh$_3$)$_3$ or [RhCl(PPh$_3$)$_2$]$_2$ are heated in boiling alcohols [8, 14].

When the reaction was completed, the catalyst was filtered off and the resulting light-grey powder was used again in the presence of 0.05 mmol of PPh$_3$. The initial turnover frequency TON(i) decreased from 4.2 h^{-1} (Fig. 1, curve A) to 1.5 h^{-1} (Fig. 1, curve B). When the catalyst was filtered off and PPh$_3$ was added again, the experiment could be performed a third time, although the reaction was slower by 67% $(TON$(i) = 0.5 h^{-1}; Fig. 1, curve C).

Figure 2 shows a comparison between the homogeneous (curve A, [8]) and heterogeneous SAP system (curve B). At the experimental conditions given, the maximum TON is 120. The homogeneous RhCl(PPh$_3$)$_3$ catalyst induces a faster initial reaction rate; however, its turnover frequency decreases already after 10 to 15 h. Contrary to that, the SAP catalyst induces a lower rate, but its activity stays constant even up to 48 h. Whereas the amount of the secondary product **2** is rather low in the homogeneous case (Fig. 2, curve C), a TON of about 25 was observed in the heterogeneous reaction (Fig. 2, curve D).

Summing up, it may be stated that the SAP catalyst system Rh(I)/$TPPTS$/SiO$_2$/ PPh$_3$ utilizes the precious rhodium component much more efficiently than its more traditional homogeneous and heterogeneous (SiO$_2$/RhCl(PPh$_3$)$_3$, [7, 13]) counterparts. In none of these latter cases the catalytic activity stays constant during the entire reaction nor can the catalyst be recycled as observed for the SAP system.
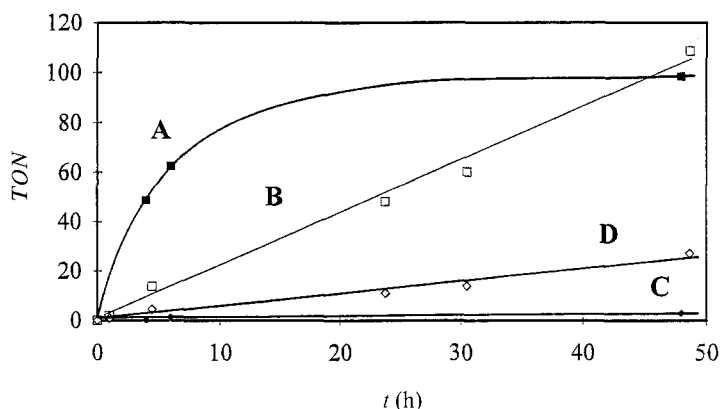
Fig. 2. Variation of turnover number (*TON*) with reaction time; 6 mmol of azobenzene and diphenylacetylene; curve A (sum of **1** + **2**): 0.05 mmol of RhCl(PPh₃)₃ in 50 ml of 1-butanol with 15 μl of HOAc [13]; curve B (sum of **1** + **2**): 1.1 g of Rh(I)/*TPPTS*/SiO₂ (0.05 mmol of Rh(I), 0.05 mmol of PPh₃, 1 g of SiO₂, 15 μl of HOAc, 25 ml of 1-butanol; curves C and D correspond to *TON* of **2** as measured for the homogeneous (curve A) and heterogeneous (curve B) reaction

Experimental

Unless otherwise noted, all experiments were performed under nitrogen. 1-Butanol was dried over K_2CO_3 and sodium and distilled under N_2. Water was distilled, degassed in an ultrasonic water bath, and stored under N_2. The silica gel (MERCK; 230–400 mesh ASTM, 550 m²/g; water content: 9%) was stored under N_2. Azobenzene and diphenylacetylene were dried *in vacuo* overnight. The products were analyzed by HPLC (pump: KNAUER HPLC pump 64; column: 250 × 8 mm, spherisorb OD52, particle size 5 μm; detector: KNAUER UV/Vis filter photometer ($\lambda = 220$ nm); integrator: SHIMADZU CR3A Chromatopac; solvent: acetonitrile/H_2O = 5/1 v/v). ^{31}P NMR spectra were recorded with a JEOL FT-NMR spectrometer JNM-DX270 at 109 MHz (δ in ppm relative to 85% H_3PO_4 as external standard). The IR spectra were recorded with a FT-IR PERKIN ELMER 16PC spectrometer. Elemental analyses were performed with a CARLO Elemental Analyser 1106 (CHN).

Synthesis of TPPTS [10]

3.15 g (12 mmol) of PPh₃ were dissolved in 20 ml of concentrated H_2SO_4. 140 ml of oleum (20% of SO_3) were added slowly at 0 °C in 1–2 hours and the solution was stirred at r.t. for seven days. The reaction mixture was slowly poured onto 120 g of ice. After adding 200 ml of water, the solution was neutralized; 90% of the solvent were removed and the resulting suspension was treated with 150 ml of methanol. Precipitated Na_2SO_4 was filtered off and the filtrate was concentrated to 10% of its volume. The suspension was treated with 100 ml of methanol again. The last three steps were repeated three to four times to remove all Na_2SO_4. 810 mg (1.3 mmol; 11%) of *TPPTS* were finally obtained. ^{31}P NMR (D_2O): $\delta = -5.5$ ppm (s); IR (KBr): $\nu = 1465$ (m; C=C), 1400 (m), 1204 (s; S=O) cm^{-1}; calc. (for *TPPTS*·$3H_2O$): C 34.73%, H 2.89%, S 15.43%; found: C 35.67%, H 2.81%, S 15.27%.

Synthesis of Rh(I)/TPPTS/SiO₂

13 mg (0.05 mmol) of $RhCl_3$·$3H_2O$ and 93 mg (0.15 mmol) of *TPPTS* were dissolved in 2 ml of water. The solution was refluxed for 5 min, the colour of the solution changing from orange-red to dark-red. 1 g of SiO_2 was added and the water was removed *in vacuo*. The resulting orange powder was used as catalyst.

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 1-butanol was added dropwise within 10 minutes to 10 ml of a refluxing 1-butanol suspension containing 1.1 g of catalyst, 15 μl of HOAc, and 0.05 mmol (13.1 mg) of PPh$_3$ (or 6 μl (0.05 mmol) of P(OMe)$_3$, or 7.5 μl (0.05 mmol) of Et$_3$N). 250 μl samples were withdrawn, the solvent was removed *in vacuo* and the residue was dissolved in 5 ml of acetonitrile prior to analysis by HPLC. When the reaction was completed and Rh(I)/*TPPTS*/SiO$_2$ filtered off, RhCl(CO)(PPh$_3$)$_2$ precipitated as a yellow, microcrystalline powder (IR (KBr): v(CO) = 1964 cm^{-1} [14]).

Observed concentrations of **1** and **2** in the experiments as described in Figs. 1 and 2: Fig. 1: curve A: **1** (mmol/l): 10 (1 h 45 min), 40 (4 h 45 min), 78 (21 h 10 min); curve B: **1** (mmol/l): 5 (1 h), 12 (4 h), 17 (6 h), 60 (23 h), 70 (25 h), 75 (27 h); curve C: **1** (mmol/l): 1 (1 h), 15.5 (17 h), 20.5 (21 h 30 min), 24.5 (24 h 40 min), 42 (41 h 20 min), 44 (47 h); Fig. 2: curve B: 6 mmol each of azobenzene and diphenylacetylene: **1** and **2** (mmol/l): 4 and 2 (1 h), 27 and 9 (4 h 35 min), 74 and 22 (23 h 45 min), 92 and 28 (30 h 30 min), 163 and 54 (48 h 40 min); curve A: data from Ref. [13].

Recycling of the catalyst

After the reaction, the catalyst was filtered off, washed several times with petroleum ether, and dried *in vacuo*. The resulting light-grey powder was used again in the presence of additional PPh$_3$ as described above.

Acknowledgements

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