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Kinetic and mechanistic investigation of the sequential hydrogenation of phenylacetylene catalyzed by rhodium(I) phosphine complexes of the type $[Rh(\eta^2\text{-}O_2Z)(PR_3)_2]$ [1]

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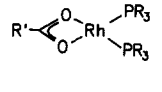
Abstract

Chelate complexes of the type $[Rh(\eta^2\text{-}O_2Z)(PR_3)_2]$ ($Z = CCH_3$, CCF_3, $CtBu$, $S(O)\text{-}p\text{-}C_6H_4\text{–}CH_3$; $PR_3 = PiPr_3$, $PPhiPr_2$, PPh_2iPr) catalyze the hydrogenation of phenylacetylene in toluene solution at 60°C. Selectivities close to 100% are achieved for the hydrogenation of the alkyne to the alkene in the presence of the acetate and trifluoroacetate complexes $[Rh(\eta^2\text{-}O_2CR)(PiPr_3)_2]$ ($R = CH_3$ **1**, CF_3 **2**). However, in other cases the reduction of the C–C double bond is also observed. In general, the selectivity of the hydrogenation reaction depends both on the phosphine and the anionic ligand. For the reduction of PhC≡CH catalyzed by **1**, the addition of acetic acid leads to a dramatic decrease in the catalytic activity.

Keywords: Hydrogenation; Kinetics; Mechanism; Phenylacetylene; Phosphine complexes; Rhodium

1. Introduction

In the course of our investigations into the chemistry of bis(triisopropylphosphine) rhodium(I) complexes of the general type $[RhX(PiPr_3)_2]_n$ [1], we recently described the synthesis and structure of the monomeric carboxylate complexes $[Rh(\eta^2\text{-}O_2CR)(PiPr_3)_2]$ ($R = CH_3$ **1**, CF_3 **2**) [2]. These compounds readily react with CO and ethylene by partial cleavage of the chelate bond to give the square-planar 1:1 adducts *trans*-$[Rh(\eta^1\text{-}O_2CR)(L)(PiPr_3)_2]$ (L = CO, C_2H_4). On treatment of **1** and **2** with H_2, O_2 and CF_3CO_2H, an oxidative addition occurs



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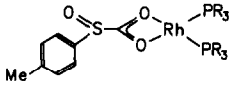

5-7

	R'	PR_3
1	CH_3	$PiPr_3$
2	CF_3	$PiPr_3$
3	CH_3	PPh_2iPr
4	tBu	PPh_2iPr

	PR_3
5	$PiPr_3$
6	$PPhiPr_2$
7	PPh_2iPr

Scheme 1. Rhodium(I) complexes of the general type $[Rh(\eta^2\text{-}O_2Z)(PR_3)_2]$

and the octahedral rhodium(III) complexes $[RhH_2(\eta^2\text{-}O_2CR)(PiPr_3)_2]$, $[Rh(\eta^2\text{-}O_2)(\eta^2\text{-}O_2CR)(PiPr_3)_2]$ and $[RhH(\eta^1\text{-}O_2CCF_3)\text{-}(\eta^2\text{-}O_2CCF_3)(PiPr_3)_2]$ are formed mostly in excellent yields [3] (Scheme 1).

The observation, that in the reaction of the dihydrido compounds $[RhH_2(\eta^2\text{-}O_2CR)(PiPr_3)_2]$ with substituted acetylenes both hydride ligands

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[1] Dedicated to Professor Walter Strohmeier on the occasion of his 75th birthday.

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are transferred to the alkyne, prompted us to study the catalytic activity of the parent carboxylate derivatives **1** and **2**. We were particularly interested to find out whether these complexes could possibly behave as catalysts for the selective hydrogenation of terminal alkynes to give the corresponding alkene as it has been observed for the hydrido-ruthenium and -osmium compounds $[RuH(\eta^2\text{-}H_2)L_4]X$ ($L=P(OR)_3$, $PPh(OR)_2$ [4]; $L_4=P(CH_2CH_2PPh_2)_3$ [5]), $[OsHCl(CO)(PR_3)_2]$ ($PR_3=PiPr_3$, $PMetBu_2$) [6], and $[OsH_4(CO)(PiPr_3)_2]$ [7]. Furthermore, we intended to compare the activity of **1** and **2** (see Scheme 1) with that of the structurally related rhodium complexes $[Rh(\eta^2\text{-}O_2CR)(PPh_2iPr)_2]$ ($R=CH_3$ **3**, *t*Bu **4**) and $[Rh(\eta^2\text{-}O_2S(O)\text{-}p\text{-}C_6H_4Me)(PR_3)_2]$ ($PR_3=PiPr_3$ **5**, $PPhiPr_2$ **6**, PPh_2iPr **7**) which were recently prepared in our laboratory [2,8]. This comparison could give us the opportunity to learn about the influence of the size and the donor properties of the phosphine as well as of the type of the anionic chelating ligand on the efficiency of the respective catalyst. In the present paper, we report the results of our catalytic studies and discuss on the basis of kinetic measurements the mechanism of the hydrogenation of PhC≡CH with **1** as the catalyst.

2. Results and discussion

2.1. Catalytic hydrogenation of phenylacetylene and styrene

Both the rhodium(I) complexes **1** and **2** catalyze the hydrogenation of phenylacetylene in toluene solution. At 1 atm H_2 and 60°C the selectivity of transforming PhC≡CH to $PhCH{=}CH_2$ is almost 100%. Whereas for **2** a further reduction of styrene has not been observed, compound **1** slowly catalyzes the hydrogenation of $PhCH{=}CH_2$ to ethylbenzene after the alkyne has been consumed. The difference in the behaviour of **1** and **2** has been confirmed by using pure styrene as the substrate.

As is illustrated in Fig. 1, the catalytic activity of the carboxylate complexes **1** and **2** in the reduction of PhC≡CH differs not too much. In contrast, the tosylate compound **5** which has been used for comparison is less efficient than **1** and **2** in the hydrogenation of phenylacetylene but catalyzes the reduction of styrene already before the complete conversion of PhC≡CH to $PhCH{=}CH_2$ has taken place. We assume that the difference in activity between **1**, **2** and **5** is mainly due to the different strengths of the chelate bond between the anionic ligand and the metal the stability of which decreases in the order $p\text{-}TolS(O)O_2^- <$

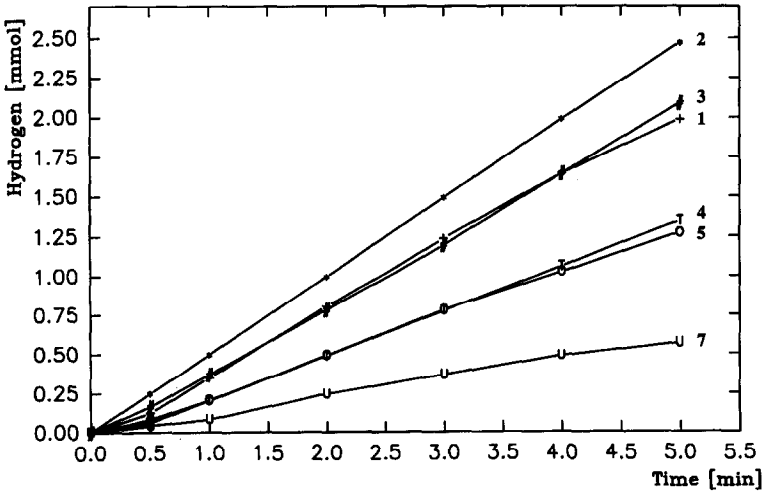


Fig. 1. Hydrogen uptake during the reduction of phenylacetylene catalyzed by **1**, **2**, **3**, **4**, **5** and **7**.

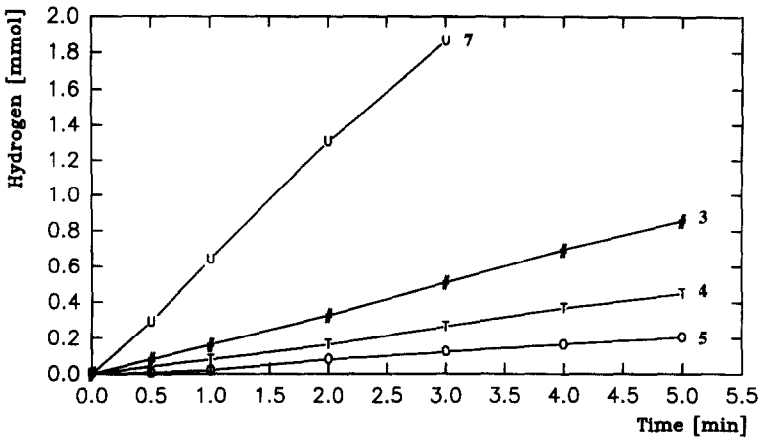


Fig. 2. Hydrogen uptake during the reduction of styrene catalyzed by **3**, **4**, **5** and **7**.

$CH_3CO_2^- < CF_3CO_2^-$. The somewhat higher reactivity of **2** compared with **1** is in agreement with the behaviour of the two carboxylate compounds towards CO and C_2H_4 [3].

The influence of the carboxylate ligand on the activity of the corresponding rhodium(I) complexes $[Rh(\eta^2\text{-}O_2Z)(PR_3)_2]$ in the hydrogenation of phenylacetylene as well as of styrene becomes even more evident if the three compounds **3**, **4** and **7**, all containing PPh_2iPr as phosphine ligand, are compared. While the tosylate complex **7** is significantly less effective for the reduction of PhC≡CH to styrene (see Fig. 1), it is more active in the hydrogenation of styrene to ethylbenzene than the related compounds **3** and **4** (see Fig. 2). The influence of the phosphine ligand on the catalytic activity is seen by comparing the tosylate rhodium(I) derivatives **5**, **6** and **7** of which that with the bulkiest phosphine ($PiPr_3$) which equally is the complex having the highest Lewis basicity, is the most active (see Fig. 3).

A difference in behaviour between **5** and **7** is also observed in the catalytic hydrogenation of styrene (see Fig. 2) where the complex with the smaller ligand (PPh_2iPr) is much more efficient than that with the larger one ($PiPr_3$). Fig. 4 summarizes the course of a typical reaction of PhC≡CH and H_2 with **7** as the catalyst. As can be seen from the change in concentration of the three hydrocarbons involved, the reduction of styrene already starts when only ca. 50% of the alkyne has been hydrogenated to the olefin. The rate of the reaction of $PhCH{=}CH_2$ to ethylbenzene, however, is significantly slower than that of PhC≡CH to styrene. In this context it is interesting to note that the hydrido-osmium compounds [OsHCl

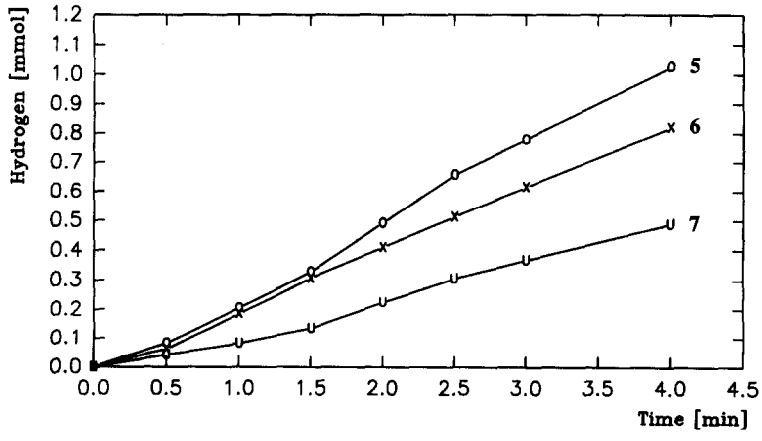


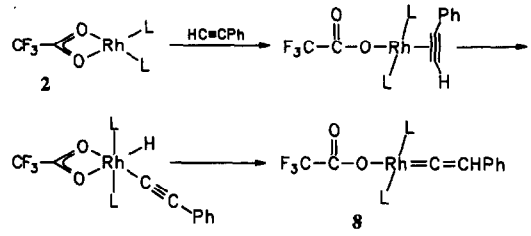
Fig. 3. Hydrogen uptake during the reduction of phenylacetylene catalyzed by **5**, **6** and **7**.

$(CO)(PiPr_3)_2]$ and $[OsHCl(CO)(PMetBu_2)_2]$ in the absence of phenylacetylene catalyze the hydrogenation of styrene to ethylbenzene at rates of about one order of magnitude higher than those observed for the reaction of PhC≡CH [6].

The catalytic activity of the carboxylate complexes $[Rh(\eta^2\text{-}O_2CR)(PiPr_3)_2]$ in reducing C≡C triple bonds is not limited to phenylacetylene. For compound **1** as the catalyst and PhC≡CPh as the substrate, the hydrogenation to (*E*)-stilbene is, however, slower by a factor of 4, the exact rate data at 60°C in toluene being 0.41 mol PhC≡CH/mol **1** · h and 0.11 mol PhC≡CPh/mol **1** · h, respectively.

2.2. *Kinetic and mechanistic studies*

Although the trifluoroacetate complex **2** facilitates the hydrogenation of phenylacetylene to styrene and also shows the highest selectivity with regard to the reduction of the C≡C bond, it is nevertheless among the compounds of general composition $[Rh(\eta^2\text{-}O_2CR')(PR_3)_2]$ not the catalyst of choice. The main disadvantage is that it quite rapidly loses its catalytic activity which is indicated by a change of color of the reacting solution from yellow to green. The reason for this is the formation of the vinylidenerhodium(I) derivative **8** which is generated from **2** and PhC≡CH in a stepwise fashion as shown in



Scheme 2.

Scheme 2 [9]. In contrast, the acetate compound **1**, although somewhat less active, is significantly more stable and thus allows more catalytic runs than complex **2**. Fig. 5 illustrates this result.

To explain the difference in the efficiency between compounds **1** and **2**, we have to take into consideration that we know already from our synthetic studies [9] that the reaction of **1** with phenylacetylene which yields the corresponding vinylidene complex **10** (see Scheme 3) proceeds much slower than that of the trifluoroacetate derivative **2**. In solution, compound **10** is in equilibrium with the alkynyl(hydrido) isomer **9** and this species reacts with H_2 to give styrene and the dihydrido compound **11**.

Since it is obvious from the data summarized in Figs. 1 and 3 that the anionic ligand of the bis(phosphine)rhodium(I) complexes has a pronounced effect on the catalytic activity of these compounds, we were interested to learn whether the presence of free acetic acid influences the rate of the reduction of phenylacetylene catalyzed by

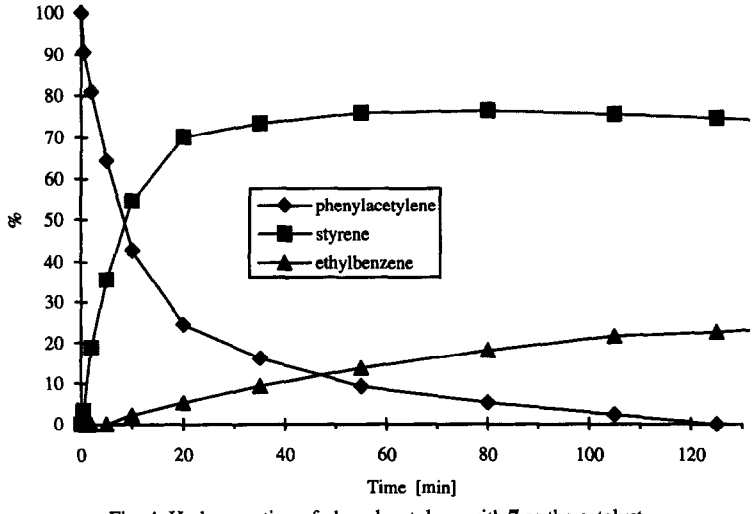


Fig. 4. Hydrogenation of phenylacetylene with **7** as the catalyst.

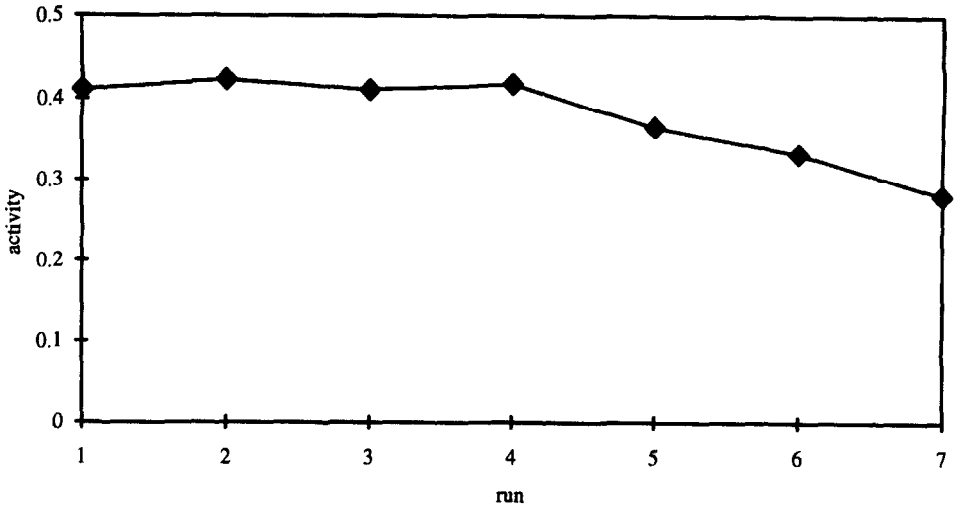
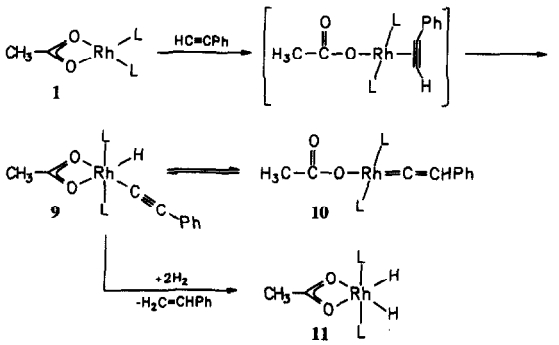


Fig. 5. Plot of the activity vs. run for the hydrogenation of phenylacetylene with **1** as the catalyst; (activity [mol $PhCH{=}CH_2$/mol **1**·h]).



Scheme 3.

the acetate derivative **1**. In addition, we set out to study the catalytic activity of **1** upon addition of NaOH because this could give us a hint whether free acetic acid is formed during the hydrogenation reaction. If NaOH does increase the rate of the reduction of phenylacetylene to styrene, hydrido(phosphine)metal species such as $[Rh_2H_2(PiPr_3)_4]$ or $[Rh_2H_4(PiPr_3)_4]$ [10] could play an active role in the catalytic cycle.

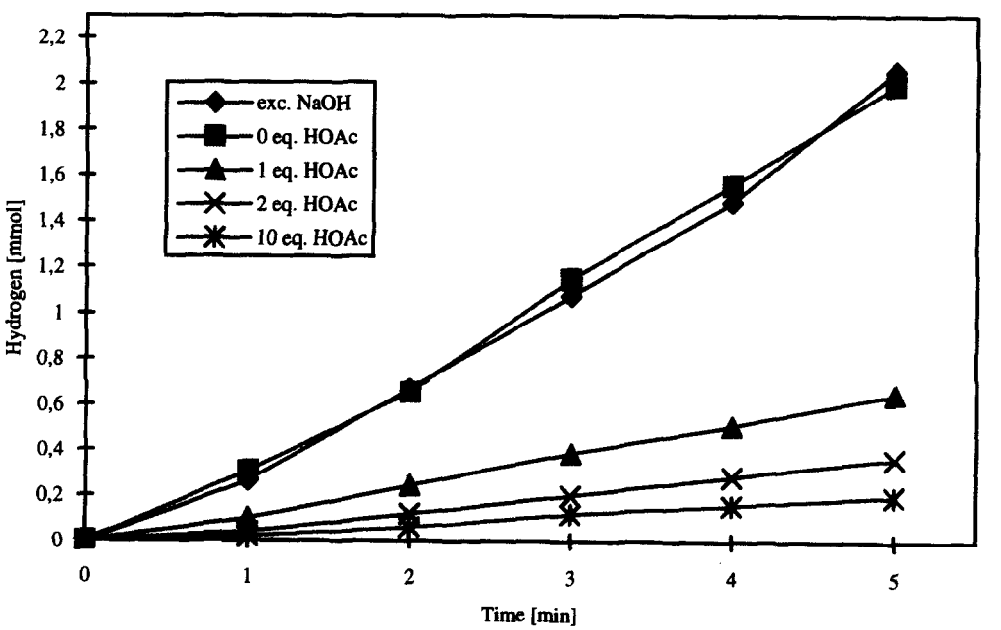
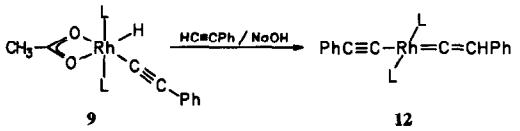


Fig. 6. Hydrogen uptake during the reduction of phenylacetylene with **1** as a function of the concentration of CH_3CO_2H.



Scheme 4.

Table 1
Kinetic data for the hydrogenation of phenylacetylene to styrene catalyzed by **1**

10^3[**1**]/M	[PhC≡CH]/M	$10^3[H_2]$/M	$p(H_2)$/atm	$10^2V_{ini}/h^{-1}$
0.83	0.25	0.87	1	0.96±0.24
1.50	0.25	0.87	1	1.20±0.12
2.00	0.25	0.87	1	1.86±0.18
2.50	0.25	0.87	1	2.34±0.12
2.50	0.33	0.87	1	2.10±0.06
2.50	0.50	0.87	1	1.92±0.24
50	0.75	0.87	1	2.10±0.12
1.50	0.50	0.73	1	1.20±0.12
1.50	0.50	1.46	2	1.32±0.42
1.50	0.50	2.93	4	1.92±0.12
1.50	0.50	4.39	6	2.52±0.06

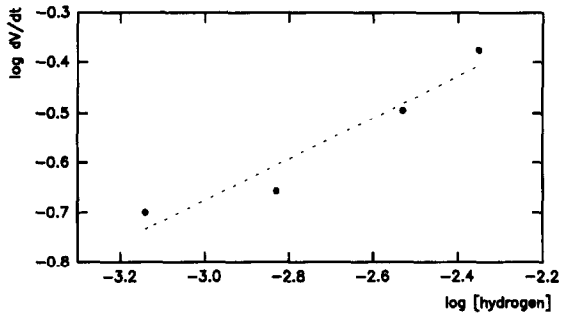


Fig. 7. Plot of the rate of hydrogen uptake vs. the hydrogen concentration in the reduction of phenylacetylene catalyzed by **1** (conditions see Table 1).

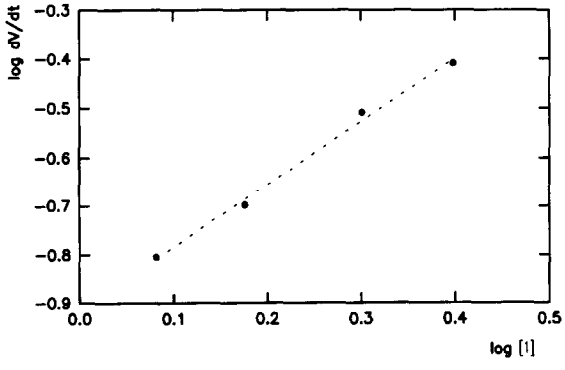


Fig. 8. Plot of the rate of hydrogen uptake vs. the catalyst concentration in the reduction of phenylacetylene catalyzed by **1** (conditions see Table 1).

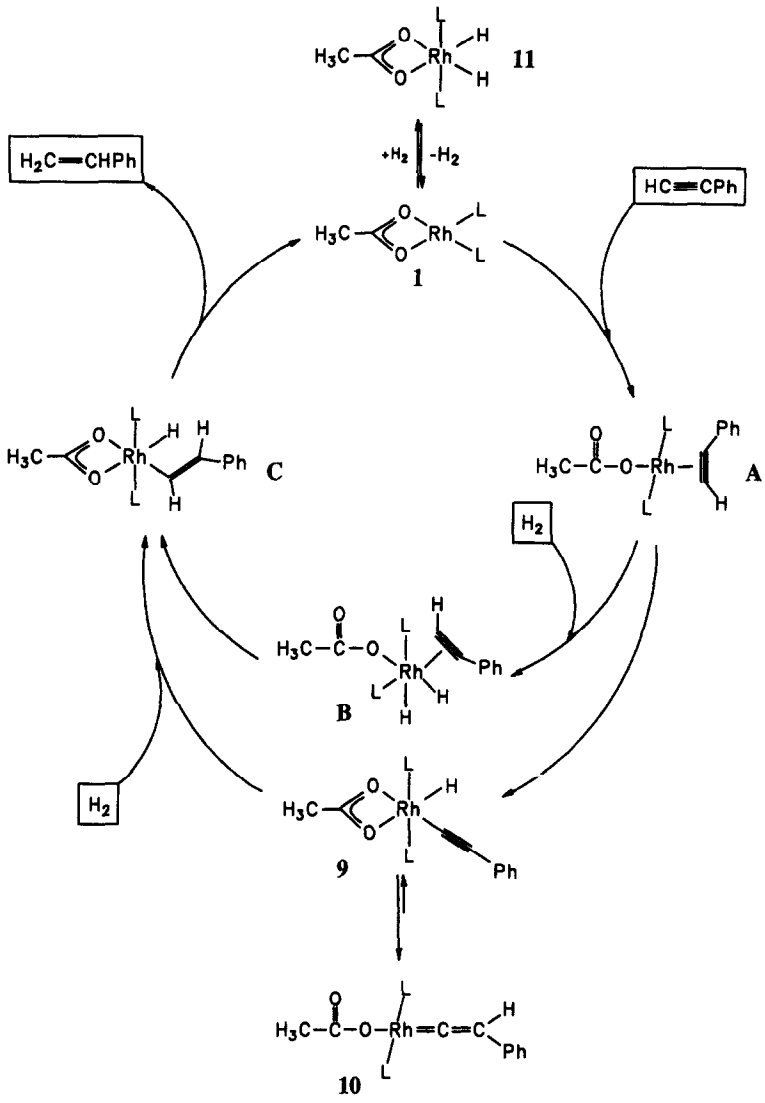
The rate of hydrogen uptake as a function of time in presence of different amounts of acetic acid is illustrated in Fig. 6. As can be seen from the data, already the addition of one equivalent of CH_3CO_2H leads to a significant decrease in the rate of the reaction and this trend continues if a higher concentration of acetic acid is used. We assume that excess CH_3CO_2H blocks the free coordination site of the catalyst, possibly by the formation of an octahedral compound [RhH(η^1-O_2CCH_3)(η^2-O_2CCH_3)($PiPr_3$)$_2$], and due to this the addition of the alkyne (or of hydrogen) to the metal centre is severely hindered.

The addition of NaOH to the reaction mixture containing **1** as the catalyst, at least in the initial stage, seems to have no effect on the rate of the hydrogenation of the alkyne. If, however, the course of the reaction is followed over a longer period of time, a gradual change of color from yellow to green occurs and a slow decrease in the rate of hydrogen uptake is observed. As has been confirmed by separate experiments, the green color originates from the formation of the alkynyl(vinylidene)rhodium(I) complex **12** (see Scheme 4) which has originally been prepared from [Rh(η^3-C_3H_5)($PiPr_3$)$_2$] and excess PhC≡CH [11] and also from compound **9** and phenylacetylene in the presence of NaOH [9].

Inspection of the kinetic data which are summarized in Table 1 reveals that the rate of the reduction of PhC≡CH to $PhCH=CH_2$ does not depend on the concentration of the alkyne. The reaction rate, therefore, is of zero order in [PhC≡CH]. A plot of log(dV/dt) versus log[H_2] yields an almost straight line of slope 0.42 (see Fig. 7), indicating that the reaction is approximately 0.5 order in hydrogen concentration. Since the plot of log(dV/dt) versus log [**1**] (see Fig. 8) produces a straight line of slope 1.2, the rate law probably is

$$-d[PhC{\equiv}CH]/dt = k[H_2]^{0.5}[\mathbf{1}]$$

By taking the kinetic data into account, the catalytic cycle for the selective hydrogenation of phenylacetylene to styrene shown in Scheme 5 can



Scheme 5. Postulated mechanism for the hydrogenation of phenylacetylene with **1** as the catalyst (L = P*i*Pr$_3$).

be proposed. Compound **1** reacts in the initial step with the alkyne to give the labile intermediate **A** which either undergoes an isomerization to the alkynyl(hydrido) complex **9** or reacts with H_2 by oxidative addition to yield **B**. While **B** could rearrange by alkyne insertion to give **C**, this intermediate could equally be formed from **9** and H_2. Finally, the hydrido(vinyl)metal species **C** on reductive elimination of styrene would regenerate the catalyst **1**. Although we know (see Scheme 3), that complex **9** can be transformed to the isomeric vinylidene compound **10**, it is to be assumed that this equilibrium does not stop the catalytic cycle. Recently we have observed that acetato(vinylidene) complexes such as **10** are obtained *photochemically* from the alkynyl(hydrido)rhodium isomers but in the absence of light this rearrangement is reversed [9]. The latter result explains why the trifluoroacetate compound **2** is catalytically less active than **1** because the reaction of the alkynyl(hydrido)rhodium derivative [RhH(C≡CPh)(η^2-O_2CCF_3)(P*i*Pr$_3$)$_2$] to give the vinylidene isomer **8** (see Scheme 2) occurs more readily than in the case of the corresponding acetate complex.

The dihydridorhodium(III) compound **11** is probably not part of the catalytic cycle since control experiments have shown that the reaction of **1** with phenylacetylene is faster than that with H_2 and also than that of **11** with PhC≡CH. Although it is known [9] that the alkynyl(hydrido) complex **9** reacts with H_2 to yield **11** and styrene (see Scheme 3), also this process is also rather slow and probably does not contribute to the formation of $PhCH{=}CH_2$ under the catalytic conditions. We are therefore left with the conclusion that the alkyne compound **A**, regardless of whether it reacts with H_2 to give **B** or rearranges to give **9**, forms the hydrido(vinyl)rhodium(III) intermediate **C** which reductively eliminates styrene to regenerate the starting material **1**. The observation that the rate of the alkyne reduction catalyzed by **1** is approximately of the order of 0.5 in hydrogen concentration can be taken as supporting evidence for the assumption that from **A** two parallel pathways are possible. For both the first step (to give **B** or **9**) is rate-determining.

3. Concluding remarks

In summary, the present investigation has shown that the anionic as well as the phosphine ligand of the rhodium(I) complexes [$Rh(\eta^2\text{-}O_2Z)(PR_3)_2$] have a pronounced influence on the catalytic activity in the hydrogenation of phenylacetylene. For compounds with those anions ZO_2^-, which form a relatively strong chelate bond with the metal centre, an undiminishing activity is observed which, however, is accompanied by a loss of selectivity. A similar conclusion can be drawn for the phosphine: the smaller this ligand is (e.g., by going from $PiPr_3$ to PPh_2iPr), the less active the corresponding complex appears. The problem of whether a replacement of PR_3 by AsR_3 or SbR_3 [12] and of phosphine by phosphite ligands would change the catalytic efficiency is currently being investigated in our laboratory.

4. Experimental

All manipulations were conducted with rigorous exclusion of air. Solvents were dried by standard procedures and distilled under argon prior to use. Phenylacetylene (Merck) was purified by distillation and styrene (Merck) by distillation and passage through an alumina column. The rhodium complexes **1–7** were prepared by literature methods [2,8].

The catalytic reactions were followed by measuring, at constant pressure, the hydrogen consumption as a function of time on a gas buret. The conversion of reactants in the catalytic reactions were followed up to 90%. In order to use the initial rates method in the calculations we considered conversions up to 20%. The stirrer was operated in such a manner that the rate of dissolution of hydrogen was much faster than its rate of absorption by the catalyst and there was no limitation due to diffusion control. The solubility of hydrogen in toluol was considered to be constant for every run. The concentration of H_2 was determined as a function of temperature and hydrogen pressure by the assumption of the linear dependence on $p(H_2)$. Plots of kinetic data were fitted by the use of conventional linear regression programs to $r^2 > 0.98$ (for Fig. 7: $r^2 = 0.964$) but the absolute error in any single measurement is large as 30%. The analysis of the products of the catalytic reactions were carried out on a Shimadzu GC-8A chromatograph connected to a Shimadzu C-R3A calculation integrator. A FFAP on Chromosorb WAW/DCMS column was used for analysis of stilbene (250°C), styrene (200°C) and ethylbenzene (200°C).

4.1. Catalytic reactions

The reactions with H_2 were carried out at 60°C in an 150 ml flask attached to a gas buret, which was in turn connected to a Schlenk manifold. The catalyst (0.06 mmol) was introduced in a glove box and connected to the gas buret. The system was evacuated and refilled with hydrogen three times, and then the flask was brought to constant

temperature by a thermostat. The substrate (6 mmol) and the solvent (filled up to 24 ml) were introduced through a septum and the mixture was vigorously stirred during the run.

4.2. *Reaction of* **1** *with phenylacetylene in the presence of* H_2

In a NMR tube, to 20 mg (0.04 mmol) of **1** a solution of 42 μl (0.40 mmol) PhC≡CH in 0.5 ml of H_2-saturated C_6D_6 was added at room temperature under an atmosphere of hydrogen. The ^{31}P-NMR spectrum, immediately recorded, of the orange–yellow solution shows a strong resonance for **9** (47.69 ppm) and a small resonance for **11** (61.78 ppm).

The induction period of ≈ 2 min in the catalytic reaction, if **11** is used as the catalyst, supports the conclusion that **11** is not a part of the catalytic cycle.

Acknowledgements

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