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New rhodium(I)-π-chelate complexes with coordinated amidine bases (dbu, dbn) and their catalytic properties to polymerize phenylacetylene

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Abstract

In dichloromethane solution the halogeno-bridged complexes $[Rh(\mu\text{-}Cl)(diene)]_2$ (diene = 2,5-norbornadiene, nbd and *cis,cis*-1,5-cyclooctadiene, cod) give with four molar equivalents of the amidine bases L (L = 1,5-diazabicyclo[4.3.0]non-5-en, dbn and 1.8 diazabicylo[5.4.0]undec-7-en, dbu) at 25 °C in 2 h in the presence of the halogen scavenger $TlPF_6$ the salts $[Rh(diene)L_2]PF_6$ (**I** cod, dbn; **II** dbu; **III** nbd, dbn; **IV** dbu). In its absence of $TlPF_6$ in THF the reaction affords the neutral complexes RhCl(nbd)L (**V** dbn; **VI** dbu). The not frequently observed coordination pattern of the monodentate ligands dbu and dbn in **I–VI** were characterized by means of FTIR and NMR measurements. All compounds obtained polymerize the substrate phenylacetylene in 1,4-dioxane solution at 25°C in a homogeneous catalytic reaction process to polyphenylacetylene (PPA) with stereospecific *cis*-transoidal microstructure. With the complexes **I–VI** TON values between 2520 (**I**) and 14 170 h^{-1} (**III**) are obtained. The average molecular weight (Mw) is between 196 900 (**I**) and 1 745 060 (**III**). A kinetic study of the polymerization process has been undertaken.

Keywords: Rh(I) complexes; Catalysts; Polymerization of phenylacetylene; Kinetic data

1. Introduction

Phenylacetylene (PA) was first polymerized by Ziegler–Natta coordinative catalysts [1]. Since then PA has also been shown to polymerize by cationic [2,3], thermal [4,5], radical [6] mechanisms as well as by metathesis with transition metal halides [7]. Later, Furlani et al. [8] studied the PA polymerization process by some rhodium(I) salts $[Rh(diene)NN]PF_6$ (diene = cod, nbd, NN = bidentate aromatic nitrogen bases) by adding the base NaOH. Without addition of this cocatalyst this process could still be sucessful using the catalysts RhCl(cod)L (L = dbu, dbn) and $[Rh(cod)\textit{o}\text{-}Py(CH_2)_2P(Ph)(CH_2)_3ZR]PF_6$ ($ZR = OC_2H_5$, OPh, NHPh, NH-*cyclo*-C_6H_{11}) which were reported previously by ourselves [9] and are portrayed in Scheme 1.

We continue this previous report by describing further rhodium(I) complexes containing the amidine bases dbu and dbn as monodentate ligands. They surpass the homogenous catalytic properties of earlier Rh(I) compounds used in the polymerization of the substrate PA. Furthermore, a first kinetic study for this reaction process is included.

2. Results and discussion

2.1. Preparation

In dichloromethane solution the complex salts $[Rh(diene)(L)_2]PF_6$ (see Scheme 1; **I–IV**) were generated by reaction of $[RhCl(diene)]_2$ (diene = nbd, cod) [10,11] with four molar equivalents of the amidine bases L (dbn, dbu) in the presence of the halogen scavenger $TlPF_6$ at 25°C, whereas the neutral complexes RhClL(nbd) (**V–VI**) could be prepared in THF solution by reacting $[RhCl(nbd)]_2$ [11] with two molar equivalents of each base L at the same reaction temperature. All products obtained were separated as yellow, air-stable solids. Their NMR and IR spectroscopic data (see Section 3) confirm previous findings that the coordination pattern of both diene ligands is bidentate [10,11] and the ligand L is monodentate, coordinating via the

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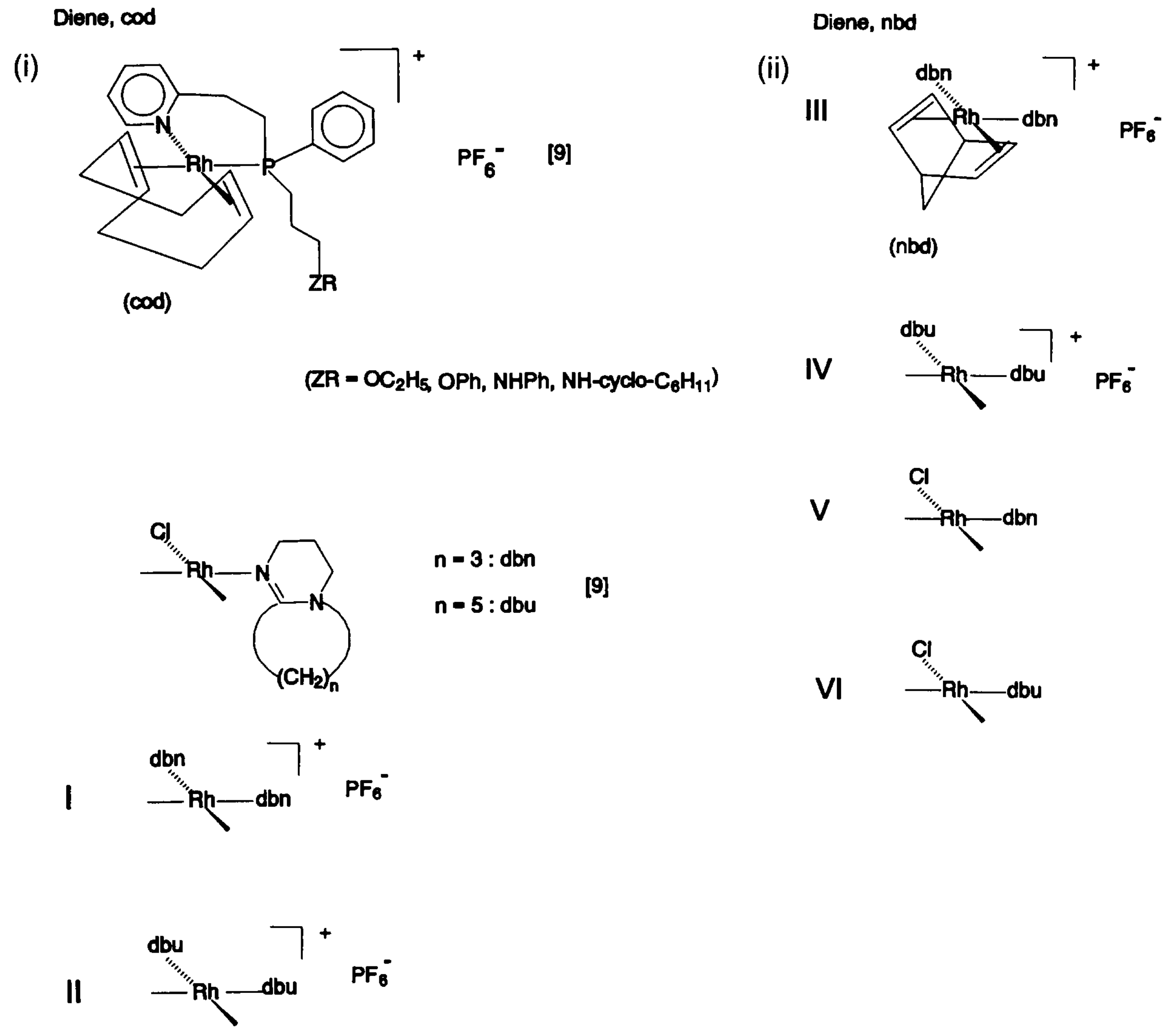
imine nitrogen atom. Consequently the $\nu(C{=}N)$ IR absorption band is lowered on going from the free to the coordinated ligand L in **I–VI** (e.g. $\Delta\nu = 18$ (dbn, **I**); 13 (dbn, **III**); 21 (dbu, **II**); 13 (dbu, **IV**) cm^{-1}). In addition, the extent of the shifts indicates that the amidine ligands are more strongly bound to the Rh(I) atom in the cod complexes than in the nbd ones. Furthermore, the ^{13}C NMR data of such comparisons show a typical low-field shift of the imine carbon atom signal [12,13] ($\Delta\delta = 2.2$ (**V**); 3.1 (**VI**)) which also supports the aforementioned coordination of the imine nitrogen atom in L. This is further confirmed in **V** by the result of a single crystal X-ray analysis [14]. The coordination sphere of the Rh(I) central atom is square planar. This typical geometry should be also present in the other complexes. Finally the salt character of **I–III** is proven by the absence of $^{103}Rh–^{31}P$ coupling in the NMR spectra.

2.2. Polymerization of phenylacetylene (PA)

Before 1991 the polymerization of PA by rhodium catalysts was examined by Furlani et al. giving polymers with only low average molecular weights of between 10000 and 100000 [8]. Afterwards Yang et al. [15] described, surprisingly, that the substrate PA could be polymerized with the in situ catalytic system $[Rh(nbd)Cl]_2$ / trietylamine to give polyphenylacetylene (PPA) with a much higher Mw value of 4428800 (gpc analysis with PS calibration) and a turnover number (TON) of 3055 h^{-1}. Careful repetition of these experiments did not confirm such large Mw values. The maximum measured Mw was only 895000. To obtain an insight on factors influencing such findings we developed the Rh(I) catalysts **I–VI** shown in Scheme 1. With respect to the results of Yang et al. our first



Scheme 1. Catalysts.

Table 1
Polymerization of PA

Catalysts	Yield (%)	TON (h^{-1})	*Mw* [c]
I [a]	42 ± 2.6	2520	196900
II [a]	53 ± 1.7	3180	180700
III [b]	94.5 ± 0.5	14175	1745060
IV [b]	85.4 ± 3.6	12960	1230120
V [a]	78.1 ± 3.3	11745	1386030
VI [a]	86.3 ± 2.3	12945	1466400

[a] Catalyst:monomer ratio 1:5000, 0.36 mol l^{-1} phenylacetylene, 1,4-dioxane solution 25°C, reaction time 20 min.

[b] Catalyst:monomer ratio 1:2000, 0.36 mol l^{-1} phenylacetylene, 1,4-dioxane solution 25°C, reaction time 20 min.

[c] GPC analysis with polystyrene calibration, the breadth of error for the *Mw* values amounts to ±5% (90% confidence interval).

attempts using the catalysts $[Rh(cod)\textit{o}\text{-}Py(CH_2)_2P(Ph)(CH_2)_3ZR]PF_6$ ($ZR = OC_2H_5$, OPh, NHPh, NH-*cyclo*-C_6H_{11}) with an uncoordinated side chain $-(CH_2)_3ZR$ (Scheme 1) for the polymerization of PA [9] ($c_{cat} = 1.3$ mmol l^{-1}, $c_{PA} = 1.3$ mol l^{-1}, solvent 1,4-dioxane, 25°C) gave lower TON as well as lower *Mw* values (352–876 h^{-1}; 199000–230000). Going from ZR = OR to NHR the TON values obtained increased [9]. In an attempt to improve at least the unsatisfactory TON values this observation led to the preparation of the catalysts RhCl(cod)L (L = dbn, dbu) which contain the sterically demanding amidine bases dbn or dbu instead of the bidentate *o*-$Py(CH_2)_2P(Ph)(CH_2)_3ZR$ as ligand. These catalysts delivered under the same reaction conditions higher TON values of 1292 (L = dbn) and 1325 (dbu), h^{-1}, although the *Mw* values (133200 and 166200, respectively) remained somewhat lower than before. The advantageous dependence on the TON suggests the replacement of the chloro ligand in RhCl(cod)L by a further amidine ligand which was realized in the catalysts **I**–**II**. The results of the polymerization of PA to PPA with a *cis*-transoidal microstructure, which is thermodynamically favored based on MNDO calculations [9], are illustrated in Table 1. The increase of the TON value was nearly twofold but the *Mw* values remain low. The number and the kind of the amidine bases ligated in Rh(I)diene complexes influences mainly the TON values. To obtain higher *Mw* and perhaps even better TON values simultaneously, it seems reasonable to vary the π-chelate ligand, particularly given the known effectiveness of the in situ system $[RhCl(nbd)]_2/NEt_3$ [15]. This means that exchange of the cod with the conformationally more rigid chelate nbd in **I** and **II** to **III** and **IV** must be helpful. Indeed, both catalysts **III** and **IV** achieved an approximately tenfold increase of the TON (**III**, 14175; **IV**, 12960 h^{-1}) and *Mw* values (**III**, 1745060; **IV**, 1230120) under comparable conditions. To support the fact that the kind of the bidentate π-ligand in catalysts **I**–**III** is really the dominant factor, substitution of one amidine base by a chloro ligand to give catalysts **V** and **VI** should not lead to dramatic changes in the TON and *Mw* values. Experiments with these catalysts gave the following values: **V**, TON 11745 h^{-1}, *Mw* 1386030; **VI**, TON 12945 h^{-1}, *Mw* 1466400. These figures are similar to those obtained with **III** and **IV**, supporting the above hypothesis. It can be concluded therefore that the stereospecific course of the polymerization process to PPA depends predominantly on the kind of π-chelate ligand coordinated in the Rh(I) complex, whereas the type and number of the coligands has less importance. The catalyst **V** is at the moment the most active in the series of Rh(I) complexes studied. **V** gives after 20 min at a catalyst/monomer ratio of 1:5000, a yield of 95.5% with a TON of 14170 h^{-1} and *Mw* of 1745060. Even at high dilution (1:10000) the yield is 72.8% and the *Mw* 1652570. This demonstrates the great utility of this Rh(I) complex for catalyzing the polymerization of PA and probably similar aromatic alkines [16].

2.3. Kinetic measurements

First kinetic investigations for the polymerization of PA with rhodium complexes were carried out with the catalyst $[Rh(cod)\textit{o}\text{-}Py(CH_2)_2P(Ph)(CH_2)_3OPh]PF_6$ (Scheme 1, TON = 349 h^{-1}, *Mw* = 232800 in 1,4-dioxane) in dichloromethane solution at 25°C [12,17]. The rate law was determined as first order with regard to the catalyst and as a fractional order of 1.7 with regard to the monomer PA by the method of initial rate. To characterize the catalytic reaction the plausible mechanistic pathway with the steps (i)–(iv) shown in Scheme 2 was proposed. This mechanism has often been proposed for the polymerization of alkynes by such complex-catalysts [8,18,19], but until now it had not been confirmed by kinetic data. As shown in Scheme 2, the catalysts undergo in the presence of PA in excess a rapid uptake of PA in an equilibrium reaction (i) which is followed by an oxidative addition reaction (ii). The subsequent propagation reaction (iii) is divided into uptake of PA (α) and insertion of coordinated PA (β); these steps are repeated. The repetition of theses steps is concluded by a reductive elimination reaction (iv).

(i) Association
$[Rh(I)Cl(diene)L] + PA \rightleftharpoons [Rh(I)Cl(diene)(PA)L]$
(ii) oxidative addition
$[Rh(I)Cl(diene)(PA)L]$
$\rightleftharpoons [Rh(III)Cl(diene)L(C{\equiv}CPh)(H)]$ (**A**)
(iii) propagation
α association
$A + PA \rightleftharpoons [Rh(III)Cl(diene)L(C{\equiv}CPh)(H)(PA)]$ (**B**)
β insertion
$B \rightarrow [Rh(III)Cl(diene)L(CH{=}C(Ph)\text{-}C{\equiv}CPh)(H)]$ (C)
(iv) reductive elimination after *n* repetitions of (iii) α and (iii) β
C $[Rh(I)Cl(diene)L]$ + polymer (PPA).

Scheme 2. Proposed mechanism for the polymerization of PA with rhodium (I) catalysts.

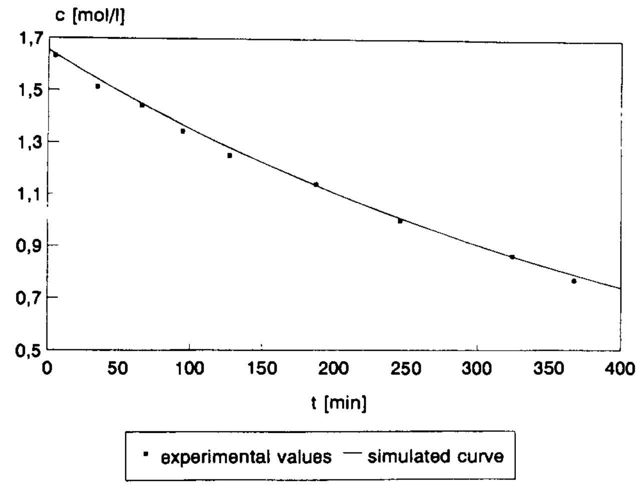


Fig. 1. Simulation of the concentration/time curve for the polymerization of PA with [Rh(cod)o-Py(CH$_2$)$_2$P(Ph)(CH$_2$)$_3$OPh]PF$_6$

Through accompanied ^{1}H and ^{13}C NMR measurements it could be confirmed only that the reaction process is initiated above −70°C. Because of the fast rate of the reaction the intermediates could not be detected, but from the known coordination chemistry of Rh it can be assumed that a facile formation of Rh–H and σ-bonded Rh–C takes place during step (ii) [20–22]. To support this hypothesis it can be noted that analogs of PA add to the Rh(I) central atom forming Rh(III)-H and Rh(III)-C≡C-R (oxidative addition) [21,23]. Further, the insertion of another π-coordinated acetylenic group into the Rh(III)–C bond in the course of the propagation is supported by the Ziegler–Natta-type coordination mechanism [19,24].

To verify the proposed mechanism, we selected the computer program Predici [25] to simulate the concentration/time curves of the polymerization of PA by [Rh(cod)o-Py(CH$_2$)$_2$P(Ph)(CH$_2$)$_3$OPh]PF$_6$ (Scheme 1, co, PA = 1.68 mol l^{-1}; co, cat = 2.6 mmol l^{-1}; 25°C; CH$_2$Cl$_2$) under consideration of the course of the steps (i)–(iv). This catalyst system is suitable because the polymerization rate is relatively low and the catalytically active species is not deactivated in the course of the reaction. The computional treatment demands that the rate constants for the single elementary processes (i)–(iv) are fitted until the divergence of the calculated values for the concentrations of PA and the measured values is as small as possible. Fig. 1 shows that the regression curve correlates well with the data obtained experimentally. This indicates that the mechanistic course shown in Scheme 1 is an acceptable proposal for the polymerization of the subtrate PA with the rhodium catalysts. To estimate the stepwise rate constants on the basis of the data measured in the concentration/time curve, it was necessary to diminish the actual number of rate constants from eight to six. This was done by reducing the steps (i) and (ii) to one step. This is reasonable because the substrate is present in excess. It must be further assumed that an intermediate formed after the insertion reaction of one PA molecule does not change its reactivity in subsequent α,β cycles of step (iii). This means that the steps (iii) α and (iii) β are independent of the length of the polymer chain, which seems to be true, in general [26]. With these restrictions the subsequent rate constants for the steps are fitted: steps (i) and (ii): $k_{\text{ox,add}} = 208.9$ l mol^{-1} min; (i) α association: $k_{\text{ass}} = 1.00$ l mol^{-1} min^{-1}; $k_{\text{ass}\rightarrow} = 0.169$ l mol^{-1} min^{-1}; (i) β insertion $k_{\text{insert}} = 16.7$ l mol^{-1} min^{-1}; propagation $k_{\text{propa}} = 6.95$ l mol^{-1} min^{-1}; (iv) $k_{\text{term}} = 0.002$ l mol^{-1} min^{-1}. For the more active rhodium catalysts **V** and RhCl(cod)(dbn) [9] the concentration / time curves could be simulated for the first 6 min without catalyst deactivation. Adding a deactivation step for the active catalytic species (**C**, Scheme 2) the whole fitting becomes satisfactory. The fitted rate constants for RhCl(cod)(dbn) [9] are: $k_{\text{ox,add}} = 31\,078.5$ l mol^{-1} min^{-1}; $k_{\text{ass}} = 200.1$ l mol^{-1} min^{-1}, $k_{\text{ass}} = 45$ l/mol min; $k_{\text{insert}} = 406.3$ l mol^{-1} min^{-1}; $k_{\text{propa}} = 15013.7$ l mol^{-1} min^{-1}; $k_{\text{term}} = 2.49$ l mol^{-1} min^{-1}; $k_{\text{deact}} = 9.85$ l mol^{-1} min^{-1}.

2.3.1. Formal kinetics

For the complexes **V** and RhCl(cod)(dbn) [9] the rate law was examined by initial rate study (Section 3). Through these measurements the aforementioned reactions orders and the rate law (eqn (1)) are confirmed [12,17].

$$\frac{-\mathrm{d}c_{\mathrm{PA}}}{\mathrm{d}t} = k_{\mathrm{obs}}(c_{\mathrm{PA}})^{1.7}(c_{\mathrm{cat}})^{1.0} \qquad (1)$$

After the rearrangement of eqn (1) and integration [27], the rate constants k_{obs} of the rate determining step can be calculated from the slopes of the plot based on eqn (2) at each of the three temperatures used.

$$(c_{\mathrm{PA}})^{-0.7} = 0.7k_{\mathrm{obs}}(c_{\mathrm{cat}})^{1.0}t + \text{const.} \qquad (2)$$

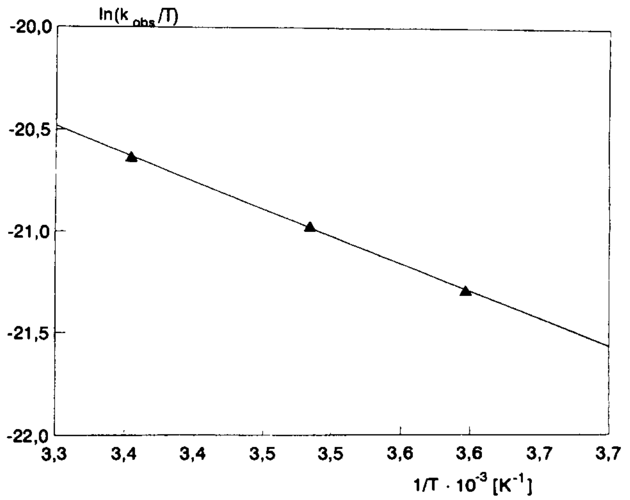


Fig. 2. Eyring plot for the polymerization of PA with **V**.

Table 2
Activation parameters

Catalyst	RhCl(nbd)(dbn) V	RhCl(cod)(dbn)
ΔH (kJ mol^{-1})	21.7 ± 3.1	7.1 ± 1.1
ΔS (J mol^{-1} K^{-1})	−98.9 ± 10.7	−173 ± 7.6
ΔG_{298} (kJ mol^{-1})	51.1 ± 4.4	58.6 ± 3.1

The data set of 5 or 6 substrate concentrations, measured over the reaction times of 5–6 min, delivers linear plots which belong to 40% turnover or more. For example, the Eyring plot for the polymerization process with catalyst **V**, based on k_{obs} at 5, 15 and 25°C is illustrated in Fig. 2. The obtained values of $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ including $\Delta G^{\ddagger}$ for the catalysts **V** and RhCl(cod)(dbn) [9] are given in Table 2. Striking amongst these activation parameters are the large negative $\Delta S^{\ddagger}$ values of -170 J mol^{-1} K^{-1} for RhCl(cod)(dbn) and -98.9 J mol^{-1} K^{-1} for **V**. They indicate that the rate determing step is associative. To decide between the possible steps (i) and (iii) α, the deuterated substrate PhC≡CD (98 at% D) instead of PA was taken to measure the H/D isotopic effect via the UV spectroscopically determined rate constants (see Section 3.4). In the case of the so-called primary isotopic effect [28], no change should be observed because the oxidative addition reaction is a single event per Rh(I) atom which is present in very low concentrations. Conversely, the H/D effect, which is a secondary one, should be strongly influencial in associative propagation which is one of numerous cycles. In order to measure the effect dichloromethane solutions of the catalyst RhCl(cod)(dbn) and the substrates PA and PhC≡CD were polymerized at 25°C (see Section 3.4). From the data obtained both average k_{obs} were calculated with eqn (2) to give a k_{obsH}/k_{obsD} ratio of 0.56 ($\pm$0.018). This presence of an inverse secondary H/D effect demands the assignment of the step (iii) α as the rate determining step. The extent of this effect indicates that steric factors could be determined for the course of the polymerization process considered [28,29].

Compared with $\Delta G^{\ddagger}$ values of 85 kJ mol^{-1} for the catalysts of the type [Rh(cod)*o*-Py(CH$_2$)$_2$P(Ph)(CH$_2$)$_3$-ZR]PF$_6$ [12,17] those of 51.1 kJ mol^{-1} (**V**) and of 58.6 kJ mol^{-1} RhCl(cod)(dbn) are smaller. The values of the activation enthalpy $\Delta H^{\ddagger}$ and the entropies of activation $\Delta S^{\ddagger}$ are strikingly different from those for **V**: the value of $\Delta H^{\ddagger}$ is lower at 7.1 kJ mol^{-1} and $\Delta S^{\ddagger}$ is more negative for RhCl(cod)(dbn) compared with the corresponding values for **V** (21.7 kJ mol^{-1} and -98.9 J mol^{-1} K^{-1}, respectively). Since the values of $\Delta G^{\ddagger}$ for both catalysts are in the same range, the aforementioned observations also demonstrate that steric features must be a dominant factor of influence on the polymerization of PA. For the more active catalyst **V** a decreasing steric hindrance accelerates the course of the polymerization. This explanation is in accordance with an evaluation with the steric factor of reaction *p*, defined as $p \approx \exp(-\Delta S^{\ddagger}/R)$ [28]. For the improvement of TON and *Mw* values the most important factor is steric hinderance, as shown by the changes caused by replacing nbd by cod as ligand.

3. Experimental details

All reactions were carried out under argon. The solvents were dried according to literature methods and distilled twice before use. To record experimental data the following instruments were used: NMR spectrometer (Bruker WR 300); FTIR spectrometer (Nicolet P510) and GPC device (eluent THF; pump, Merck Hitachi L6200); UV detector, Merck Hitachi L4000 (254 nm)). A complete spectroscopic data set was obtained only for compound **I**.

3.1. Preparation of [Rh(diene(L))$_2$]PF$_6$ (I–III)

A total of 100 mg of the starting materials [Rhμ-Cl(cod)]$_2$ (0.2 mmol) and [Rhμ-Cl(nbd)]$_2$ (0.22 mmol) [10,11] in 3 ml dichloromethane was stirred at 25°C with four molar equivalents of dbu or dbn. The chloride scavenger TlPF$_6$ was added to the mixture which led to the precipitation of TlCl. The reaction mixture was then stirred for 5 h and the TlCl was separated off by use of a centrifuge. For product separation the solvent was removed by distillation (10^{-3} mbar). The yellow residue obtained was purified with n-hexane/dietylether (1:1), filtered and dried under vacuum. Yields: 149.8 mg (61%) **I**; 233.2 mg (87%) **II**; 204.3 mg (80%) **III**; 249.3 mg (89%) **IV**.

I: Anal. Calc. $C_{22}H_{36}F_6N_4PRh$: C 43.72; H 6.00; N 9.27%. Found C 43.84; H 6.08; N 9.23%. FTIR (KBr): ν(CN) 1641.63s cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 3.75 (s, 4H, cod (olef.)); 3.31 (t ^3J(HH) 6.9 Hz, 4H, dbn); 3.16 (t 3*J*(HH) 5.1 Hz, 4H, dbn); 3.08 (t 3*J*(HH) 5.9 Hz, 4H, dbn); 2.86 (t ^3J(HH) 7.6 Hz, 4H, dbn); 2.30 (m, 4H, cod); 1.96 (p, 4H, dbn); 1.76–1.70 (m, 4H, cod); 1.66 (p, 4H, dbn). ^{13}C NMR (CD$_2$Cl$_2$): δ 163.12 (s, 2C, dbn); 81.00 (d, 4C, ^1J(RhC) 12.1 Hz, cod (olef.)), 52.51 (s, 2C, dbn); 46.64 and 42.74 (s, 2C, dbn); 30.94 (s, 4C, cod); 21.10 and 20.27 (s, 2C, dbn). ^{31}P NMR (CD$_2$Cl$_2$): δ −144.08 (h, ^1J(PF) 710.67 Hz, PF$_6$)).

II: Anal. Calc. $C_26H_44F_6N_4PRh$: C 47.28; H 6.71; N 8.48%. Found C 47.22; H 7.00, N 8.63%. FTIR (KBr): ν(CN) 1601.12s cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 3.80 (d, 4H, cod (olef.)). ^{13}C NMR (CD$_2$Cl$_2$): δ 164.57 (s, 2C, dbu); 80.76 (d0, 4C, ^1J(RhC) 11.6 Hz, cod (olef.)).

III: Anal. Calc. $C_{21}H_{32}F_6N_4PRh$: C 42.87; H 5.48; N 9.52%. Found C 42.50; H 5.29; N 9.14%. FTIR (KBr): ν 1647.42s cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 3.84

(dd, 4H, ^2J(HH) 2.2 Hz, nbd (olef.)). ^{13}C NMR (CD_2Cl_2): δ 163.14 (s, 2C, dbn); 57.59 (d, 4C, ^1J(RhC) 10.1 Hz, nbd (olef.)).

IV: Anal. Calc. $C_{25}H_{40}F_6N_4PRh$: C 46.59; H 6.26; N 8.69%. Found C 46.43; H 6.30; N 8.48%. FTIR (KBr): ν(CN) 1608.84 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 3.74 (s, 6H, nbd). ^{13}C NMR (CD_2Cl_2): δ 164.13 (s, 2C, dbu); 57.22 (d, 4C, ^1J(RhC) 10.1 Hz, nbd (olef.)).

3.2. Preparation of RhCl(nbd)L (V and VI)

[RhCl(nbd)]$_2$ (**V**: 150 mg, 0.33 mmol; **VI**: 200 mg, 0.43 mmol) and dbn (**II**; 82 μl, 0.66 mmol) or dbu (**VI**: 131 μl, 0.86 mmol), respectively, were stirred in 3 ml THF at 25°C for 2 h. The solvent was removed by distillation (10^{-3} mbar). With addition of n-hexane/diethylether (1:1) a yellow solid was precipitated in both cases. This was filtered, washed with n-hexane and dried under reduced pressure. Yield: 200 mg (86%) **V**; 236 mg (60%) **VI**.

V: Anal. Calc. $C_{14}H_{20}ClN_2Rh$: C 47.41; H 5.68; N 7.89%. Found C 47.42; H 5.56; N 7.62%. FTIR (KBr): ν(CN) 1639.7vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.05 (s, 2H, nbd (olef.)); 3.72 (s, 2H, nbd); 3.55 (s, 2H, nbd (olef.)). ^{13}C NMR ($CDCl_3$): 162.59 (s, 1C, dbn); 57.86 (s, 2C, nbd (olef.)); 48.75 (s, 2C, nbd (olef.)).

VI: Anal. Calc. $C_{16}H_{24}ClN_2Rh$: C 50.21; H 6.32; N 7.32%. Found C 50.04; H 6.14; N 6.97%. FTIR (KBr): ν(CN) 1612.7s cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 3.93 (s, 2H, nbd (olef.)); 3.71 (s, 2H, nbd); 3.51 (s, 2H, nbd (olef.)); ^{13}C NMR (CD_2Cl_2): δ 163.89 (s, 1C, dbu); 57.09 (s, 2C, nbd (olef.)); 48.35 (s, 2C, nbd (olef.)).

3.3. Polymerization of phenylacetylene (PA)

To 8 ml of solutions of the complexes **I–VI** (c = 0.18–0.072 mmol l^{-1}) in 1,4-dioxane 4 ml of a solution of PA in dioxane (0.36 mol l^{-1}) was added dropwise at 25°C. After 20 min the polymer fraction (PPA) was precipitated with methanol, washed and dried under reduced pressure (10^{-3} mbar). The purity was checked by microanalysis and the yield was determined by gravimetry (PPA fraction). For determination of the molecular weight averages (Mw) of polyphenylacetylene (PPA) size exclusion chromatography (GPC) with polystyrene calibration was used (column: phenogel 106 Å, 50 × 0.8 cm, solvent THF, flow rate 0.5 ml min^{-1}, Mw determination of the THF soluble part of PPA). The given GPC molecular weight in polystyrene equivalent is only approximate. These values can normally differ from those of light scattering or viscosity measurements but to compare our results with those of other authors we also use the PS method (DIN 55672, 1993) [7,8,9,30]. The yellow polymers PPA with *cis* transoidal microstructure proved by ^{1}H NMR data [8,9] were stored under vacuum conditions.

3.4. Kinetic studies

The experiments were carried out in a two-necked round bottomed 25 ml flask. The flask containing the monomer solution in CH_2Cl_2 was thermostated at the desired temperature in the range -5 to 25°C ($\Delta T = \pm 1$°C, as measured in the reaction solutions) for 10 min. The catalyst dissolved in dichloromethane was added. The samples were taken through the septum with a syringe. Samples of 40 μl were diluted with 1 ml THF. The sample (20 μl) was injected into the GPC device to separate the polymer from the monomer (column Knaur Eurogel SEC 100, 25 × 1 cm, 1.5 ml THF min^{-1}). Conversion of monomer was determined by UV spectroscopy (UV detector 254 nm, three point calibration). For the determination of the rate constants an initial monomer concentration of 0.289 mol l^{-1} (RhCl(nbd)(dbn)) and 0.535 mol l^{-1} (RhCl(cod)(dbn)) was used. The catalyst concentrations were 0.0438 mmol l^{-1} (RhCl(nbd)(dbn)) and 0.488 mmol l^{-1} (RhCl(cod)(dbn)). In the GPC chromatograms taken to evaluate k_{obs} no oligomers and cyclotrimers were observed. This underlines the fact that PPA did not decompose during the measurements.

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