APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2004; **18**: 124–129

# Polymerization of phenylacetylene catalysed by RhTp(cod) and RhBp(cod) in ionic liquids: effect of alcohols and of tetraammonium halides

**Anna M. Trzeciak and Józef J. Ziółkowski***

Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie St., 50-383 Wrocław, Poland

Received 30 August 2003; Accepted 31 October 2003

**RhTp(cod) (1) and RhBp(cod) (2), almost inactive in $CH_2Cl_2$, became good catalysts of phenylacetylene polymerization in ionic liquids ([bmim]Cl, [bmim]$BF_4$: *bmim* = 1-butyl-3-methylimidazolium, [mokt]$BF_4$: *mokt* = 1-methyl-3-oktylimidazolium, [bumepy]$BF_4$: 1-butyl-4-methylpyridinium) and in $CH_2Cl_2$ in the presence of tetraammonium halides ($[R_4N]X$, R = Bu, Et; X = Cl, Br). The highest yields of polyphenylacetylene with catalyst 1 were obtained in [bmim]Cl at 65 °C (64% after 2 h) and in [mokt]$BF_4$ at 20 °C (56% after 24 h). In alcohols ($CH_3OH$, $(CH_3)_2CHOH$, $(CH_3)_3COH$) as solvents, up to 100% of the polymer was produced. When a mixture of an ionic liquid and $CH_3OH$ was used as the reaction medium, the polymer yield was similar to the yield achieved in an ionic liquid only, but the molecular weight increased remarkably.**

**Tetraammonium salts, $[R_4N]X$, are co-catalysts for 1, and the yield of the polymer increased in the order $[Et_4N]Br < [Bu_4N]Br < [Et_4N]Cl < [Bu_4N]Cl$. Polymers with molecular weights from 6900 to 38 800 Da were obtained with catalyst 2 in $[R_4N]Br$ or $[R_4N]Cl$, whereas in ionic liquids ([bmim]Cl, [bmim]$BF_4$) the corresponding molecular weights were higher, from 51 300 to 60 300 Da. Copyright © 2004 John Wiley & Sons, Ltd.**

**KEYWORDS:** phenylacetylene polymerization; rhodium(I); pyrazolylborate; ionic liquids; ammonium halides

## INTRODUCTION

Ionic liquids, compounds having no vapour pressure, have been the subject of intense focus as environmentally friendly media of various catalytic reactions.[1–4] The use of ionic liquids makes it possible to eliminate toxic organic solvents and offers new ways to separate organic products from catalysts.[1–4] Ionic liquids have been tested in different catalytic processes, and recently also in phenylacetylene polymerization with rhodium catalysts.[5]

Those rhodium complexes that are known as active polymerization catalysts usually contain coordinated diene (cyclooctadiene (cod), norbornadiene (nbd)) ligands. Rhodium complexes of the formula [Rh(L–L)]X (L–L = cod, nbd, nitrogen chelating ligand; X = $PF_6^-$, $ClO_4^-$, $BPh_4^-$) catalyse phenylacetylene polymerization when applied in the presence of NaOH.[6] Rhodium imidazole complexes, e.g. $[Rh(cod)(imH)_2]BF_4$, $[Rh(cod)(im)]_3$ (imH = imidazole; im = imidazolate), produce polyphenylacetylene (PPA) of $M_w$ = 10 000–22 000 but their activity is not influenced by NaOH.[7] Rhodium diene complexes, $[RhCl(cod)]_2$ and $[RhCl(nbd)]_2$, are good catalysts of polymerization in polar solvents, e.g. tetrahydrofuran (THF) or $H_2O$, but in toluene the yield of the polymer was *ca* 1% only.[8] Water-soluble complexes, $[Rh(diene)(tos)(H_2O)]$ (diene = cod, nbd; tos = tosylate), are active in THF or $H_2O$ but not in toluene.[8] $[Rh(cod)(tos)(H_2O)]$ yielded PPA with higher stereoregularity than that obtained from a reaction catalysed by $[Rh(nbd)(tos)(H_2O)]$ in the same solvent system.[8]

The $[RhCl(nbd)]_2$ complex used as a catalyst for the polymerization of phenylacetylenes with cyano groups produces soluble, stereoregular, and high-molecular-weight polymers in THF–$NEt_3$ and dimethylformamide (DMF)–$NEt_3$ media.[9]

Three dinuclear complexes obtained in reaction of $[RhCl(cod)]_2$ with $1,3\text{-}(PPh_2CH_2)_2C_6H_4$ are catalytically active for polymerization of phenylacetylene; however, the activity

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*Correspondence to: Józef J. Ziółkowski, Faculty of Chemistry, University of Wrocław, 14 F. Joliot–Curie St., 50-383 Wrocław, Poland.
E-mail: jjz@wchuwr.chem.uni.wroc.pl
Contract/grant sponsor: State Committee for Research (KBN); Contract/grant number: PBZ-KBN 15/09/T09/99/01d.

has been observed only for complexes containing the Rh(cod) moiety.[10]

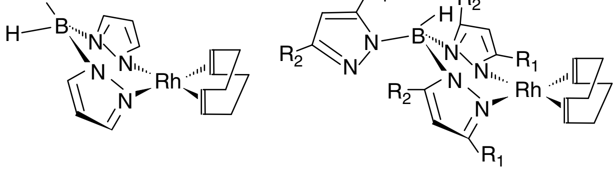
Rhodium complexes with oxygen ligands, Rh(AAEMA)(cod) (AAEMA = deprotonated form of 2-(acetoxy)ethyl-methacrylate) and Rh(acac)(diene) (acac = acetylacetonate; diene = cod, nbd), are active catalysts of phenylacetylene and *p*-tolylacetylene polymerization under homogeneous and heterogeneous conditions.[11] Higher stereoregularities and molecular weights of PPA have been obtained in a heterogeneous system than in a homogeneous one.[11]

The rhodium complexes Rh(acac)(nbd) and Rh(acac)(cod) in ionic liquids ([bmim]$BF_4$, [bupy]$BF_4$) are active in phenylacetylene polymerization only when the $Et_3N$ co-catalyst is added to the system.[5] The yield of the polymer (79–92%) as well as $M_w$ of 100 000–196 000 Da are higher in the case of the application of Rh(acac)(nbd)–$NEt_3$ than in the case of Rh(acac)(cod), regardless of the kind of ionic liquid used.[1] The yields of PPA obtained in reactions catalysed by $[RhCl(cod)]_2$ and $[RhCl(nbd)]_2$ with the $NEt_3$ co-catalyst in ionic liquids are 10–20% lower than with acetylacetonato complexes.[5]

Rhodium(I) tris(pyrazolyl)borate complexes with homo- and hetero-scorpionates, RhTp′(cod), are efficient catalysts of stereoregular polymerization of phenylacetylene derivatives.[12,13] Catalytic activity has been observed only for complexes with substituents (R) in the 3- and 5-positions of the pyrazolyl ring, and the more bulky R-groups usually cause higher catalytic activity. In contrast, rhodium complexes with unsubstituted tris(pyrazolylborate) (Tp) and bis(pyrazolylborate) (Bp) ligands (RhTp(cod) (**1**), RhBp(cod) (**2**); Fig. 1) have, till now, been known as almost inactive.[12]

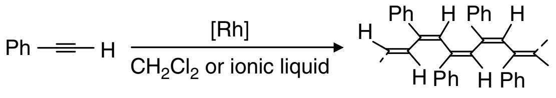
In this paper we describe two rhodium(I) pyrazolyl borates, **1** and **2**, as active catalysts when used in ionic liquids or with tetraammonium salts as co-catalysts and alcohols as solvents. The aim of the studies presented in this paper was to construct an active catalytic system for the polymerization of phenylacetylene (Scheme 1) based on rhodium complexes, RhTp(cod) (**1**) and RhBp(cod) (**2**).

The very low catalytic activity of these complexes used without co-catalysts has been reported earlier by other authors.[12] We have found that ionic liquids, as well as ammonium salts, are efficient co-catalysts, especially in polymerization catalysed by RhTp(cod) (**1**). Very good results have also been obtained with alcohols as solvents. On the basis of the results presented, new, very effective catalytic systems could be developed.



**RhBp(cod)** **RhTp(cod)** ($R_1$, $R_2$ = H, Me)

**Figure 1.** Structures of rhodium complexes **1** and **2**.



**PPA**

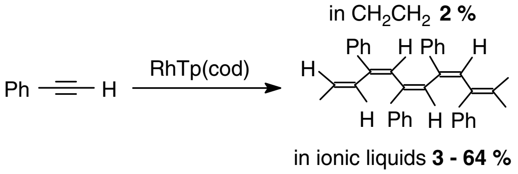
**Scheme 1.**

## RESULTS AND DISCUSSION

### Phenylacetylene polymerization in ionic liquids

RhTp(cod) (**1**) itself, used as a catalyst for phenylacetylene polymerization in $CH_2Cl_2$, shows very low activity (*ca* 2% PPA) compared with that (over 40% PPA) obtained for RhBp(cod) (**2**) (with relatively low $M_w = 21\,800$ Da and a polydispersity index of 2.9); see Scheme 2 and Table 1. The application of ionic liquids as solvents resulted in a significant increase in polymer yield in reactions catalysed by **1** (Table 2). In reactions catalysed by complex **2**, the effect of the application of ionic liquids is seen as a two- to three-fold increase in polymer molecular weight and decrease in its polydispersity (Table 1).

To standardize the polymerization reaction conditions, we selected a temperature of 65 °C for all ionic liquids used, since at that temperature [bmim]Cl also becomes liquid, whereas other ionic liquids, like [bmim]$BF_4$, [mokt]$BF_4$, and



**Scheme 2.**

**Table 1.** The phenylacetylene polymerization catalysed with RhBp(cod) **2** in ionic liquids[a]

| Ionic liquid | PPA yield (%) | $M_w$ (Da) | $M_w/M_n$ |
|---|---|---|---|
| —[b] | 40 | 21 800 | 2.9 |
| [bmim]$BF_4$ | 38 | 55 000 | 2.0 |
| [mokt]$BF_4$ | 58 | 60 000 | 1.7 |
| [bumepy]$BF_4$ | 28 | 51 300 | 1.8 |
| [bmim]Cl | 2 | | |
| [bmim]Cl (1 h) | 16 | | |
| [bmim]Cl (1 h) | 54[c] | 60 300 | 1.8 |

[a] Reaction conditions: 65 °C, [PhC≡CH] : [Rh] = 114, 30 min.
[b] Reaction in $CH_2Cl_2$.
[c] Recycle of the previous run (see text).

**Table 2.** The phenylacetylene polymerization catalysed with RhTp(cod) (**1**) in ionic liquids

| Ionic liquid | PPA yield (%) | $M_w$ (Da) | $M_w/M_n$ |
|---|---|---|---|
| Reaction conditions: 65 °C, 1 h[a] | | | |
| [bmim]BF$_4$ | 3 | 50 800 | 1.7 |
| [bmim]BF$_4$ | 16[b] | 43 200 | 2.0 |
| [mokt]BF$_4$ | 12 | 67 800 | 1.7 |
| [bmim]Cl | 43 | 84 000 | 1.8 |
| [bmim]Cl (2 h) | 64 | 84 000 | 1.8 |
| [bmim]Cl | 51[b] | 33 100 | 1.8 |
| [bmim]Cl | 75[c] | 60 113 | 2.0 |
| Reaction conditions: 20 °C, 24 h[d] | | | |
| [bmim]BF$_4$ | 19 | 58 300 | 1.7 |
| | 100[c] | 66 000 | 1.8 |
| | 35[e] | 98 500 | 1.7 |
| | 61[e,f] | 78 600 | 1.8 |
| [bmim]PF$_6$ | 25 | 57 500 | 1.7 |
| | 75[c] | 75 500 | 1.9 |
| | 19[e] | 107 700 | 1.8 |
| | 48[e,f] | 137 500 | 1.9 |
| [mokt]BF$_4$ | 56 | 80 400 | 1.8 |
| | 27[c] | 64 000 | 1.8 |
| | 19[e] | 113 500 | 1.8 |
| [bumepy]BF$_4$ | 17 | 74 700 | 1.7 |
| | 19[c] | 62 900 | 1.8 |
| | 46[e] | 89 800 | 1.7 |

[a] [PhC≡CH] : [Rh] = 114.
[b] [PhC≡CH] : [Rh] = 50.
[c] Recycle of the previous run (see text).
[d] [PhC≡CH] : [Rh] = 72.
[e] Solvent: ionic liquid (0.5 cm$^3$) + MeOH (0.5 cm$^3$).
[f] 48 h.

[bumepy]BF$_4$, are already dense liquids at room temperature. Both complexes, **1** and **2**, are weakly soluble in ionic liquids. Therefore, before introducing phenylacetylene, sufficient quantities of the complex and the ionic liquid were mixed with a small amount of CH$_2$Cl$_2$ to obtain a totally homogeneous solution. CH$_2$Cl$_2$ was then removed by evaporation *in vacuo* and the remaining solution of the complex in the ionic liquid was used for the polymerization test. A similar procedure has previously been used earlier by other authors.[5]

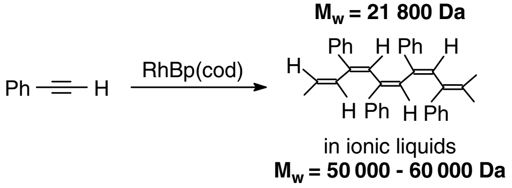
Complex **1** in [bmim]BF$_4$ and [mokt]BF$_4$ was found to be a rather weak catalyst of phenylacetylene polymerization, giving only 3% and 12% of PPA respectively. However, when a higher concentration of **1** was used, the polymer yield increased in [bmim]BF$_4$ to 16% (Table 2). The highest yield of PPA was obtained in the reaction in [bmim]Cl: 43% after 1 h and 64% after 2 h. Comparing the yield of polymerization with **1** in [bmim]Cl and in [bmim]BF$_4$, one may note the effect of the anion in the ionic liquid. We consistently observed higher yields of polymerization in the ionic liquid containing chloride ions (3% of PPA in [bmim]BF$_4$ and 43% of PPA in [bmim]Cl) (Table 2). It is worth noting that in all polymerization reactions in ionic liquids the yield of the polymer was higher than that obtained in a CH$_2$Cl$_2$ solution. This observation warrants the conclusion that, for both the rhodium catalysts **1** and **2**, the ionic liquids are not only solvents but also act as co-catalysts. A good result (75% PPA) was obtained in an experiment with reused catalyst separated from the reaction mixture after precipitation of the polymer with methanol.

In polymerization reactions catalysed by **2** (Scheme 3) we observed a positive effect of ionic liquids on the quality of the polymer produced, but not on its yield. The molecular weight of the polymer $M_w$ increased and the polydispersion factor decreased compared with the results of polymerization reaction in CH$_2$Cl$_2$ only (Table 1).

In [bmim]Cl, 2% of the polymer was obtained after 0.5 h and only 16% after 1 h. However, a much higher yield, 54% of PPA, was obtained with reused catalyst. This was later explained by the effect of traces of methanol, left in the sample during the recycling procedure.

When Cl$^-$ in the ionic liquid was replaced by BF$_4^-$ ([bmim]BF$_4$ was applied), 38% of PPA was obtained after 0.5 h. The best result, 58% PPA, was obtained for [mokt]BF$_4$, whereas for [bumepy]BF$_4$ the yield was only 28%. Generally, the yields of phenylacetylene polymerization catalysed by RhBp(cod) **2** in ionic liquids are similar to those obtained in CH$_2$Cl$_2$, except for the reaction in [mokt]BF$_4$.

Further experiments with **1** as a catalyst in ionic liquids were conducted at 20 °C. In such reaction conditions, ionic liquids, as previously, act as co-catalysts, increasing the yield of the polymer compared with that obtained in CH$_2$Cl$_2$ (Table 2). In two reactions, with [bmim]BF$_4$ and [bmim]PF$_6$ as solvents, the highest yields of the polymer were obtained with reused catalysts. Such an effect was not observed in reactions with [mokt]BF$_4$ and [bumepy]BF$_4$ as solvents. We supposed that the polymer yield increase might be caused by small amounts of methanol left in the reaction mixture after separation of the precipitated polymer. This is a reasonable explanation when methanol is not carefully removed by vacuum evaporation from the mixture containing the catalyst dissolved in the ionic liquid. Consequently, further reactions were conducted in a medium composed of an ionic liquid and methanol, and in all cases higher molecular-weight polymers were obtained compared with the previous reactions in ionic liquids only (Table 2). The methanol caused an increase in



**Scheme 3.**

polymer molecular weight; however, its positive effect on the reaction yield was smaller than expected. In one experiment only, with $[bumepy]BF_4$ and methanol as solvent, the polymer yield increased significantly from 17% to 46%. In all other cases the differences in PPA yield were smaller. Complex **1** is not readily soluble in ionic liquids or in methanol, and this may be the reason for the relatively low reaction rate.

## Phenylacetylene polymerization in alcohols

The results presented in Table 3 show an important contribution of methanol to the reaction rate and the yield of the polymer. The highest molecular weight of the polymer ($M_w = 130\,700$ Da) was obtained in a reaction conducted in methanol; however, the reaction yield was only 50%. This may have been caused by, first, the low solubility of **1** in methanol and, second, its being tied up in the polymer precipitated during the reaction. For comparison, several experiments with different alcohols in the mixture with $CHCl_3$ (volume ratio $CHCl_3 : ROH = 5$) were done (Scheme 4).

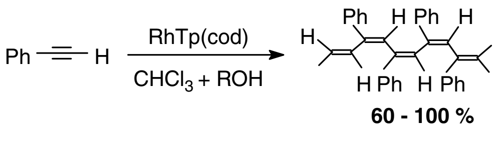
The alcohols were found to be the most attractive co-solvents for catalytic polymerization reactions, with the following effectiveness towards the yield of the polymer:

$CH_3OH$, $(CH_3)_2CHOH$, $(CH_3)_3COH$ > $PhCH_2OH$, $PhOH$
100% 80%
> $C_2H_5OH$, $CH_3CH_2CH_2OH$, $(CH_3)_2CHCH_2OH$,
$CH_3CH_2CH_2CH_2OH$
60%

**Table 3.** The phenylacetylene polymerization[a] catalysed with RhTp(cod) (**1**) in $CHCl_3 + ROH$[b] solution: effect of alcohol

| ROH | PPA yield (%) | $M_w$ (Da) | $M_w/M_n$ |
|---|---|---|---|
| $CH_3OH$ | 100 | 41 300 | 1.9 |
| | 50[c] | 130 700 | 2.0 |
| $(CH_3)_2CHOH$ | 100 | 44 900 | 2.1 |
| $(CH_3)_3COH$ | 96 | 80 700 | 2.0 |
| PhOH | 81 | 25 000 | 1.9 |
| $PhCH_2OH$ | 81 | 30 100 | 2.1 |
| $CH_3CH_2OH$ | 75 | 39 000 | 1.9 |
| $CH_3CH_2CH_2OH$ | 65 | 32 100 | 1.9 |
| $(CH_3)_2CHCH_2OH$ | 62 | 60 700 | 1.2 |
| $CH_3CH_2CH_2CH_2OH$ | 49 | 69 400 | 2.4 |

[a] Reaction conditions: 20 °C, 24 h, $[PhC{\equiv}CH] : [Rh] = 75$.
[b] $CHCl_3$ (0.5 $cm^3$) + ROH (0.1 $cm^3$).
[c] Reaction in pure $CH_3OH$.



**Scheme 4.**

The most effective alcohols are those with short carbon–carbon chains (e.g. methanol, t-butanol). The molecular weight of the polymers obtained ranged from 32 000 to 80 000 Da, like in $CH_2Cl_2$ or in ionic liquids, and was smaller than that obtained in reactions proceeding in methanol only. Our studies clearly showed that the addition of even small amounts of alcohol to the reaction mixture significantly increases the reaction rate and the yields of polymers. It is worth noting that, as far as we know, there are no literature data about the positive effect of alcohols on polymerization catalysed by other rhodium complexes or by iridium complexes.[14]

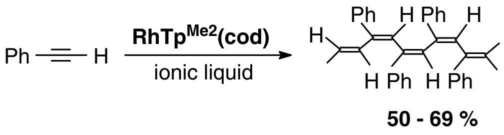
In contrast to alcohols, other solvents, like DMF, $C_6H_6$, or pyridine, used in a mixture with $CH_2Cl_2$ show no noticeable influence on the polymer yield, which remains at *ca* 10%.

## Phenylacetylene polymerization with $RhTp^{Me2}$(cod) (3)

Another tris-pyrazolylborate rhodium(I) complex, $RhTp^{Me2}$(cod) (**3**), was tested as a catalyst in ionic liquids and in methanol (Scheme 5).

According to the literature data, complex is more active than **1**, although only 5% of the polymer was obtained in $CH_2Cl_2$ after 3 h at 40 °C.[12] However, we found that in methanol the polymerization yield increased to 91% ($M_w = 60\,000$ Da; Table 4). Complex **3** also shows very high catalytic activity in ionic liquids (over 50% yield of the polymer after 2 h; Table 4). Although complex **3** itself is not soluble in ionic liquids, it forms a homogeneous solution briefly after the addition of phenylacetylene to the reaction mixture; therefore, other co-solvents were not used.

For the separation of the catalyst from the polymer, a method described in the literature was successfully applied.[5] The polymer was extracted with toluene and then precipitated



**Scheme 5.**

**Table 4.** The phenylacetylene polymerization catalysed with $RhTp^{Me2}$(cod) (**3**) in ionic liquids[a]

| Ionic liquid or $CH_3OH$ | PPA yield (%) | $M_w$ (Da) | $M_w/M_n$ |
|---|---|---|---|
| $[bmim]BF_4$ | 58 | 61 600 | 1.8 |
| $[bmim]PF_6$ | 69 | 81 400 | 1.8 |
| $[mokt]BF_4$ | 65 | 94 800 | 1.8 |
| $[bumepy]BF_4$ | 50 | 80 100 | 1.8 |
| $CH_3OH$ | 91 | 180 700 | 1.9 |

[a] Reaction conditions: 20 °C, 2 h, $[PhC{\equiv}CH] : [Rh] = 75$.

with methanol. The catalyst remains in the ionic liquid and may be used in the next reaction. Polymerization of phenylacetylene with catalysts **1**, **2**, and **3** leads to the formation of structurally identical products, cis–transoidal polymers (92–100% of the isomer, according to IR analysis[11]).

## Phenylacetylene polymerization in the presence of tetraammonium salts

The positive results of phenylacetylene polymerization in ionic liquids as solvents and the discovery that they also act as co-catalysts prompted us to study the expected similar properties of tetraammonium salts. Table 5 collects the results of the polymerization reaction catalysed by **1** in $CH_2Cl_2$ with the addition of tetraammonium salts. The reactions were conducted at room temperature over a period of 48 h, and then the polymer was precipitated with methanol and analysed. Although a rather small excess of $[R_4N]X$ versus **1** was used, $[R_4NX] : [Rh] = 4$, increased yields of PPA compared with the yield obtained with just **1** were observed in all tests (Table 5). The best result, 81% PPA ($M_w = 66\,900$ Da), was obtained in a reaction carried out with $[{}^n\mathrm{Bu_4N}]\mathrm{Cl}$ (Scheme 6). The data collected in Table 3 point to a noticeable positive effect of chloride versus bromide salts on the reaction yield.

The following activity order of tetraammonium salts used in polymerizations with **1** may be proposed (Table 5):

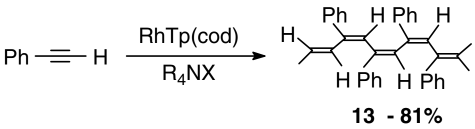
$$[\mathrm{Et_4N}]\mathrm{Br} < [{}^n\mathrm{Bu_4N}]\mathrm{Br} < [\mathrm{Et_4N}]\mathrm{Cl} < [{}^n\mathrm{Bu_4\ N}]\mathrm{Cl}$$

All polymers have similar molecular weights, *ca* 50 000 Da, which is consistent with results obtained for other rhodium catalyst precursors containing cod as a ligand.[11] The polydispersity indexes of the polymers obtained range from 2.0 to 2.7. Application of $Et_3N$ as a co-catalyst in the polymerization reaction of phenylacetylene with rhodium catalysts has been reported by other workers;[5,6,9] therefore, for the sake of comparison, we tested a catalytic system composed of $\mathbf{1} + Et_3N$. The reaction yield increased from 2% with just **1** to 13% PPA for $[Et_3N] : [Rh] = 4$. The molecular weight of the polymer was relatively high (94 400 Da, Table 3), similar to that in other polymerization reactions involving $Et_3N$.[11]

**Table 5.** The phenylacetylene polymerization catalysed with RhTp(cod) (**1**) and addition of tetraammonium halides or $Et_3N$[a]

| $[R_4N]X$ | PPA yield (%) | $M_w$ (Da) | $M_w/M_n$ |
|---|---|---|---|
| — | 2 | — | — |
| $[Et_4N]Cl$ | 28 | 51 400 | 2.0 |
| $[Bu_4N]Cl$ | 81 | 66 900 | 2.3 |
| $[Et_4N]Br$ | 13 | 38 600 | 2.2 |
| $[Bu_4N]Br$ | 25 | 61 500 | 2.7 |
| $NEt_3$ | 13 | 94 400 | 2.1 |

[a] Reaction conditions: 25 °C, $[[R_4N]X] : [Rh] = 4$, $[PhC{\equiv}CH] : [Rh] = 114$, 48 h.



**Scheme 6.**

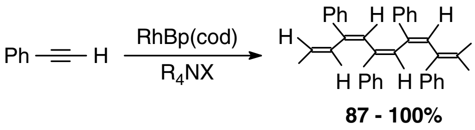
Under the reaction conditions that we applied (25 °C, 24 h), complex **2** catalysed polymerization of phenylacetylene with a 68% yield ($M_w = 11\,700$ Da). The addition of tetraammonium salts increased the yield of the polymerization reactions to 87–100%. The best result, 100% PPA ($M_w = 38\,800$ Da) was obtained for $[Et_4N]Cl$ (Scheme 7, Table 6).

Generally, the polymers obtained in reactions catalysed by RhBp(cod) **2** are of lower molecular weight than those obtained with RhTp(cod) **1**. Polymerization reaction products obtained with **2** and tetraammonium bromides stand out particularly: they are characterized by a low molecular weight ($M_w = 6900$ Da) and a relatively high polydispersity index (3.9). These polymers also show low solubility in chloroform. Tetraammonium halides were found to be attractive co-catalysts for both rhodium catalysts, **1** and **2**. To our knowledge, they had not been used for such purposes before.

## CONCLUDING REMARKS

The results of studies on the application of RhTp(cod) **1** as a polymerization catalyst reported above proved that this compound, inactive itself, became catalytically active when used with ionic liquids and/or ammonium salts as reaction media.

What is a very interesting and practically important result is the discovery of a positive effect of alcohols, both on the polymer yield and on the molecular weight. This



**Scheme 7.**

**Table 6.** The phenylacetylene polymerization catalysed with RhBp(cod) (**2**) and addition of tetraammonium halides[a]

| $[R_4N]X$ | PPA Yield (%) | $M_w$ | $M_w/M_n$ |
|---|---|---|---|
| — | 68 | 11 700 | 2.2 |
| $[Et_4N]Cl$ | 100 | 38 800 | 2.0 |
| $[Bu_4N]Cl$ | 87 | 34 600 | 2.9 |
| $[Et_4N]Br$ | 93 | 6800 | 3.9 |
| $[Bu_4N]Br$ | 94 | 6900 | 3.9 |

[a] Reaction conditions: 25 °C, $[[R_4N]X] : [Rh] = 4$, $[PhC{\equiv}CH] : [Rh] = 114$, 24 h.

phenomenon remained unexplained, because spectroscopic studies ($^1$H and $^1$C NMR) did not make it possible to detect any intermediate species formed *in situ* during the polymerization reaction, nor in the mixture of **1** and [bmim]$BF_4$. In the post-reaction mixtures, only unchanged complexes **1**, **2**, and **3** were identified, and signals of free cod were not observed in $^1$H NMR. This was in contradiction to literature data relating to an iridium polymerization catalyst, where free cod was found in the reaction solution.[14]

Small amounts of the new compound were, however, found in the methanol solution obtained after several catalytic cycles with catalyst **1**. Unlike **1**, this new compound is soluble in methanol and is characterized by rather low symmetry, demonstrated by inequivalence of the three pyrazolyl rings of the tris(pyrazolylborate) ligand. This compound has not been characterized structurally yet, but one may assume that it initiates catalytic polymerization. Its formation and accumulation during the reaction may be responsible for the increase in the activity of the catalyst recovered from the reaction mixture.

## EXPERIMENTAL

The rhodium complexes RhTp(cod), RhBp(cod), and $RhTp^{Me2}$(cod) were prepared according to the literature methods.[15] $CH_2Cl_2$ and $NEt_3$ were purified using standard procedures.[16] $PhC{\equiv}CH$ was purchased and used without purification. Ionic liquids were used as purchased.

### Catalytic procedure

Polymerization reactions were carried out in 50 $cm^3$ Schlenk flasks under a nitrogen atmosphere. In a typical experiment, 0.014 mmol of the catalyst was dissolved in 0.5 $cm^3$ of $CH_2Cl_2$ and 0.2 $cm^3$ (1.82 mmol) of phenylacetylene was added. The mixture was stirred under nitrogen at 25 °C for 24 or 48 h; then, the polymer was precipitated by the addition of methanol (2 $cm^3$), filtered, and dried *in vacuo*.

Polymerization reactions in ionic liquids were carried out in a 30 $cm^3$ thermostated glass reactor under a nitrogen atmosphere. In a typical experiment, 0.014 mmol of the catalyst was stirred in 0.5 $cm^3$ of $CH_2Cl_2$ and 0.5 $cm^3$ of the ionic liquid (or 0.5 g of [bmim]Cl) at 65 °C for 10 min. After this time the rhodium complex was dissolved, $CH_2Cl_2$ was evaporated under a reduced pressure, the reactor was cooled to room temperature, and 0.2 $cm^3$ (1.82 mmol) of phenylacetylene was added. The mixture was heated again to 65 °C and stirred for 30 min or 1 h. The formation of an orange polymer, which was not soluble in the ionic liquid, was observed. After the appropriate reaction time, the mixture was cooled, treated with 4 $cm^3$ of methanol, and the polymer was filtered and dried *in vacuo*.

### Catalyst reuse

The polymer, obtained in reaction in [bmim]Cl, was precipitated from the post-reaction mixture with methanol, separated by filtration, and dried. Methanol and unreacted phenylacetylene were evaporated from the filtrate under vacuum. Next, 0.2 $cm^3$ of phenylacetylene was added to the reactor (containing the catalyst and the ionic liquid), heated, and stirred for 1 h. Then, the reactor was cooled to room temperature and 4 $cm^3$ of methanol was added to precipitate the new portion of the polymer.

Polymer yields were determined by weighing. The number- and weight-average molecular weights ($M_n$ and $M_w$) and polydispersity ($M_n/M_w$) were determined using a Hewlett-Packard gas chromatography–mass spectrometry system ($CHCl_3$ solutions), a refractive index detector, and a Plgel 10 m MIXED-B column.

## Acknowledgements

Grant no PBZ-KBN 15/09/T09/99/01d (KBN, State Committee for Research) is gratefully acknowledged.

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