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Catalytic activity of a half-sandwich Ru(II)-N-heterocyclic carbene complex in the oligomerization of alkynes

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Abstract

The ruthenium(II)-N-heterocyclic carbene complex, [$RuCl_2$(1-butyl-3-methylimidazol-2-ylidene)(*p*-cymene)] selectively catalyzes oligomerization of phenylacetylene (PA) and its derivatives to linear oligomers, containing positively charged imidazolium end-group and uncharged ones. The charged oligomer chain consists of maximum 9–11 PA monomer units after 36 h reaction at 80 °C whereas mainly pentamers are formed as other products. The H_2 atmosphere retards oligomerization of PA and hydrogenation to vinylbenzene and ethylbenzene is observed instead.

Keywords: Ruthenium(II); N-heterocyclic carbene; Phenylacetylene; Alkyne; Oligomerization

1. Introduction

The application of N-heterocyclic carbenes (NHC) as ligands for transition metals led to advances in several important catalytic reactions [1,2]. Fascinating results have been achieved in the area of olefin metathesis [3,4], and in a variety of other reactions such as polymerization [5], hydrogenation [6], hydrogen transfer [7], hydrosilylation [8] and hydroformylation [9]. Since in many cases the NHC – transition metal complexes show enhanced stability and catalytic activity compared to the corresponding phosphine compounds [2,10], there is an interest in detailed studies of their catalytic properties.

The direct coupling of terminal alkynes may result in the formation of enynes of various lengths. Polyvinylenes, as a subclass of conjugated polymers, are generally prepared with the aim to examine their photoelectrical and photonic properties [11], whereas other oligo- and dienynes have found increasing application in natural products synthesis [12]. Terminal alkynes can also be converted into aromatic products by cyclotrimerization process [13,14].

The linking of alkyne building blocks into dimers, cyclotrimers, oligomers and polymers can be carried out with the use of different metal-complexes, however the rate and the regio- and stereo-selectivity of the reaction, as well as the properties of the products, are strongly affected by the applied catalyst and the reaction conditions.

Rhodium complexes containing coordinated diene (e.g. cyclooctadiene (cod), norbornadiene (nbd)) ligands are widely used in alkyne polymerization reactions [15–19]. The polybenzimidazole-supported $[Rh(cod)Cl]_2$ catalyst has been applied to convert substituted acetylenes into readily available high molecular weight polymers without the formation of oligomer side-products [20]. In some cases the reaction conditions have dramatic effect on the polymerization process. While [RhTp(cod)] and [RhBp(cod)] (Tp, tris-pyrazolylborate; Bp, bis-pyrazolylborate) are almost entirely inactive in CH_2Cl_2, they become good catalysts of phenylacetylene polymerization in ionic liquids [21].

A group of effective catalysts include molybdenum complexes. The generation of the 14-electron [(2-$i$$Pr_2PC_6H_4$-$\eta^7$-

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$C_7H_6)Mo(P\text{-}Mo)]^+$ complex in the presence of phenylacetylene gives rise to the corresponding alkyne complex, which can be used for the catalytic oligomerization of phenylacetylene affording, besides linear oligomers, predominantly the 1,3,5- and 1,2,4-triphenylbenzene cyclotrimers [22]. Other molybdenum catalysts, such as the dinuclear $[Mo_2Cl_4(MeOH)_2(PPh_3)_2]$ complex show medium activity in the coupling of phenylacetylene, however, these reactions lead to a mixture of cyclotrimers and oligomers [23].

The solvent-free reaction of phenylacetylene in the presence of nickelocene ($[(\eta\text{-}Cp)Ni(CO)]_2$, $[(\eta\text{-}Cp)Ni(PPh_3)]Cl$, etc.) gives rise to a mixture of cyclotrimers, linear oligomers and polyphenylacetylene. Lower reaction temperatures favour linear oligomer and polymer formation [24].

The application of a palladium/imidazolium chloride system for the dimerization of alkynes has been reported, where the catalytically active Pd-carbene was prepared in situ from $Pd(OAc)_2$ and IMes.HCl in the presence of Cs_2CO_3 as a base [25].

Recently, several ruthenium alkylidene complexes have been found highly active in the polymerization of acetylenes [26–30]. More generally, however, ruthenium catalysts transform alkynes to di- or oligoenynes. The reactions of alkynes with the substitutionally labile pseudo 14e complexes RuCp′(cod)Cl (Cp′ = Cp or Cp*) and with the cationic complexes $[CpRu(CH_3CN)_2L]^+$ and $[Ru(\eta^5\text{-}C_5H_4CH_2CH_2\text{-}\kappa^1P\text{-}PPh_2)]^+$ were studied in much detail [31]. The $[CpRu(CH_3CN)_3]^+$ complex catalyzes cyclotrimerization of alkynes with preference of 1,2,4-trisubstituted arene, however the reaction was quenched because of the formation of inactive ruthenium sandwich arene complexes [32]. The μ-methylene complex, $[Ru_2(\mu\text{-}CH_2)(CO)_4(\mu\text{-}dppm)_2]$ (dppm: $Ph_2PCH_2PPh_2$) catalyzed the selective dimerization of $PhC{\equiv}CH$ to give the head-to-tail dimer. In the case of a large excess of phenylacetylene, further oligomerization occurred, and the major products were identified as a hexamer and octamer [33]. The $[C_5Me_5Ru(L)H_3]$ (L = PPh_3, PCy_3, PMe_3) ruthenium hydride complexes were also found to catalyze the dimerization of terminal alkynes to produce *cis*- and *trans*-1,4 and 1,3 disubstituted enynes [34].

1,10,15,20-Tetraphenylporphirinato ruthenium(II) carbonyl, Ru(TTP)(CO), catalyzes cyclooligomerization of arylethynes in ionic liquids to naphthalene derivatives as the main reaction products [35].

Ruthenium complexes of the type Cp*Ru-[C(R)N(H)C=C(H)N(R)]Cl were active in the dimerization of terminal alkynes and their selectivity was strongly influenced by the substituents of the N-heterocyclic carbene ligand [36].

We have recently reported the synthesis and characterization of a new water soluble ruthenium(II)-N-heterocyclic carbene complex ($[RuCl_2$(1-butyl-3-methylimidazol-2-ylidene)(*p*-cymene)]) (**1**) (Fig. 1), which catalyzed the hydrogenation of a variety of olefines, aldehydes and ketones and the redox isomerization of allyl alcohol in aqueous solutions under mild conditions [37].

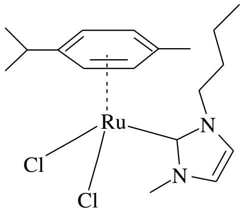


Fig. 1. The structure of ($[RuCl_2$(1-butyl-3-methylimidazol-2-ylidene)(*p*-cymene)]) (**1**).

It has been shown that the monohydroxo and dihydroxo species formed by hydrolysis in the aqueous solutions of **1** are stable in a wide pH range (2–12), and the ruthenium–carbene carbon bond is not effected by water [37].

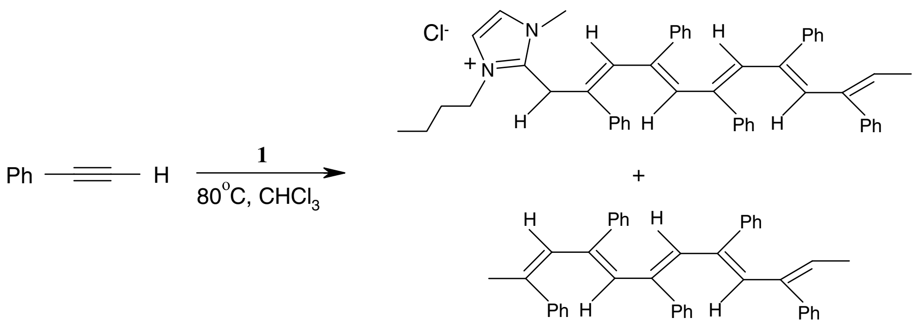
Here we report on the homogeneous catalytic oligomerization of phenylacetylene and its derivatives in the presence of **1**, and the structural changes of **1** observed during oligomerization and hydrogenation reactions. In the former case the Ru(II) complex not only acts as a catalyst, but also as a source of the oligomer end group. These reactions are the first examples of ruthenium–carbene catalyzed alkyne oligomerizations, giving rise mainly to the formation of linear oligomers. Polymerization products were not observed and the yield of cyclotrimers was lower than 2%.

2. Results and discussion

In the course of the oligomerization of phenylacetylene (PA) catalyzed by **1** the initially yellowish-brown solution became dark brown, indicating significant changes in the structure of the catalyst. The newly formed PA oligomers were detected by means of ESI-MS, which revealed that **1** not only catalyzed the oligomerization process, but provided the positively charged imidazolium end-group, as well (Scheme 1).

On the basis of ^1H NMR measurements carried out in $CDCl_3$ solutions containing the catalyst and the alkyne substrate in a 1:1 ratio it was concluded, that upon heating the carbene ligand migrates to a PA molecule coordinated to **1** and a new C–C bond is formed (Fig. 2). The coupling of the next PA molecules (insertion into Ru–C bond) led to the oligomer containing a 1-butyl-3-methylimidazolium end-group with a chloride counter ion. Due to the presence of the positive charge on the end-group the oligomers are conveniently detected by mass spectrometry. ^1H NMR signals originating from free 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) were not observed in reaction mixture which confirms that the reaction proceeds in the coordination sphere of **1**.

Fig. 2 presents ^1H NMR spectra measured during oligomerization of PA in the presence of **1**. The most characteristic changes are observed in the region of the carbene C–H protons of the NHC-ligand, at ca. 7 ppm. During the reaction the intensity of two signals at 6.99 and 7.03 ppm decreased whereas a new signal appeared at 7.08 ppm. This new signal can be attributed to two protons



Scheme 1. The structure of oligomers formed from PA in the presence of **1**.

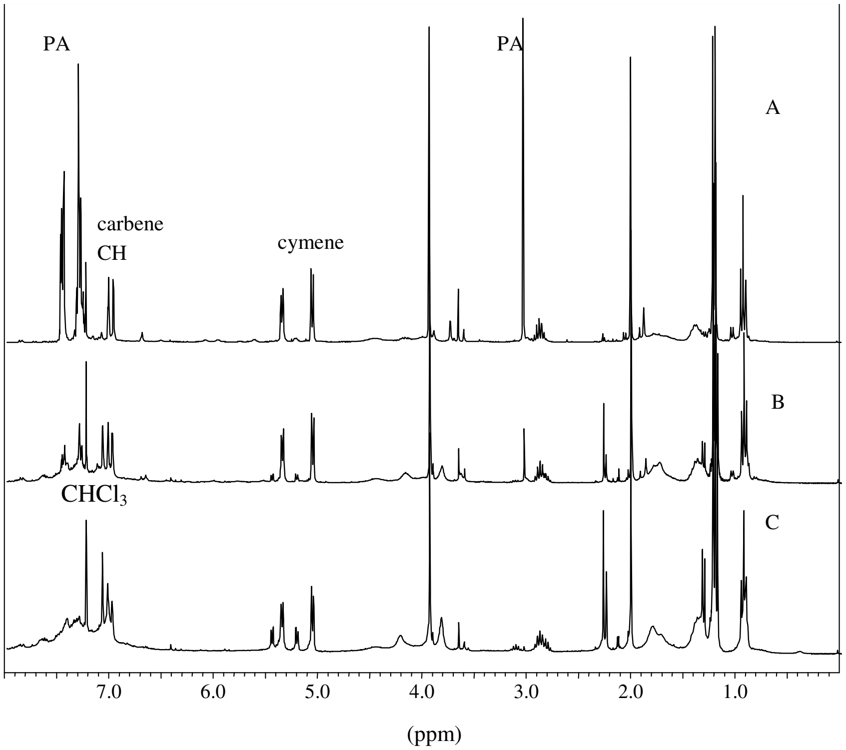


Fig. 2. ^{1}H NMR spectra of the reaction mixture containing **1**:PA = 1:1 in $CDCl_3$. [Ru] = 3×10^{-2}M. (A) Before the reaction; (B) after 10 h in RT; (C) sample B after 2 h heating at 60 °C. Assignment of all signals of **1** is given in [37].

of imidazolium cation which became equivalent as a result of positively charged oligomer formation.

In addition ^{13}C NMR spectrum shows a shift of carbene-C signal of the NHC-ligand from 173.17 to 172.97 ppm. The formation of oligomer in this sample was confirmed by ESI-MS measurement in which a high intensity peak appeared at $m/z = 240$, as expected for $[BMIM + PA]^+$.

The excess of added [BMIM]Cl (C = 0.15 M) has no significant effect on either the conversion or the length of the oligomer chains formed in the process. This observation shows that the imidazolium end group originates exclusively from **1**, whereas the coupling between PA and free [BMIM]Cl is not favoured under these conditions. The fundamental role of ruthenium was confirmed by the reaction of PA with the highly reactive silver carbene complex [38] obtained in situ in the reaction of [BMIM]Cl with Ag_2O in which oligomers were not formed.

The *p*-cymene signals of **1** were slightly shifted during the reaction, however, new signals characteristic to free *p*-cymene were not observed. On the basis of these findings it is assumed that the *p*-cymene ligand remains attached to the ruthenium during the catalytic process. The oligomer chains eventually consist of maximum 9–11 PA monomer units after a 36-h reaction (Fig. 3).

The oligomers have *trans* head-to-tail structure, since the characteristic signal of *cis* olefin protons of polyphenylacetylene at δ 5.8–5.9 was not detected in ^{1}H NMR spectra [39], whereas at the same time, a broad signal between δ 6.8 and 7.7 was observed, suggesting the existence of the *trans* isomer [40] (Fig. 2).

Analysis of the reaction mixture with application of GC–MS and HPLC methods showed the presence of

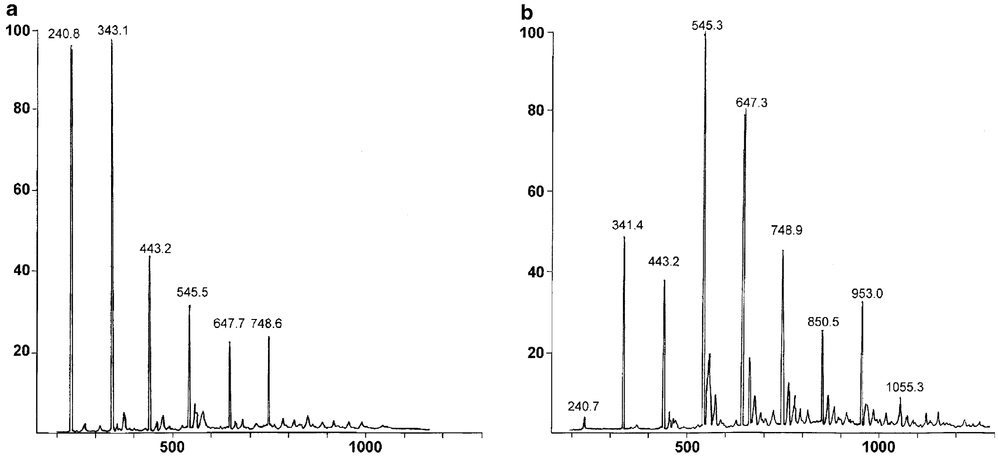


Fig. 3. ESI-MS spectra obtained after 6.5 h (a) and 36 h (b) oligomerization reaction of PA in the presence of **1**. $[Ru] = 3 \times 10^{-3}$ M, $[PA] = 0.3$ M, $T = 80$ °C, $CHCl_3$. 240: $[BMIM + PA]^+$, 343: $[BMIM + 2PA]^+$, 443: $[BMIM + 3PA]^+$, 545: $[BMIM + 4PA]^+$, 647: $[BMIM + 5PA]^+$, 748: $[BMIM + 6PA]^+$, etc.

uncharged oligomers, formed besides of charged ones identified with ESI-MS method. 1,2,4-Triphenylbenzene was identified with GC–MS in amount not exceeded 2% of PA total conversion. The low yield of cyclotrimer is surprising since PA easily forms cyclotrimers and also decompose under relatively mild conditions [41–46]. HPLC analysis indicated the presence of pentamers of average M_w estimated as 520, which are the main reaction products under applied reaction conditions ([PA]:[Ru] = 100). Their formation can be attributed to the activity of 16 electron complex formed after breaking the Ru(II)–C bond. It can be proposed, that the catalytic process starts with insertion of PA into Ru–C bond and formation of charged oligomers. Next, Ru–C bond is broken, and the new 16 electron species formed reacts with PA producing uncharged linear oligomers and trace amount of cyclotrimer.

The addition of MeOH to the post reaction solutions, generally used to precipitate PPA from organic solvents, did not produce any changes, what proves an evidence against polyphenylacetylene (PPA) formation [21].

Tolylacetylene (1-ethynyl-4-methylbenzene – TA), differing only in one methyl-group from PA was also successfully applied in oligomerization reactions (Fig. 4). It is seen from the spectrum that a 6.5-h reaction produces oligomers consisting of 2–7 monomer units and the imidazolium end-group. **1** Undergoes similar structural changes as observed in the reaction with phenylacetylene.

Interestingly, when other substrates, such as trimethylsilyl-acetylene, 1-ethynyl-cyclohexene and 1-hexyne were used under the same reaction conditions, no oligomerization occurred. Internal alkynes (e.g. diphenylacetylene – DPA) also proved to be inappropriate substrates for **1**.

It turned out thereafter, that significant conversions can exclusively be detected applying phenylacetylene derivatives. In Table 1, the reactivities of some substrates are listed. It is seen from Table 1 that the highest conversion (65%) and TOF (10.1 h^{-1}) at 3×10^{-3} M of **1** were determined when PA was used as a substrate. The reactivity of the studied alkynes toward oligomerization depends on the size and the number of the substituents present on the aromatic ring. The smaller the size, the higher yields are detected. This phenomenon is explained simply by

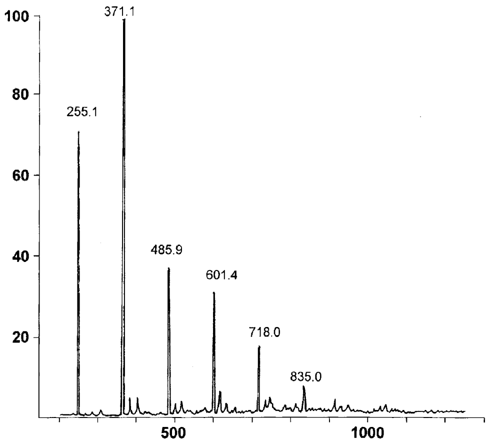


Fig. 4. ESI-MS spectrum obtained in the oligomerization reaction of TA in the presence of **1**. $[Ru] = 3 \times 10^{-3}$ M, $[TA] = 0.3$ M, $T = 80$ °C, $t = 6.5$ h $CHCl_3$. 255: $[BMIM + TA]^+$, 371: $[BMIM + 2TA]^+$, 486: $[BMIM + 3TA]^+$, 601: $[BMIM + 4TA]^+$, 718: $[BMIM + 5TA]^+$, 835: $[BMIM + 6TA]^+$, 951: $[BMIM + 7TA]^+$.

Table 1
Catalytic activity of **1** in the oligomerization reactions of various phenylacetylene derivatives

Substrate	Conversion (%)	TOF (h^{-1})[a]	M_w[b] (Da)
Phenylacetylene (PA)	65	10	399
1-Ethynyl-4-methylbenzene (TA)	49	8	418
1-Ethynyl-3-methylbenzene	50	8	663
2-Ethynyl-1,4-dimethylbenzene	41	6	562
1-Ethynyl-4-pentylbenzene	17	3	585
3-Chloro-1-ethynylbenzene	44	7	538

$[Ru] = 3 \times 10^{-3}$ M, $[PA] = 0.3$ M, $T = 80$ °C, $t = 6.5$ h, $CHCl_3$.

[a] In units of mol of converted substrate (mol of catalyst)$^{-1}$ (time)$^{-1}$.

[b] Average molecular weight of charged oligomers.

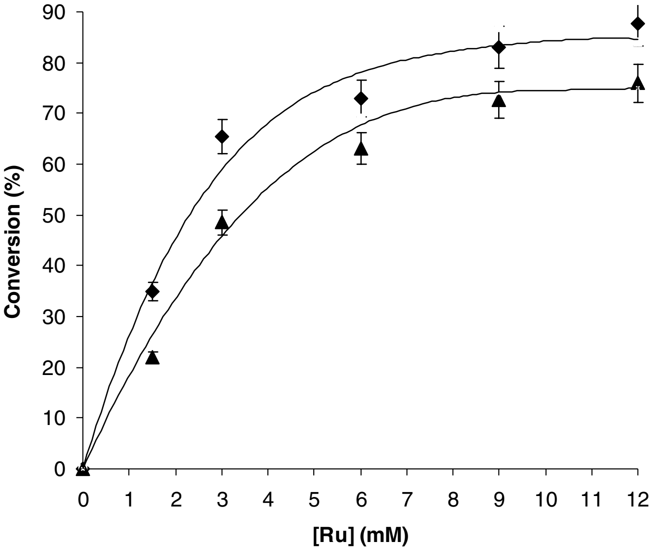


Fig. 5. The effect of the catalyst (**1**) concentration on the oligomerization of PA (◆) and TA (▲) [substrate] = 0.3 M, $T = 80$ °C, $t = 6.5$ h, $CHCl_3$.

steric effects, since the vicinity of bulky groups in the oligomer chains is energetically unfavorable. For instance, the presence of the bulky pentyl group in 1-ethynyl-4-pentylbenzene allows a conversion of only 17%, which is almost three times less than it is obtained in the reaction of 1-ethynyl-4-methylbenzene or 1-ethynyl-3-methylbenzene having small methyl groups attached to the aromatic ring (Table 1). The reactivity of 2-ethynyl-1,4-dimethylbenzene holding two methyl groups is also somewhat lower than that of the previously mentioned two methylbenzene species.

The rates of the oligomerization of PA and TA were studied as the function of the catalyst concentration under the same conditions (Fig. 5). TA proved to be less reactive than PA at all catalyst concentrations. This can be rationalized considering that TA is somewhat bulkier than the non-substituted phenylacetylene. In the low catalyst concentration region conversions increase linearly with increasing catalyst concentrations, and level off around 70–80% conversions at higher catalyst loadings.

The oligomerization reaction of PA was also studied under hydrogen atmosphere in the presence of **1**. It is concluded that the presence of hydrogen favours the hydrogenation of the triple bond resulting in the formation of a mixture of vinylbenzene and ethylbenzene, however dimerization, oligomerization or polymerization of phenylacetylene cannot be detected. When the reaction was carried out at 10 bar hydrogen pressure and 80 °C for 3 h, almost all PA was hydrogenated (43.8% $Ph{-}CH{=}CH_2$ and 54.3% $Ph{-}CH_2{-}CH_3$), whereas at atmospheric H_2 pressure conversions were significantly lower (6.5% $Ph{-}CH{=}CH_2$ and 17.7% $Ph{-}CH_2{-}CH_3$).

3. Conclusions

The $[RuCl_2$(1-butyl-3-methylimidazol-2-ylidene)(p-cymene)] (**1**) complex selectively catalyzes the oligomerization of phenylacetylene derivatives, and provides the positively charged 1-butyl-3-methylimidazolium end-group, whereas the *p*-cymene ligand of **1** remains coordinated to the ruthenium in the process. The rate of oligomerization depends on the size of the substrate. Bulky substrates undergo less conversions under the same conditions. In the absence of hydrogen exclusively oligomerization is observed while its presence allows the hydrogenation of the triple bond of the alkyne substrates and does not favour the formation of oligoenynes.

4. Experimental

All manipulations were carried out in air without previous evacuation of the reaction vessels. Phenylacetylene (PA), diphenylacetylene (DPA), 1-ethynyl-4-methylbenzene (tolylacetylene, TA), 1-ethynyl-3-methylbenzene, 1-ethynyl-4-pentylbenzene, 2-ethynyl-1,4-dimethylbenzene, 3-chloro-1-ethynylbenzene and 1-hexyne were purchased from Aldrich and used directly without any purification. Solvents were used as received, except tetrahydrofurane (THF), which was distilled before application.

1 was prepared by the carbene transfer methodology [38] from $[\{RuCl_2(p\text{-cymene})\}_2]$ and 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) according to the method described in our previous paper [37].

Oligomerization reactions were performed in NMR tubes. 0.5–4 mg (1.13–9.01 μmol) catalyst (**1**) and 0.23 mmol substrate were dissolved in 0.75 mL $CDCl_3$. 18.3 μl (0.23 mmol) THF was used as an internal standard. NMR tubes containing the reaction mixtures were closed, sealed with parafilm and their ^1H NMR spectra were recorded. The tubes were then placed into an oil bath and kept at 80 °C for 6.5 or 36 h, respectively. After the reaction solutions were cooled, ^1H NMR data were collected again. Conversions were calculated by comparing the integrals of the $-CH_2$ signals of the standard and the $-C{\equiv}C-H$ signals of the alkyne compounds before and after the oligomerization process. The $CDCl_3$ solutions of the oligomers were directly analyzed by ESI-MS. The catalytic experiments performed without THF, with TMS as an internal standard gave similar results. This allowed to exclude the important role of THF in studied reactions. For comparison conversions were also determined by GC using toluene as an internal standard. The differences between results obtained by both methods (NMR and GC) did not exceed 5% and average values are given in Table 1. 1,2,4-Triphenylbenzene was identified using HP 5890 II – 5971 A GC–MS equipment and its yield was determined by GC. Oligomers were identified by HPLC method using Hewlett-Packard system, a refractive index detector, and a Plgel 10 m MIXED-B column. Polystyrene samples of known M_w were used for standardization.

The reaction of **1** with phenylacetylene (PA) and tolylacetylene (TA) was investigated in solutions containing the catalyst and the alkyne in a ratio of 1:1. 10 mg (22.52 μmol) catalyst (**1**) was dissolved in 0.75 mL $CDCl_3$, and 12.35 (PA) or 14.25 (TA) μL (22.52 μmol) of the substrate and 18.3 μL (0.23 μmol) of the internal standard (THF) were added. The resulting solutions were heated in an oil bath at 80 °C for 18 h. ^{1}H NMR spectra were recorded before and after the reactions. Reactions performed without THF (with TMS as a standard) gave the same results.

Hydrogenation reactions of PA were carried out in a teflon coated autoclave. In a typical reaction 74 μL (0.68 mmol) PA and 1.5 mg (3.38 μmol) catalyst were taken up in 1.5 mL $CDCl_3$. The solutions were stirred for 3 h at 80 °C and 10 bar hydrogen pressure. The volatiles were pumped off the catalyst and collected at liquid N_2 temperature; the obtained clear solutions were directly analyzed by GC–MS.

Nuclear magnetic resonance spectra were recorded at ambient temperature on a Bruker AMX 300 instrument. Mass spectra were obtained on a Finnigan Mat TSQ 700 ESI mass spectrometer equipped with a high voltage electron multiplier detection system. The conversions in the hydrogenation of phenylacetylene (PA), and the identity of the products were determined using a HP 5890 II – 5971A GC–MS equipment (column: HP5, programmed heating 70–200 °C, 25 °C/min).

Acknowledgements

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