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Selective dimerization of terminal acetylenes in the presence of PEPPSI precatalysts and relative chloro- and hydroxo-bridged *N*-heterocyclic carbene palladium dimers

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ABSTRACT

Highly regio- and stereoselective dimerization of terminal acetylenes occurs in the presence of [$PdCl_2$(IPr)(3-chloropyridine)], other members of the family of PEPPSI precatalysts and the structurally related *N*-heterocyclic carbene palladium dimers, i.e. [{Pd(μ–Cl)Cl(IPr)}$_2$] and [{Pd(μ–OH)Cl(IPr)}$_2$] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene). The reaction leads to exclusive formation of *E*-isomer of head to head dimerization product. [{Pd(μ–OH)Cl(IPr)}$_2$] catalyzes dimerization of a broad spectrum of aryl- and silylacetylenes at room temperature and is able to act in base-free conditions.

1. Introduction

1 The catalytic dimerization of terminal acetylenes is an attractive method for the preparation of disubstituted 1,3-enynes (Scheme 1) [1]. Conjugated enynes are of great importance in organic synthesis [2], medicinal chemistry [3] and material sciences [4]. In general, catalytic alkyne dimerization produces a mixture of regio- or stereoisomeric enyne products (Scheme 1) [1]. In some systems formation of disubstituted buta-1,2,3-trienes has been also observed [1a,5].

A variety of catalytic systems using various transition metals [4], main group elements [6] and lanthanides [7] have been reported over the past few decades. However, there is a limited number of systems enabling nearly exclusive formation (selectivity exceeding 99%) of single isomers **I** [4c,8], **II** [7d-f,9] or **III** [10] (Scheme 1). Therefore, the search for new active systems permitting fully selective formation of single isomers for a wide range of acetylenes at the highest possible catalytic activity is highly desirable.

Within the catalytic systems based on transition metals, numerous palladium complexes have been found to promote dimerization of terminal acetylenes with relatively high activity and selectivity. Palladium based catalytic systems have been reported to enable efficient synthesis of both head to head [1,8i,11] and head to tail dimers [1,12]. Pd-catalyzed head to head dimerization of terminal alkynes usually leads to mixtures of stereoisomeric 1,4-disubstituted enynes (**I** and **II**, Scheme 1).

The use of *N*-heterocyclic carbene complexes contributed to further progress in catalysis of the reaction. In 2001 Herrmann reported that diiodo(triphenylphosphine){1,3-di[(R)-1-phenylethyl]imidazol-2-ylidene}palladium(II) are able to catalyze dimerization of phenylacetylene [13]. Nolan has used $Pd(OAc)_2$ in combination with different imidazolium chlorides in dimerization of high range of terminal aryl- and aliphatic terminal alkynes and shown the dependence of selectivity on steric bulk of NHC precursors used. In the catalytic system $Pd(OAc)_2$/imidazolium chloride/Cs_2CO_3, significant selectivity toward isomer *trans* of head to head dimerization product was observed when precursors of steric IMes (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) or IPr (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) ligands were used [14]. The catalytic system $Pd(OAc)_2$/SIMes·HCl/Cs_2CO_3 permits *E*-selective head to head polyaddition of 2,7-diethynyl-9,9-dioctylfluorene [4c]. Gevorgyan has proposed highly regio- and stereoselective palladium-catalyzed head-to-head dimerization reactions of a high variety of terminal acetylenes. The use of palladium complex [$Pd(IPr)_2$] in the presence of electron-rich

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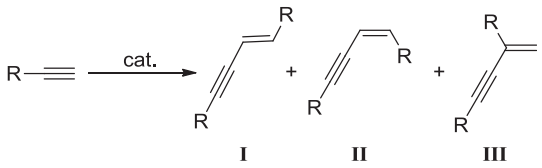
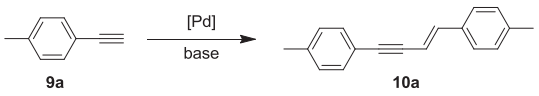


Scheme 1. Dimerization of terminal alkynes.



Scheme 2. Dimerization of 4-tolylacetylene.

and bulky phosphine TDMPP (TDMPP = P[(2,6-OMe)$_2$C$_6$H$_3$]$_3$) permitted dimerization of terminal acetylenes leading to exclusive formation of *E*-isomers of head to head dimers. This reaction has been demonstrated via PDF calculations to proceed via hydropalladation pathway [8e]. Analogous selectivity has been observed by using a number of *N*-heterocyclic carbene palladium complexes [15]. Recently, Nechaev has shown that cinnamyl palladium chloride complex [PdCl(cinnamyl)(SIPr)] [where SIPr = 1,3-bis(2,6-diisopropylphenyl)-(4,5-dihydroimidazol-2-ylidene)], used in the presence of KOH as a base, permitted efficient, regio- and stereoselective dimerization of terminal arylalkynes under mild conditions [8c].

In 2005, Organ described a structurally defined group of [PdCl$_2$(NHC)(pyridine)] complexes, the so-called PEPPSI precatalysts (Pyridine-Enhanced Precatalyst Preparation Stabilization and Initiation) [16]. These precatalysts exhibit attractive catalytic properties in a number of coupling processes [17]. Despite numerous literature reports regarding the activity of palladium complexes of the PEPPSI type in a number of C-C bond forming reactions, there are no reports on their use in the dimerization of terminal acetylenes.

Herein we report on the high catalytic activity of a series of PEPPSI precatalysts (1–6, Fig. 1) and relative dimeric chloro- and hydroxo-bridged complexes (7 and 8, Fig. 1) in homo-dimerization of aryl- and silylacetylenes. We provide convenient procedures of efficient, regio- and stereoselective synthesis of *E*-1,4-disubstituted but-1-en-3-ynes.

2. Results and discussion

As a model reaction, we have chosen homo-dimerization of 4-tolylacetylene, a reagent widely tested in the study of this reaction, which makes it possible to compare the results obtained with literature data. The reactant has a relatively high boiling point, which allows the reaction to be studied over a wide temperature range, while the presence of methyl groups permits a convenient analysis of the reaction mixture by ^{1}H NMR spectroscopy. Treatment of 4-tolylacetylene with 5 mol% of PEPPSI-IPr (**1**) at 75 °C for 24 h does not lead to any transformation. The addition of the one equivalent of KO^{t}Bu (with respect to the catalyst) led only to a trace conversion. In the presence of 4 equiv. of KO^{t}Bu an immediate change in color from yellow to orange and then brown was observed and the GC analysis of the reaction mixture performed after one hour of the reaction course indicated complete conversion of the reagent and formation of a single product, which was afterwards identified by ^{1}H NMR spectroscopy as (*E*)-1,4-bis(4-methylphenyl)-but-1-en-3-yne (Scheme 2).

A similar efficient course of the reaction was also observed in the presence of an excess of other bases. Optimization experiments permitted specification of conditions of effective and selective course of the reaction (Table 1).

Complete conversion was observed when the reaction was performed in toluene at 60 °C for 1 h by using 1 mol% of complex **1** and the presence of four equivalents of KO^{t}Bu relative to the catalyst. From among all bases tested the highest yields were achieved in the presence of KO^{t}Bu and Cs_2CO_3. Efficient conversion requires the presence of a fourfold molar excess of the base in relation to complex **1**. The reaction must be performed in an inert atmosphere as otherwise competitive oxidative coupling of acetylenes is observed. It has been found that the use of non-dried toluene promotes the course of the reaction. The addition of 10 μL of water to dry and degassed toluene (2 mL) enabled practically quantitative yields at the loading of complex **1** reduced down to 0.5 mol% (Table 1, entry 14). Because in the presence of water, KO^{t}Bu undergoes hydrolysis, another test another test was carried out, in which KOH was used instead of KO^{t}Bu. Also in this case, the quantitative yield of the product was observed (entry 15). The efficiency of the process in the presence of water can be explained by the improved solubility of KOH in the reaction medium. Performance of the reaction in such solvents as hexane or THF enables high conversion, but the reaction leads to mixtures of isomers

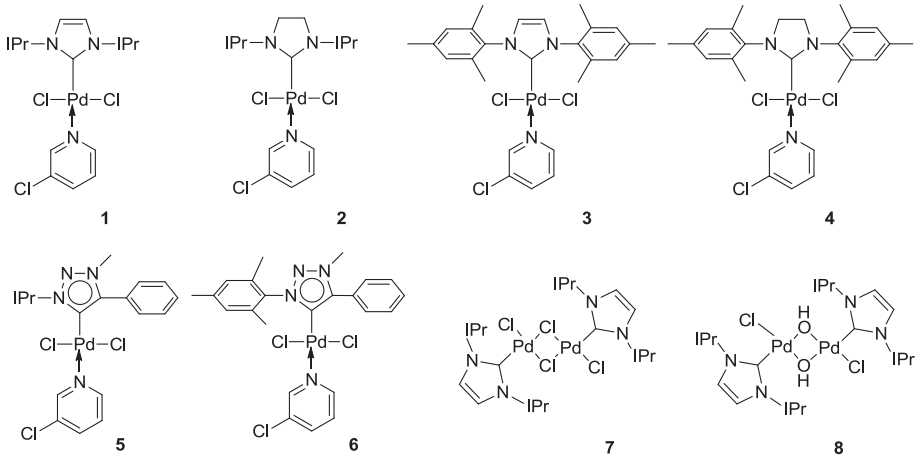


Fig. 1. PEPPSI precatalysts and related dimeric complexes tested in dimerization of terminal acetylenes.

Table 1
Dimerization of 4-tolylacetylene in the presence of PEPPSI-IPr (**1**). Optimization of the reaction conditions.

Entry	Solvent/T [°C]	Cat.**1** [mol%]	Base ([Pd]/[base])	Time [h]	Conv. [%][a]	*E/Z/gem*[b]
1	toluene/75	5	–	24	0	-
2	toluene/75	5	KO^{t}Bu (1/1)	24	<5	*E*
3	toluene/75	5	KO^{t}Bu (1/2)	24	55	*E*
4	toluene/75	5	KO^{t}Bu (1/3)	1	93	*E*
5	toluene/75	5	KO^{t}Bu (1/4)	1	>99	*E*
6	toluene/75	5	Cs_2CO_3 (1/4)	24	99	*E*
7	toluene/75	5	K_2CO_3 (1/4)	24	80	*E*
8	toluene/75	5	AgOAc (1/4)	24	52	*74/0/26*
9	toluene/75	5	KOH (1/4)	6	82	*E*
10	toluene/60	5	KO^{t}Bu (1/4)	1	>99	*E*
11	toluene/45	5	KO^{t}Bu (1/4)	1	>80	*E*
12	toluene/60	1	KO^{t}Bu (1/4)	1	>99	*E*
13	toluene/60	0.5	KO^{t}Bu (1/4)	**6**	92	*96/0/4*
14	toluene/60	0.5	KO^{t}Bu (1/4)	1	>99[c]	*E*
15	toluene/60	0.5	KOH (1/4)	1	>99[c]	*E*
16	toluene/60	0.1	KO^{t}Bu (1/10)	24	70	*95/0/5*
17	hexane/60	0.5	KO^{t}Bu (1/4)	6	89	*92/0/8*
18	THF/60	0.5	KO^{t}Bu (1/4)	6	94	*78/0/12*
19	EtOH/60	0.5	KOH (1/4)	1	93	*E*
20	EtOH/60	0.5	KOH (1/4)	1	>99[c]	*E*
21	EtOH/60	0.25	KOH (1/4)	24	57	*E*
22	EtOH/22	0.5	KOH (1/4)	24	54	*E*

Reaction conditions: solvent (2 mL), argon.
[a] Determined by GC analysis.
[b] Determined by ^{1}H NMR spectroscopy of the crude reaction mixture.
[c] 10 μL H_2O was added to reaction mixture.

(Table 1, entries 17 and 18). High conversion and selective course of the reaction was observed by using ethanol as a solvent and KOH as a base (entry 20). In this case, the efficient progress of the reaction was observed at 60 °C, at catalyst loading of 0.5 mol% and in the presence of four equivalents of the base (relative to the catalyst). In the presence of silver acetate as a base, a decrease in selectivity and the formation of a mixture of regioisomers is observed (entry 8). Such phenomenon has been previously described and explained by Gevorgyan and Ananikov [15]. Lowering the concentration of complex **1** in the reactions performed in toluene in the presence of KO^{t}Bu, results in a slight decrease in the selectivity of the reaction. The formation of small amounts of head to tail dimer under the conditions of reduced reaction rates can be the result of the competitive reaction pathway, in which O^{t}Bu$^-$ plays the similar role to that described by Gevorgyan and Ananikov for carboxylate anion [15]. In the optimized reaction conditions, the activity of complex **1** was compared with that of selected members of the family of PEPPSI complexes as well as structurally related chloride (**7**) [18] and hydroxide dimers (**8**) [19] (Fig. 1). Results are collected in Table 2.

In the presence of catalysts **1**–**3** and **8**, high acetylene conversion and exclusive formation of *E*-isomer of head to head dimer (**10a**) was observed (Scheme 2).

Table 2
Dimerization of 4-tolylacetylene. Comparison of different palladium catalyst (**1**–**8**).

Entry	Cat.	Time [h]	Conv. [%][a]	*E/Z/gem*[b]
1	**1**	1	>**99**	**100/0/0**
2	**2**	1	90	100/0/0
3	**3**	1	94	100/0/0
4	**4**	1	95	80/3/4
5	**5**	24	0	–
6	**6**	24	0	–
7	**7**	1	94	96/4/0
8	**8**	1	>**99**	**100/0/0**

Reaction condition: toluene, 60 °C, [Pd] (1 mol %), [Pd]/[KO^{t}Bu] = 1/4, argon.
[a] Determined by GC analysis.
[b] Determined by GC/MS and ^{1}H NMR spectroscopy of the crude reaction mixture.

Under the conditions used, no catalytic activity of complexes **5** and **6** was observed. For complex **4** and chloride dimer **7** high conversions were observed (95%) but the reactions proceeded to form a mixture of isomers (Table 2, entries 4 and 7). In order to precisely identify the difference in activities of complexes **1**, **7** and **8**, the course of dimerization over time was investigated. The reaction profiles obtained are shown in Fig. 2 and indicate that complex **8** enables complete conversion already after 15 min of the reaction. In the presence of complexes **1** and **7** full conversion was observed after approx. 1 h of the reaction. In the initial stage of the reaction, dimer **7** exhibited higher activity than complex **1**.

The high activity of complex **8** prompted us to look for optimal reaction conditions in the presence of this catalyst. Results are collected in Table 3.

Complex **8** was found to exhibit activity in base-free conditions, however, high catalyst loading (7 mol%) was required to get quantitative conversion. The use of four equivalents of the base relative to **8** ([Pd]/[KOH] = 1/4) allowed efficient progress of the reaction at a catalyst loading down to 0.25 mol%. The use of ethanol as a solvent and excess of KOH allows the reaction to proceed at room temperature in the presence of 0.25 mol% of catalyst.

Optimization tests (Tables 1 and 3) permitted specification of the conditions for efficient progress of the reaction in the presence of catalysts **1** and **8**. In selected optimized reaction conditions dimerization of a series of arylacetylenes was tested to determine the versatility of the method. The results are shown in Fig. 3.

For all the arylacetylenes tested, nearly quantitative yields of products were obtained. The slight differences in catalytic activity of both palladium complexes tested were observed for more sterically congested acetylenes. In the dimerization of 1-ethynylnaphthalene, 9-ethynylphenanthrene and 4-ethynylbiphenyl catalyzed by **1**, efficient conversion required extension of the reaction time. ^{1}H NMR analyzes of the reaction mixtures made after completion of the reaction showed in each case the exclusive formation of head to head dimers with *E* geometry around the double bond. Only in the case of phenylacetylene and 9-ethynylphenanthrene, formation of up to 3% of the *Z*-isomer was observed.

Table 3
Dimerization of 4-tolylacetylene in the presence of [{Pd(μ-OH)Cl(IPr)}$_2$] (**8**). Optimization of the reaction conditions.

Entry	Solvent/T [°C]	Cat. **8** [mol %]	[Cat.]/[KOH]	*T* [h]	Conv. [%][a]	*E*/*Z*/*gem*[b]
1	toluene/60	7	–	24	72	100/0/0
2[c]	toluene/60	0.5	–	24	–	–
3[c]	toluene/60	1	–	24	<5	100/0/0
4[c]	toluene/60	2	–	24	35	100/0/0
5[c]	toluene/60	5	–	24	93	100/0/0
6[c]	toluene/60	7	-	24	>99	100/0/0
7[c]	toluene/60	0.5	1/4	1	>99	100/0/0
8[c]	toluene/60	0.25	1/4	1	>99	100/0/0
9	EtOH/60	0.25	1/4	1	95	100/0/0
10[c]	EtOH/60	0.25	1/4	1	>99	100/0/0
11[c]	EtOH/60	0.1	1/4	24	91	100/0/0
12[c]	EtOH/22	0.25	1/4	2	>99	100/0/0

[a] Determined by GC analysis.
[b] Determined by ^{1}H NMR spectroscopy on the crude reaction mixture.
[c] 10 μL H_2O was added to reaction mixture.

Further determination of the scope of the reaction revealed the reactivity of terminal silylacetylenes. The catalytic tests performed showed completely regio- and stereoselective course of the reaction (Scheme 3). Table 4 summarizes the results of optimization tests for dimerization of triethylsilylacetylene.

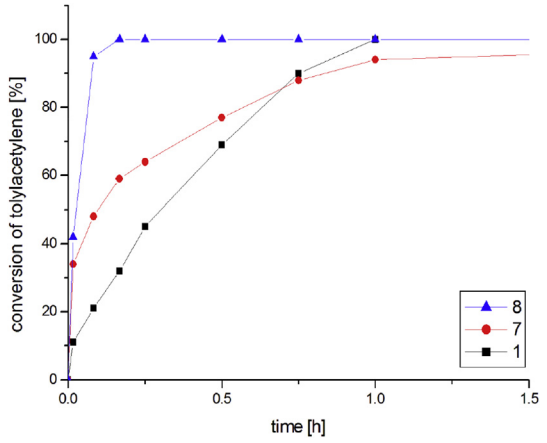
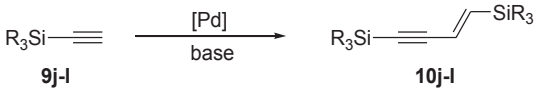


Fig. 2. Reaction profiles. Dimerization of 4-tolylacetylene in the presence of complexes **1**, **7** and **8**. Reaction conditions: toluene 2 mL, 4-tolylacetylene 0.017 mmol, 60 °C, [Pd] (1 mol%), [Pd]/[KO^{t}Bu] = 1/4, argon.

Efficient course of silylacetylene dimerization requires higher catalyst concentrations (up to 2 mol%) and longer reaction times. A drop in selectivity and formation of a mixture of stereoisomers was observed when the reaction was run at temperatures exceeding 100 °C. Effect of the addition of small amounts of water was found to improve the reaction efficiency (compare entries 6 and 7, 8 and 9) as it was observed for dimerization of arylacetylenes. The use of ethanol as a solvent and KOH as a base allows the reaction to proceed at room temperature.

Under optimized reaction conditions, high yield and completely selective course of reaction were observed (Fig. 4). However, silylacetylenes **9k** and **9l** did not undergo efficient conversion at room temperature.

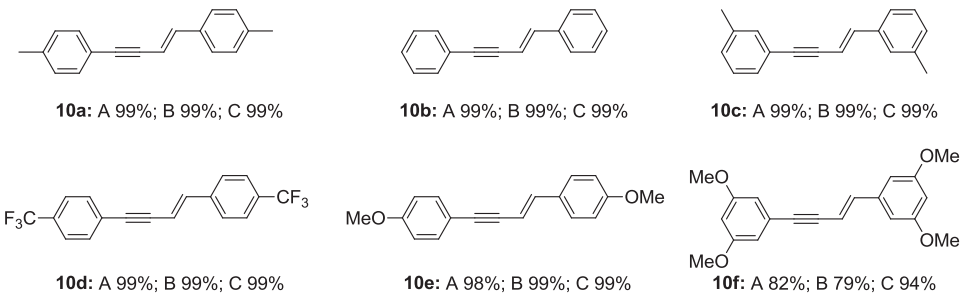
From the point of view of the reaction mechanism, alkyne dimerization catalyzed by palladium systems proceeds through the



9j-l **10j-l**

SiR_3 = $SiEt_3$ (**j**), $SiMe_2{}^tBu$ (**k**), $SiMe_3$ (**l**)

Scheme 3. Dimerization of silylacetylenes in the presence of complexes **1** and **8**.



10a: A 99%; B 99%; C 99%
10b: A 99%; B 99%; C 99%
10c: A 99%; B 99%; C 99%
10d: A 99%; B 99%; C 99%
10e: A 98%; B 99%; C 99%
10f: A 82%; B 79%; C 94%
10g: A[a] 98%; B 99%; C 99%
10h: A[b] 99%; B[c] 99%; C[d] 92%
10i: A[b] 69%; B[c] 78%; C[d] 89%

Fig. 3. Dimerization of arylacetylenes in the presence of complexes **1** and **8**. Reaction conditions: **A** toluene, cat. **1** (1 mol%), [Pd]/[KO^{t}Bu] = 1/4, 60 °C, 1 h, argon; **B** toluene, cat. **8** (1 mol%), [Pd]/[KO^{t}Bu] = 1/4, 60 °C, 1 h, argon; **C** EtOH (99.8%), cat. **8** (1 mol%), [Pd]/[KOH] = 1/4, 22 °C, argon; [a] 6 h; [b] 24 h; [c] 3 h; [d] 60 °C.

Table 4
Dimerization of triethylsilylacetylene in the presence of complexes **1** and **8**. Optimization of the reaction conditions.

Entry	Solvent	Base	T [°C]	Cat. (mol %)	*t* [h]	Conv. [%][a]	*E*/*Z*[b]
1	toluene	KO^{t}Bu	60	**1** (1)	1	19	*E*
2	toluene	KO^{t}Bu	60	**1** (1)	24	75	*E*
3	toluene	KO^{t}Bu	60	**1** (2)	2	98	*E*
4	EtOH	KOH	60	**1** (2)	24	95	*E*
5	EtOH	KOH	22	**1** (2)	24	10	*E*
6	toluene	KOH	60	**8** (0.25)	24	9	*E*
7	toluene	KOH	60	**8** (0.25)	24	40[c]	*E*
8	toluene	KOH	60	**8** (1)	24	52	*E*
9	toluene	KOH	60	**8** (1)	24	63[c]	*E*
10	toluene	KOH	60	8 (2)	2	>99[c]	*E*
11	toluene	KOH	100	**8** (1)	24	92[c]	*E*
12	toluene	KOH	110	**8** (1)	6	75[c]	*80/20*
13	EtOH	KOH	60	**8** (2)	2	>99	*E*
14	EtOH	KOH	22	**8** (2)	24	>99	*E*

Reaction condition: [Pd]:[base] = 1:4, argon.
[a] Determined by GC analysis.
[b] Determined by ^{1}H NMR spectroscopy of the crude reaction mixture.
[c] 10 μL of degassed water was added to the reaction mixture.

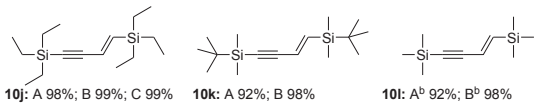
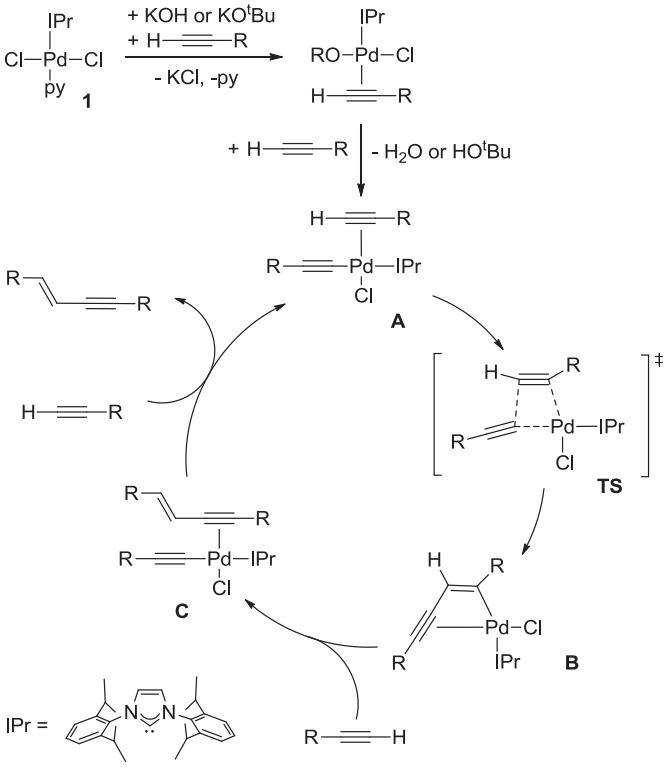


Fig. 4. Dimerization of silylacetylenes in the presence of complexes catalysts **1** and **8**. Isolated yields of products. Reaction conditions: A cat **1** (2 mol%), toluene, 60 °C, [Pd]/[KO^{t}Bu] = 1/4, 2 h, argon; B cat. **8** (2 mol%), toluene, 60 °C, [Pd]/[KOH] = 1/4; 2 h, argon; C cat **8** (2 mol%), EtOH, 22 °C, 24 h; [a)] 24 h; [b)] Reaction performed in a closed system.



Scheme 4. Proposed mechanism of dimerization of terminal acetylenes in the presence of complex **1**.

formation of an σ-alkynyl/π-alkyne intermediate which undergoes subsequent carbopalladation or hydropalladation. For the *N*-heterocyclic palladium complexes, Ananikov and Gevorgyan have shown by means of DFT calculations a clear kinetic preference for an alkyne insertion into the Pd-H bond over the Pd-C bond for both aryl and alkyl acetylenes [8e,15]. In the systems containing basic carboxylate anion hydropalladation may be deactivated due to the reaction of the base with hydride ligand. In such systems, the reaction proceeds via carbometallation pathway [15].

The catalytic systems described in this work contain Pd(II) complexes in the presence of small excess (relative to the catalyst) of tert-butoxide or hydroxide base. In such a system deactivation of the hydropalladation pathway is to be expected. Indeed, all attempts to detect palladium hydride species in a system containing catalyst **1** or **8**, KO^{t}Bu (4 equiv.) and fivefold excess of p-tolylacetylene in C_6D_6 using ^{1}H NMR spectroscopy have failed.

We proposed that the formation of σ-alkynyl palladium(II) complexes (A, Scheme 4) from chloride palladium(II) complexes of PEPPSI type, in the presence of KOH or KO^{t}Bu, proceeds as a result of electrophilic substitution and is preceded by the formation of palladium hydroxide or tert-butoxide complexes (Scheme 4). Our previous studies confirmed the formation of hydroxide complexes in a system containing PEPPSI-IPr and an excess of KOH [19]. Monitoring of the reaction of complex **8** with 5 equiv. of tolylacetylene (C_6D_6 at 60 °C) shows minor (9%) decrease in the intensity of the signal of hydroxide ligand and formation of water. Formation of π-acetylene complex from **1** proceeds via substitution of pyridine ligand. ^{1}H NMR monitoring of the substitution process shows the presence of only minor amount of free pyridine, which suggests that the substitution of pyridine by acetylene is an equilibrium process.

Once the palladium(II) σ-alkynyl/π-alkyne complex (**A**, Scheme 4) is formed π-coordinated acetylene undergoes migratory insertion into the palladium carbon bond (in the absence of hydride ligand). Ananikov and Gevorgyan have demonstrated for anionic palladium(II) NHC complex that the formation of head to head dimer is kinetically preferred over the head to tail one [15]. Moreover, the calculated molecular structure of transition state of carbometallation indicates that the preferred formation of the E-isomer [15] results from the absence of steric interactions between the phenyl ring of the dimer and the isopropyl groups of the 2,6-diisopropylphenyl substituent in the IPr ligand. Such steric crowding would be expected in the case of the formation of *Z*-isomer. Selective formation of *E*-isomer of head to head dimer in the presence of palladium complexes containing IPr ligands (or NHC ligands with analogous steric properties) and strongly basic hydroxides reported by Nechaev [8c] and observed in our systems are in good agreement with the DFT calculation results reported by Ananikov and Gevorgyan [15].

According to the proposed mechanism (Scheme 4) migratory insertion is followed by electrophilic substitution of sigma bonded enyne in complex **B** with another acetylene molecule with the formation of complex **C**. In the presence of a strongly donating NHC ligand an increased preference for electrophilic substitution should be expected. Substitution of π-bonded enyne with another acetylene molecule liberates the product and regenerates complex **A**.

The results presented in this work confirm the high potential of *N*-heterocyclic carbene palladium complexes as catalysts for the dimerization of terminal acetylenes reported by Nolan, Ananikov and Gevorgyan, Nechaev and others [e.g. Refs. [8b,e,14,15]]. By evidencing the utility of commercially available, cost competitive, highly air and moisture stable, user friendly one component PEPPSI precatalysts in efficient and selective dimerization of acetylenes, we have increased the range of available catalysts of the process and the number of effective procedures. The procedures described allow selective syntheses of *E*-1,4-disubstituted but-1-en-3-ynes already at room temperature, using small catalyst loadings.

Complex **8** allows successful dimerization in base-free conditions. For the first time the possibility of selective dimerization of silylacetylenes in the presence of *N*-heterocyclic palladium complexes has been shown.

3. Conclusions

Convenient and highly efficient procedure for synthesis of *E*-1,4-disubstituted but-1-en-3-ynes via dimerization of terminal aryl- and silylacetylenes in the presence of PEPPSI precatalyst and structurally related palladium dimers [{Pd(μ–Cl)Cl(IPr)}$_2$] and [{Pd(μ–OH)Cl(IPr)}$_2$] was proposed.

4. Experimental

4.1. General methods and reagents

Unless otherwise indicated, all operations were carried out using standard Schlenk techniques. ^{1}H and ^{13}C NMR spectra were recorded on Varian 400 operating at 402.6 and 101.2 MHz, respectively. GC/MS analyses were performed on a Varian Saturn 2100T equipped with DB-5, 30 m capillary column and Ion Trap Detector. GC analyses were performed using Varian CP-3800 (column: RTX-5, 30 m, 0,53 mm), equipped with TCD. The chemicals were obtained from the following sources: acetylenes, benzene-d_6, chloroform-d, styrene-d_8 KO^{t}Bu, K_2CO_3, Cs_2CO_3, CH_3COOAg, KOH, decane, dodecane, PEPPSI-IPr, PEPPSI-SIPr, di-μ-chlorobis[chloro {1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene}dipalladium(II) were purchased from Aldrich. Complexes **3** [20], **4** [20], **5** [21], **6** [21] and **8** [19] were synthesized according to literature procedures. Dichloromethane, toluene ethanol (99.8%) and hexane were purchased from POCh (Poland). All solvents (except of EtOH) were dried and stored under argon prior to use. Ethanol was degassed prior to use.

4.2. General procedure of catalytic tests

Glass reactor (3 mL) equipped with a condenser and a stirring bar was charged under argon with solvent (2 mL), 1-ethynyl-4-methylbenzene 21 μL (1.66×10^{-4} mol), dodecane 7 μL (internal standard). Reaction mixture was stirred and heated up to the temperature indicated in the tables. Then catalyst (0.1–5 %mol of Pd in relation to acetylene) and (if applicable) a base was introduced ([Pd]/[base] ratio is indicated in Tables). The reaction mixture was heated and stirred for designated time. Test reactions were monitored for 24 h by GC and GC/MS techniques.

4.3. General procedure for the synthesis of 1,4-bis(aryl)but-1-en-3-ynes in ethanol

Glass reactor (3 mL) equipped with a condenser and a stirring bar was charged under argon with arylacetylene (9.11×10^{-4} mol), EtOH (99.8%) (2 mL) and catalyst **8** (0.25–2.0 mol% in relation to acetylene). The reaction mixture was stirred at 22 °C for 24 h. Then the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2 = 4/1). Evaporation of the solvent gave an analytically pure product.

4.4. General procedure for the synthesis of 1,4-bis(silyl)but-1-en-3-ynes in toluene

Glass reactor (3 mL) equipped with a condenser and a stirring bar was charged under argon with silylacetylene (5.58×10^{-4} mol) and toluene (2 mL). The reaction mixture was heated up to 60 °C. Then palladium complex (2 mol% in relation to acetylene) and KO^{t}Bu ([Pd]/[KO^{t}Bu] = 1/4) was added. The reaction mixture was heated at 60 °C for 24 h. Then the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (silica gel 60, hexane to hexane/CH_2Cl_2 = 4/1). Evaporation of the solvent gave an analytically pure product.

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