Polymerization of phenylacetylene by novel Rh (I)-, Ir (I)- and Ru (IV) 1,3-R$_2$-3,4,5,6-tetrahydropyrimidin-2-ylidenes (R = mesityl, 2-propyl): Influence of structure on activity and polymer structure

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Abstract

The preparation of novel Rh (I) and Ir (I) complexes, i.e. [Rh(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)-(COD)]$^+$[PF$_6$]$^-$ (**1**), Rh(CF$_3$SO$_3$)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD) (**2**) and Ir(CF$_3$CO$_2$)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD) (**3**) (COD = 1,5-cyclooctadiene), is described. Compounds **1** and **3** were structurally characterized by X-ray diffraction. In **1**, the *N*-heterocyclic carbene acts as a bidentate ligand with the carbene coordinating to the Rh(I) center and an arene group acting as a homoazallyl ligand. The catalytic activity of complexes **1–3** in the polymerization of phenylacetylene was studied and compared to that of RhCl(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD) (**4**), Rh(CF$_3$COO)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD) (**5**), [Rh(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD)]$^+$[BF$_4$]$^-$ (**6**), IrCl(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD) (**7**), IrCl(1,3-diisopropyl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD) (**8**), IrBr(1,3-di-2-propylimidazolin-2-ylidene)(COD) (**9**), RuCl$_2$(PCy$_3$)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(=CH–C$_6$H$_5$) (**10**), RuCl$_2$(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene) (=CH-2-(2-PrO)-5-NO$_2$-C$_6$H$_3$) (**11**), Ru(CO$_2$CF$_3$)$_2$(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(=CH-2-(2-PrO)-5-NO$_2$-C$_6$H$_3$) (**12**). Compounds **1–6** were active in the polymerization of phenylacetylene. *cis*-Poly(phenylacetylene) (PPA) was obtained with the rhodium-based catalysts **1**, **2**, **4–6**, *trans*-PPA was obtained with the Ir-based catalysts **3** and **8**. In addition, compounds **1** and **6** were found to produce highly stereoregular PPA with a *cis*-content of 100% in the presence of water. Finally, the Ru-based metathesis initiator **12** allowed for the synthesis of *trans*-PPA, representing the first example of a ruthenium complex being active in the polymerization of a terminal alkyne.
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1. Introduction

Transition metal complexes of *N*-heterocyclic carbenes (NHCs) [1–6] including those of Rh (I) and Ir (I) are widely used in organometallic catalysis as well as organic synthesis due to their stability and high activities [7–16]. During the last 2 years, we have been working

on novel NHC complexes of Ag (I), Pd (II), Rh (I), Ir (I) and Ru (IV) based on 1,3-R_2-3,4,5,6-tetrahydropyrimidin-2-ylidenes (R = mesityl, 2-propyl) [17–23] and used the novel transition metal complexes in various C–C and C–Si coupling reactions. Based on the finding that in these coupling reactions Rh(CF$_3$COO)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD) (**5**) and [Rh(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD)]$^+$[BF$_4$]$^-$ (**6**) were the most active metal complexes in comparison to all other analogues investigated, we were interested in whether this concept would also apply to polymer chemistry. In due course we synthesized novel [Rh(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD)]$^+$[PF$_6$]$^-$ (**1**), Rh(CF$_3$SO$_3$)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD)] (**2**) and Ir(CF$_3$CO$_2$)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD) (**3**). In the following, the syntheses, solid state structures and reactivity in the polymerization of phenylacetylene in comparison to existing catalysts are described.

2. Results and discussion

2.1. Synthesis and X-ray structure of compound *1*

RhCl(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD) was prepared as described previously [19,20]. Addition of 1 equiv. of silver hexafluorophosphate in freshly distilled THF resulted in the formation of [Rh(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD)]$^+$[PF$_6$]$^-$ (**1**) (Scheme 1).

The product was obtained in pure form in 75% yield by layering diethyl ether over a saturated solution of **1** in dichloromethane. Compound **1** crystallizes in the orthorhombic space group *Pbca*, with $a = 1583.17(3)$, $b = 1684.28(2)$ and $c = 4939.90(0)$ pm ($Z = 16$). As already observed for cationic [Rh(1,3-dimesityl-3,4,5,6-tetra-

hyropyrimidin-2-ylidene)(COD)]$^+$[BF$_4$],$^-$ (**6**) [24], the cationic Rh-center in **1** is stabilized by a homoazallyl bonding to the arene in the solid state (Fig. 1). The distance Rh(1)–C(9) is 203.3(5) pm, practically identical to the distance found in [Rh(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD)]$^+$[BF$_4$]$^-$ (**6**, 204.0(4) pm), however, it is somewhat shorter than the distance Rh(1)–C(9) in Rh(CF$_3$COO)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD) (**5**, 206.5(8) pm) [23]. The distance Rh(1)–C(13) is 235.3(5), somewhat shorter than in **6** (237.7(4) pm). The angle N(1)–C(9)–Rh(1) is slightly reduced to 100.7(4)°, compared to 101.5(3)° in **6**, however is significantly different from the angle N(1)–C(9)–Rh(1) in **5**, which is 119.6(5)° [23]. The distance Rh(1)–C(13) is 235.3(5) pm and must in fact be regarded a real coordinative bond since it is comparable to the distances Rh(1)–C(5), Rh(1)–C(6), Rh(1)–C(1),
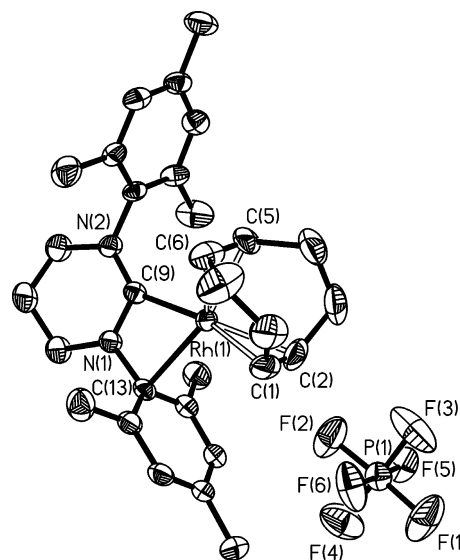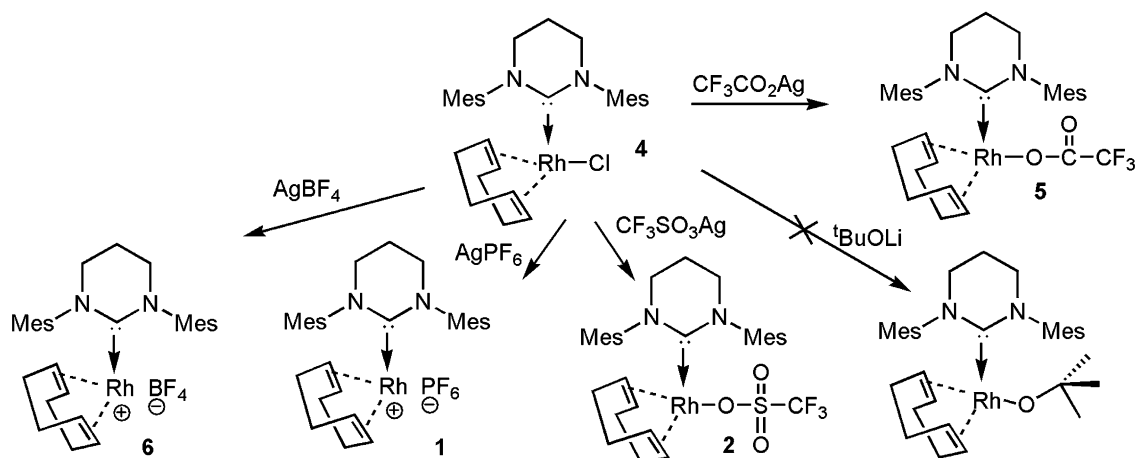

Fig. 1. X-ray structure of compound **1**.

Scheme 1. Synthesis of Rh-complexes **1**, **2**, **4–6**.

Rh(1)–C(2), which are 211.4(7), 222.6(7), 224.3(7) and 235.3(5) pm, respectively (Tables 1 and 2). However, the latter are significantly longer than the Rh–COD distances found in **5** (208.2(8), 209.3(8), 216.6(11) and 219.5(11) pm, respectively) [23], a fact that might be attributed to *trans*-effects produced by the bonding situation in **1**. In contrast to the unsymmetrical solid state structure, the room temperature ^{1}H and ^{13}C NMR solution spectrum of **1**, recorded either in THF-d$_8$ or CDCl$_3$ did not show any further additional coordination of the arene ligand. In due consequence, a symmetrical, cationic Rh(NHC)(COD) complex forms upon dissolution.

Similarly, RhCl(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)COD (**4**) underwent reaction with 1 equiv. of CF$_3$SO$_3$Ag in THF to give Rh(CF$_3$SO$_3$)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD) (**2**). Yellow crystals were obtained after recrystallization from dichloromethane-diethyl ether in 72% yield. How-ever, all attempts to synthesize Rh(O^{t}Bu)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD) from **4** and lithium *tert*-butoxide in THF failed.

In a similar manner, Ir(CF$_3$CO$_2$)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD) (**3**) was prepared from IrCl(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD) (**7**) by reaction with 1 equiv. of silver trifluoroactate (Scheme 2). The crude product was re-crystallized by layering diethyl ether and *n*-pentane over a saturated solution of **3** in dichloromethane. Compound **3** crystallizes in the monoclinic space group *C2/c*, with *a* = 1455.07(2), *b* = 1214.23(2) and *c* = 3458.03(6) pm, *β* = 97.937(2)° (*Z* = 8). The distance Ir(1)–C(9) was 207.9(4) nm. All attempts to prepare the cationic Ir-complex [Ir(1,3-dimesityltetrahydropyrimidin-2-ylidene)(COD)][PF$_6$]$^-$ failed (Fig. 2 and Table 3).

2.2. Catalytic activity of compounds **1–12** in the polymerization of phenylacetylene

Poly(phenylacetylene) (PPA) finds various applications in electronic, liquid crystalline, optical and magnetic devices [25]. Different transition metal catalysts based on W, Mo, Rh, Ir, Ni, Fe, Pd have been used so far [26–37]. Generally speaking, four possible stereoisomers of PPA can be generated from the configuration of the C=C bond as well as the conformation of the carbon–carbon single bond of the polymer main chain (Scheme 3). Farnetti pointed out that polymerization of monosubstituted alkynes (i.e. terminal alkynes) catalyzed by organorhodium compounds resulted exclusively in the formation of the corresponding *cis*-polyene with both *cis*-cisoid and *cis*-transoid structures [26,27]. Similar results were obtained with the new catalysts.

Thus, all Rh (I)–NHC complexes yielded PPA with a *cis*-transoid structure as evidenced by UV- IR-, ^{1}H and

Table 1
Crystal data and structure refinement for **1** and **3**

	1	**3**
Molecular formula	C$_{30}$H$_{40}$F$_6$N$_2$PRh · 0.5CH$_2$Cl$_2$	C$_{32}$H$_{40}$F$_3$IrN$_2$O$_2$
FW	718.98	733.86
Crystal syst	Orthorhombic	Monoclinic
Space group	*Pbca* (No. 61)	*C2/c* (No. 15)
a (pm)	1583.17(3)	1455.07(2)
b (pm)	1684.28(2)	1214.23(2)
c (pm)	4939.90(9))	3458.03(6)
α (°)	90	90
β (°)	90	97.937(2)
γ (°)	90	90
Volume (nm^3)	13.1723(4)	6.05108(17)
Z	16	8
Temperature (K)	233(2)	233(2)
Density (calc.) (Mg/m^3)	1.450	1.611
Absorption coefficient (mm^{-1})	0.705	0.4462
Color, habit	Yellow prism	Yellow plate
Number of reflections with $I > 2\sigma(I)$	7348	5272
Goodness-of-fit on F^2	1.067	1.186
R indices $I > 2\sigma(I)$	$R_1 = 0.0543$ $\omega^2 = 0.1269$	$R_1 = 0.0322$ $\omega R^2 = 0.0636$

Table 2
Bond lengths [pm] and angles [°] for **1**

Rh(1)–C(9)	203.3(5)
Rh(1)–C(6)	208.4(8)
Rh(1)–C(5)	211.4(7)
Rh(1)–C(2)	222.6(7)
Rh(1)–C(1)	224.3(7)
Rh(1)–C(13)	235.3(5)
C(9)–Rh(1)–C(13)	62.9(2)
N(1)–C(9)–Rh(1)	100.7(4)
N(1)–C(9)–Rh(1)	140.7(4)
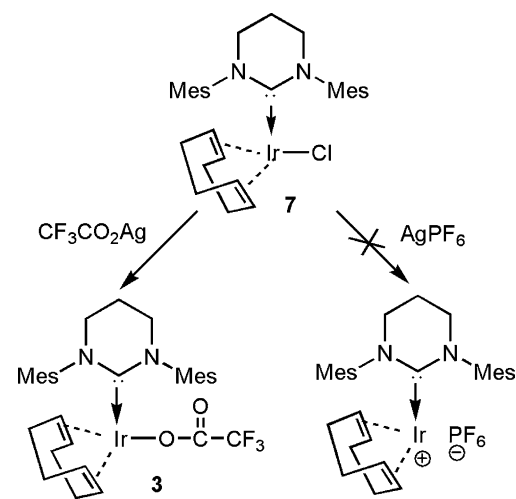
Scheme 2. Synthesis of Ir-complex **3** and attempted synthesis of [Ir-(1,3-dimesityl-4,5,6,7-tetrahydropyrimidin-2-ylidene)(COD)]$^+$[PF$_6$]$^-$.

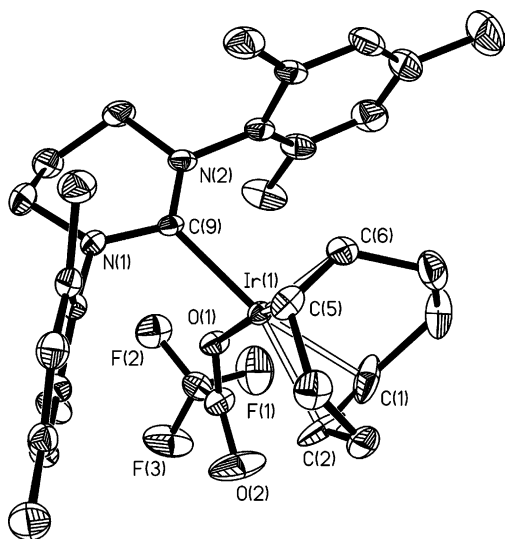Fig. 2. X-ray structure of compound **3**.

Table 3
Bond lengths [pm] for **3**

Ir(1)–C(9)	207.9(4)
Ir(1)–C(6)	210.1(4)
Ir(1)–C(5)	210.6(5)
Ir(1)–O(1)	211.8(3)
Ir(1)–C(1)	215.4(5)
Ir(1)–C(2)	216.5(5)

^{13}C NMR spectroscopy. The UV/Vis spectra displayed typical absorptions around 500 nm, typical of *cis*-transoid PPA. In the IR-spectrum, signals around 740 cm^{-1} were observed, again characteristic for *cis*-olefinic bonds. The ^{1}H NMR signal at $\delta = 5.84$ was characteristic for double bonds in *cis*-transoid sequences. The *cis*-content of the corresponding polymers was quantified according to the established equation: %-*cis* = $100 \times (A_{5.84} \times 6)/(A_{total})$, data are summarized in Table 4 [38].

Polymerization of PA with the cationic complex **1** in chlorinated solvents at either room temperature, 40 and 80 °C, respectively, resulted in the formation of PPA with 70–80% *cis*-content (Table 4, entries 1–3). Values for the polydispersity index (PDI) varied between 1.54 and 3.72. It is worth noting that NONE of the polymerizations described here fulfilled the criteria of livingness [39]. The use of triethyl amine was investigated, too (Table 4, entry 4). It was reported to act as a cocatalyst, presumably by coordinating to the metal center in a reversible way, thus improving polymerization characteristics by regulating the ratios of the rate constant of initiation (k_i) and propagation (k_p) [40]. However, it showed a diametric effect here. Thus, the PDI remained unaffected, initiation efficiency decreased, resulting in a high M_w-polymer ($M_w = 43,900$ g/mol). Since **1** is stable under ambient conditions, polymerizations were run in protic solvents in the presence of air. Interestingly, polymers with 100% *cis*-content and molecular weights up to 115,800 were obtained (Table 4, entries 6–8). To the best of our knowledge, this is the first report on the influence of such reaction conditions on polymer structure.

Similar results as obtained with **1** were achieved with complexes **2**, **4**, **5** and **6**. The use of NEt$_3$ as cocatalyst again in most cases resulted in the formation of high M_w-polymers ($M_w \leqslant 115,000$ g/mol). As observed for **1**, the use of **6** in a protic solvent and in the presence of air resulted in the formation of pure *cis*-PPA (Table 4, entry 34). Methylalumoxane, MAO, is widely used as cocatalyst and activator, respectively, in 1-olefin polymerization. Due to its pronounced Lewis acidic behavior it is capable of generation cationic and thus highly reactive complexes. Consequently, we checked whether its use in the present polymerization system was of any advantage (Table 4, entries 17–19). Disappointingly, no effect, whether on PDI or molecular weights, was observed.

In contrast to the rhodium-based systems, the iridium complexes **3** (Table 4, entry 11) and **7–9** (Table 4, entry 35–37) allowed for the formation of *trans*-polyenes, though with reduced activities. Thus, yields were generally ⩽11%. Together with the signals in the corresponding ^{1}H NMR spectra around 7.2 ppm, the ^{13}C NMR signals of the corresponding PPA at 130–126 ppm were attributed to a *trans*-structure. This was further
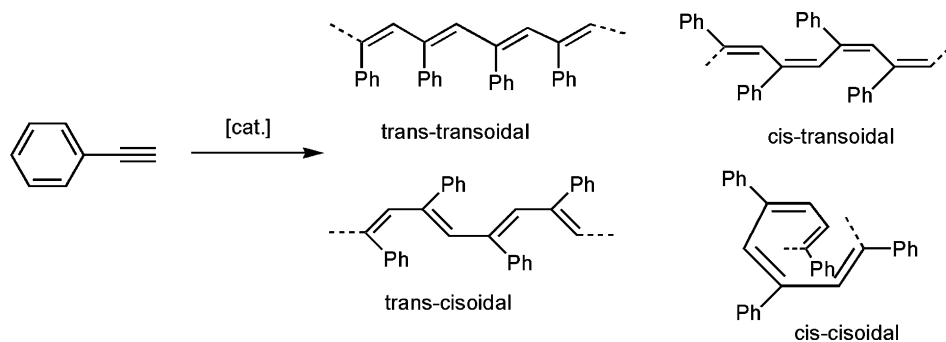
Scheme 3. Polymerization of phenyl acetylene (PA) and possible polymer structures.

Table 4
Polymerization of phenylacetylene (PA) by catalysts **1**–**12**

#	Catalyst (mol%)	Cocatalyst (mol%)	Solvent	Temperature (°C)	Time (h)	Yield (%)	*cis* (%)	M_w (g/mol)	M_w/M_n (g/mol)
1	**1** (3)	0	CH$_2$Cl$_2$	40	19	90	76	26,500	1.85
2	**1** (3)	0	CH$_2$Cl$_2$	23	19	71	75	16,700	1.95
3	**1** (2)	0	ClCH$_2$CH$_2$Cl	80	20	43	80	26,000	1.56
4	**1** (2.5)	2.5[a]	CH$_2$Cl$_2$	40	19	56	84	43,900	1.87
5	**1** (1)	0	H$_2$O/THF	23	2	62	67	58,400	3.72
6	**1** (0.5)	0[c]	H$_2$O/THF	23	2	51	~100	85,600	1.78
7	**1** (1)	0	H$_2$O/MeOH	23	6.5	66	~100	115,800	2.48
8	**1** (1)	0[c]	MeOH	23	25	32	~100	47,300	1.80
9	**2** (2)	0	CH$_2$Cl$_2$	40	20	53	64	25,500	1.55
10	**2** (2)	0	ClCH$_2$CH$_2$Cl	80	20	61	64	22,000	1.55
11	**3** (1)	0	CH$_2$Cl$_2$	23	19	11	*trans*	16,900	1.54
12	**4** (1)	0	CH$_2$Cl$_2$	23	22	29	75	27,000	2.25
13	**4** (2.5)	0	CH$_2$Cl$_2$	23	48	40	72	27,400	2.22
14	**4** (2.5)	0	ClCH$_2$CH$_2$Cl	80	45	37	58	25,400	1.59
15	**4** (1)	2[a]	CH$_2$Cl$_2$	23	19	29	71	18,500	1.98
16	**4** (2)	2[a]	ClCH$_2$CH$_2$Cl	80	19	42	54	21,200	1.48
17	**4** (1)	400[b]	Toluene	40	19	13	83	42,300	1.97
18	**4** (2)	400[b]	Toluene	40	19	19	70	34,700	1.94
19	**4** (2)	800[b]	Toluene	40	19	19	78	38,100	2.00
20	**5** (1)	0	CH$_2$Cl$_2$	23	14	22	63	42,900	1.84
21	**5** (2.5)	0	CH$_2$Cl$_2$	23	19	50	86	58,500	2.02
22	**5** (1)	0	CH$_2$Cl$_2$	40	14	17	70	49,900	2.00
23	**5** (1)	0	(MeOCH$_2$)$_2$	80	14.5	17	57	33,600	1.88
24	**5** (1)	0	THF	23	14	13	71	74,900	2.53
25	**5** (1)	0	ClCH$_2$CH$_2$Cl	80	14	24	69	33,700	1.73
26	**5** (2)	0	ClCH$_2$CH$_2$Cl	80	19	42	70	37,900	1.90
27	**5** (2)	0	ClCH$_2$CH$_2$Cl	80	19	53	56	34,200	1.84
28	**5** (2)	0	Toluene	110	19	31	50	21,300	1.72
29	**5** (1)	2[a]	CH$_2$Cl$_2$	23	19	23	61	31,500	2.14
30	**5** (2.5)	2.5[a]	CH$_2$Cl$_2$	23	19	37	71	115,000	2.88
31	**5** (2)	2[a]	ClCH$_2$CH$_2$Cl	80	19	42	52	21,300	1.60
32	**6** (2)	0	CH$_2$Cl$_2$	23	19	34	77	67,200	2.31
33	**6** (1)	0	H$_2$O/THF	23	3	33	57	71,700	3.72
34	**6** (1)	0[c]	H$_2$O/MeOH	23	6.5	70	~100	138,200	2.71
35	**7** (1)	0	ClCH$_2$CH$_2$Cl	23	19	0	–	–	–
36	**8** (2)	0	ClCH$_2$CH$_2$Cl	80	64	4.7	*trans*	9,700	1.37
37	**9** (2)	0	ClCH$_2$CH$_2$Cl	80	64	0	–	–	–
38	**10** (2)	0	ClCH$_2$CH$_2$Cl	80	19	0	–	–	–
39	**11** (2)	0	ClCH$_2$CH$_2$Cl	80	19	0	–	–	–
40	**12** (2)	0	ClCH$_2$CH$_2$Cl	80	19	30	*trans*	71,600	1.59

[a] Et$_3$N.
[b] MAO.
[c] Polymerization was conducted in air.

supported by typical IR signals at 1265 cm^{-1}. Finally, we were interested, whether highly active ruthenium-based metathesis catalysts were capable of polymerizing PPA. For this purpose, RuCl$_2$(PCy$_3$)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(=CH–C$_6$H$_5$) (**10**), RuCl$_2$(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(=CH-2-(2-PrO)-5-NO$_2$-C$_6$H$_3$) (**11**) and Ru(CO$_2$CF$_3$)$_2$(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(=CH-2-(2-PrO)-5-NO$_2$-C$_6$H$_3$) (**12**) were used. As observed in the cyclopolymerization of 1,6-heptadiynes, only the trifluoroacetate-based catalysts showed significant polymerization activity for PA [17,41,42]. Thus, the use of **12** produced PPA in moderate yield (30%) yet with comparably high PDIs (Table 4, entry 40). Despite the fact that these polymerization activity is by far to

low to be of any synthetic relevance, it should be noted that this is the *first report* on any 1-alkyne polymerization activity of a ruthenium-based initiator that provides data on molecular weights, PDIs and yields [43]. Present efforts focus on increasing this activity and relevant data will be reported in due course.

3. Summary

In summary, a series of Rh (I), Ir (I) and Ru (IV) based catalysts containing the 1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene and 1,3-di(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene ligand, respectively, was synthesized and tested for their applicability to the

polymerization of phenylacetylene. While Rh (I) compounds produced selectively *cis*-poly(phenylacetylene) (PPA), the corresponding Ir (I) compounds allowed for the selective synthesis of *trans*-PPA, albeit with significantly reduced activity. Interestingly, Ru(CO$_2$CF$_3$)$_2$(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(=CH-2-(2-PrO)-5-NO$_2$-C$_6$H$_3$) (**12**), a metathesis initiator, highly active in the cyclopolymerization of 1,6-heptadiynes, allowed for the synthesis of *trans*-PPA. However, it should be emphasized that all polymerizations described here proceeded in a non-living manner.

4. Experimental

All manipulations were performed under a nitrogen atmosphere in a glove box (MBraun LabMaster 130) or by standard Schlenk techniques. Purchased starting materials were used without any further purification. Pentane and tetrahydrofurane (THF), diethyl ether, toluene and diethyleneglycoldimethyl ether (DME) were distilled from sodium benzophenone ketyl under nitrogen. Methylene chloride and dichloroethane were distilled from calcium hydride. RhCl(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD) (**4**) was synthesized according to the literature. Phenylacetylene (Fluka) was distilled from CaH$_2$ at low pressure. NMR data were obtained at 300.13 MHz for proton and 75.74 MHz for carbon in the indicated solvent at 25 °C on a Bruker Spectrospin 300 and are listed in parts per million downfield from tetramethylsilane for proton and carbon. Coupling constants are listed in Hz. IR spectra were recorded on a Bruker Vector 22 using ATR technology. Elemental analyses were carried out at the Mikroanalytisches Labor, Anorganisch-Chemisches Institut, TU München, Germany. Molecular weights and polydispersity indices (PDIs) of the polymers were determined by GPC at 30 °C on Polymer Laboratories columns (PLgel 10 µm MIXED-B, 7.5 × 300 mm) in THF at 25 °C using a Waters Autosampler, a Waters 484 UV detector (254 nm) and an Optilab Rex refractive index detector (685 nm, Wyatt). The flow rate was 0.7 mL/min.

4.1. Rh(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD)]$^+$[PF$_6$]$^-$ (1)

Compound **4** (56.7 mg, 0.100 mmol) was dissolved in THF and added to a solution of silver hexafluorophorsphate (25.3 mg, 0.10 mmol) in THF, both cooled to −36 °C. After mixing, the solution was stirred for another 3 hours, allowing it to reach room temperature. During that time a white precipitate of AgCl formed. The mixture was filtered through celite and the THF was removed in vacuo. Methylene chloride was added to dissolve the residue and the solution was again con-

centrated in vacuo. Diethyl ether was layered over the red, saturated solution. Orange crystal formed at −36 °C. Yield: 51.0 mg, 75.3%. FTIR: $\bar{v}$ 2917 (w), 1604 (w), 1536 (m), 1476 (m), 1379 (m), 1335 (m), 1209 (m), 1075 (w), 833 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 6.99 (br, s, 4H, aromatic H), 3.39 (m, 6H, 2 · CH$_{COD}$ + 2 · NCH$_2$), 3.13 (m, 2H, CH$_{COD}$), 2.49 (br, s, 12H, Mesityl-*ortho*-CH$_3$), 2.34 (m, 2H, CH$_2$), 2.30 (br, s, 6H, mesityl-*para*-CH$_3$),1.93-1.90 (m, 4H, CH$_{2\ COD}$), 1.57–1.53 ppm (m, 4H, CH$_{2\ COD}$); ^{13}C NMR (CDCl$_3$): δ 174.0 [d, NCN, $^1J(^{103}$Rh, ^{13}C) = 40.7 Hz], 141.2, 138.0, 135.6, 134.7, 130.4, 129.5, 125.2 (s, all aromatic C), 102.35 [d, CH$_{COD}$, $^1J(^{103}$Rh, ^{13}C) = 6.7 Hz], 72.9 [d, CH$_{COD}$, $^1J(^{103}$Rh, ^{13}C) = 16.6 Hz], 48.2 (s, NCH$_2$), 32.8 (s), 26.7(s), 21.0(s), 20.4(s), 18.3(s), 17.5 ppm (s, CH$_{2\ COD}$).

4.2. Rh(CF$_3$SO$_3$)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD) (2)

A THF solution (2 mL) of AgSO$_3$CF$_3$ (51.4 mg, 0.20 mmol) was cooled to −36 °C and added to a chilled THF solution (2 mL) of compound **4** (113.4 mg, 0.20 mmol). The mixture was stirred at room temperature for 4 h and filtered through celite. THF was removed in vacuo to yield a yellow solid that was re-dissolved in CH$_2$Cl$_2$ and filtered through glass-fiber paper. The product was re-crystallized as yellow needles by laying diethyl ether over a saturated solution of **2** in methylene chloride at −36 °C. Yield: 98.7 mg, (72.3%). FTIR: $\bar{v}$ 2917 (w), 1604 (s), 1335 (m), 1266 (s), 1221 (m), 1141 (s), 1030 (s), 960 (w), 856 cm^{-1}(m); ^{1}H NMR (CDCl$_3$): δ 7.00 (br, s, 4H, aromatic H), 3.45 (m, 6H, 2 · CH$_{COD}$ + 2 · NCH$_2$), 3.08 (m, 2H, CH$_{COD}$), 2.52 (br, s, 12H, mesityl-*ortho*-CH$_3$), 2.39 (m, 2H, CH$_2$), 2.30 (br, s, 6H, mesityl-*para*-CH$_3$),1.99-1.93 (m, 4H, CH$_{2\ COD}$), 1.60-1.56 (m, 4H, CH$_{2\ COD}$); ^{13}C NMR (CDCl$_3$): δ 174.5 [d, NCN, $^1J(^{103}$Rh, ^{13}C) = 40.4 Hz], 141.1, 135.6, 130.4, 125.6 (s, all aromatic C), 102.0 [d, CH$_{COD}$, $^1J(^{103}$Rh, ^{13}C) = 6.8 Hz], 72.6 [d, CH$_{COD}$, $^1J(^{103}$Rh, ^{13}C) = 16.3 Hz], 48.4 (s, NCH$_2$), 32.8 (s), 26.7(s), 21.1(s), 20.5(s), 18.4 (s, CH$_{2\ COD}$). Elemental Anal. Calc. for C$_{31}$H$_{42}$F$_3$N$_2$O$_3$RhS (682.19): C, 54.54; H, 6.20; N, 4.10. Found: C, 54.52, H, 6.01; N, 3.79%.

4.3. Ir(CF$_3$CO$_2$)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD) (3)

Compound **7** (65.8 mg, 100 µmol) was dissolved in THF and the solution was cooled to −36 °C. A chilled solution of silver trifluoroacetate (22 mg, 100 µmol) in THF was added drop wise. A white precipitate of silver chloride immediately formed from the yellow solution. The reaction mixture was stirred for 2 h at room temperature. Silver chloride was removed by filtration through celite and the solvent was removed in vacuo.

The residue was dissolved in dichloromethane and the solution was quickly filtered through glass-fiber paper. Gray-green crystals were obtained by layering diethyl ether and *n*-pentane over a methylene chloride solution of **3** at −36 °C, Yield: 47.7 mg (65%). FT-IR (ATR mode): $\bar{v}$ 2915 (w), 1686 (s), 1607 (w), 1489 (m), 1402 (m), 1300 (m), 1189 (s), 1179 (s), 973 (s), 880 (s), 720 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.02 (br, s, 2H, aromatic H), 6.92 (br, s, 2H, aromatic H), 4.46–4.44 (m, 2H, $2 \cdot CH_{COD}$), 3.40–3.35 (m, 4H, $2 \cdot NCH_2$), 2.79–2.77 (m, 2H, $2 \cdot CH_{COD}$), 2.33 (br, s, 6H, mesityl-*para*-CH$_3$), 2.29–2.20 (m, 14H, mesityl-*ortho*-CH$_3$+CH$_2$), 1.31-1.18 (m, 4H, CH$_2$ COD), 1.03–0.97 ppm (m, 4H, CH$_2$ COD); ^{13}C NMR (CDCl$_3$): δ 204.8 (s, NCN), 161.0 [q, CO, $^2J(^{19}F, ^{13}C) = 35.1$ Hz], 141.1, 137.5, 137.0, 134.5, 129.9, 128.2 (s, all aromatic C), 116.2 [q, CF$_3$, $^1J(^{19}F, ^{13}C) = 292.9$ Hz], 79.2 (s, CH$_{COD}$), 48.8 (s, CH$_{COD}$), 48.2 (s, NCH$_2$), 32.6, 27.8, 21.1, 20.9, 18.9, 17.8 (s, CH$_2$, MesCH$_3$, CH$_{2COD}$).

4.4. Typical procedure for the polymerization of phenylacetylene

A weighed amount of catalyst (20 μmol) was dissolved in dichloromethane (1.5 mL). A solution of phenylacetylene (1 mmol) in methylene chloride (1 mL) was added and the tube was taken out of the glove box. The mixture was allowed to react under nitrogen at the indicated temperature. After the time indicated in the tables, several drops of trifluoroacetic acid were added to deactivate the catalyst. The solution was concentrated and added drop wise to *n*-pentane (60 mL) under vigorous stirring. The precipitated polymer was separated by centrifugation, washed with *n*-pentane and dried in vacuo. In the case where MAO was used, 5 mL of methanol and 15 mL of diluted HCl were added to destroy the MAO and the polymer was extracted with dichloromethane. After removal of most of the solvent, the solution was added drop wise to *n*-pentane (60 mL) under vigorous stirring. The precipitated polymer was separated by centrifugation, washed with *n*-pentane and dried in vacuo. In case polymerizations were done in presence of water, the precipitate was isolated by centrifugation, washed by acetone and dried in vacuo. The product was re-dissolved in dichloromethane and any insoluble polymer was removed by filtration.

4.5. X-ray measurement and structure determination of 1 and 3

Data collection was performed on a Nonius Kappa CCD equipped with graphite-monochromatized Mo Kα-radiation ($\lambda = 0.71073$ Å) and a nominal crystal to area detector distance of 55 mm for **1** and 40 mm for **3**. Intensities were integrated using DENZO and scaled with SCALEPACK [44]. Several scans in and ω-direction were made to increase the number of redundant reflections, which were averaged in the refinement cycles. This procedure replaces in a good approximation an empirical absorption correction. The structures were solved with direct methods SHELXS86 and refined against F^2 SHELX97 [45]. The function minimized was $\Sigma[w(F_o^2 - F_c^2)^2]$ with the weight defined as $w^{-1} = [\sigma^2(F_o^2) + (xP)^2 + yP]$ and $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms for **1** and **3** were placed on calculated positions, except for those of the double bonds of the COD ligand, which were refined regularly with isotropic displacement parameters and bond restraints to the attached carbon atoms ($d = 95$ pm). The solvent CH$_2$Cl$_2$ in compound **1** shows a 2:1 disorder of one chlorine atom.

Appendix A. Supplementary data

Crystallographic data for **1** and **3** have been deposited with the CCDC Nos. 272183 and 272184 on the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44-1223 336 033, e-mail: deposit@ccdc.cam. ac.uk or on the web www: http://www.ccdc.cam. ac.uk. Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2005.07.036.

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