Monatshefte für Chemie 129, 221–233 (1998)

Monatshefte für Chemie
Chemical Monthly

Printed in Austria

Ruthenium Catalyzed Homocoupling of Terminal Alkynes

Christian Slugovc[1], **Daniel Doberer**[1], **Christian Gemel**[1], **Roland Schmid**[1], **Karl Kirchner**[1,*], **Berthold Winkler**[2], and **Franz Stelzer**[2,*]

[1] Institute of Inorganic Chemistry, Technical University of Vienna, A-1060 Vienna, Austria
[2] Institute of Chemical Technology of Organic Materials, Technical University of Graz, A-8010 Graz, Austria

Summary. Several complexes of the type Ru*Tp*(*L*)(*L'*)Cl (*L*, *L'* = P, N, O donors) were tested with respect to their ability of promoting catalytic C–C-coupling reactions of terminal acetylenes. When *L* = tertiary phosphine, predominantly dimerization occurs, Ru*Tp*$(PPh_3)_2$H being the most efficient pre-catalyst. In the absence of a phosphine ligand, polymerization takes place with Ru*Tp*(*COD*)Cl as the most effective pre-catalyst. Both product distribution and conversion depend strongly on the substituent of the alkyne and to a lesser extent on the co-ligands of the ruthenium complex. The catalytically active species is the 16e$^-$ alkynyl complex Ru*Tp*(*L*)(–C≡C–*R*) which in case of *L* = P*Cy*$_3$ and *R* = Bu^n could be trapped as Ru*Tp*(PCy_3)(–C≡CBu^n)(CO).

Keywords. Ruthenium; Poly(acetylene); Conjugated polymers; Dimerization; Trispyrazolylborate.

Rutheniumkatalysierte Homokupplung von terminalen Alkinen

Zusammenfassung. Die Fähigkeit einiger Komplexe des Typs Ru*Tp*(*L*)(*L'*)Cl, C–C-Kupplungsreaktion terminaler Alkine zu katalysieren, wurde getestet. Ist *L* ein Phosphin und *L'* ein labiler Ligand, so dimerisieren die Alkine, während sie in Abwesenheit von Phosphinen polymerisieren. Ru*Tp*$(PPh_3)_2$H ist der beste Katalysator für die Dimerisierung, Ru*Tp*(*COD*)Cl für die Polymerisation. Produktverteilung und Ausbeute sind in erster Linie vom Substituenten am Alkin abhängig, aber auch von den Liganden am Ruthenium. Die katalytisch aktive Spezies ist der 16e$^-$-Alkinyl-Komplex Ru*Tp*(*L*)(–C≡C–R), der im Falle von *L* = P*Cy*$_3$ und R = Bu^n als Ru*Tp*(P*Cy*$_3$)(–C≡C–Bu^n)(CO) abgefangen werden konnte.

Introduction

The transition metal catalyzed dimerization of terminal alkynes is an effective method for the formation of enynes. Its synthetic application in organic synthesis has been limited, however, due to the low selectivity on dimeric products [1]. Recent advances in transition metal mediated selective dimerization reactions fueled a resurgence of interest in this type of reaction [2]. We have recently shown that Ru*Tp*$(PPh_3)_2Cl$ (**1** *Tp* = hydrido*tris*(pyrazolyl)borate) is an efficient pre-

* Corresponding author

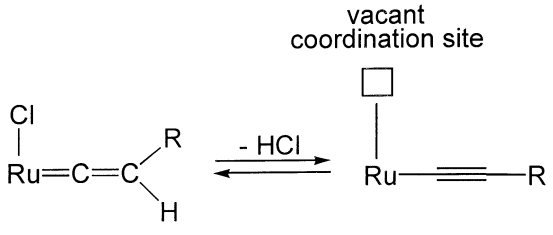
catalyst for the selective coupling of HC≡C*R* (*R* = Ph, $SiMe_3$, *n*-Bu, and *t*-Bu) to give 1,4- and 2,4-disubstituted butenynes [3]. If two pyridine moieties are substituted for the PPh_3 units, no dimeric but instead polymeric products are obtained. Interestingly, in the presence of an excess of allyl alcohol this pathway becomes of minor importance, and predominantly allyl vinyl ethers are obtained [4].

In order to establish the factors that control the reactivity of the catalyst and consequently the selectivity of the C–C coupling process, we report here on the coupling of HC≡CPh with complexes **1**, Ru*Tp*(PPh_3)(=C=CHPh)Cl (**2**), Ru*Tp*(PPh_3)(*py*)Cl (**3**), Ru*Tp*(PPh_3)(PMe_3)Cl (**4**), Ru*Tp*(PPh_3)(CO)Cl (**5**), Ru*Tp*(PBu^n_3)$_2$Cl (**6**), Ru*Tp*(PCy_3)(OMe)Cl (**7**, *Cy* = cyclohexyl), Ru*Tp*(*dppe*)Cl (**8**, *dppe* = $Ph_2PCH_2CH_2PPh_2$), Ru*Tp*(*pn*)Cl (**9**, *pn* = $Ph_2PCH_2CH_2NMe_2$), Ru*Cp**(*pn*)Cl (**10**, *Cp** = pentamethylcyclopentadienyl), Ru(*pn*)$_2Cl_2$ (**11**), and Ru*Tp*(PPh_3)$_2$H (**12**) acting as catalyst precursors. Mechanistic details will be presented and, in addition, we describe the polymerization of some terminal alkynes [5] mediated by Ru*Tp*(*COD*)Cl (**13**, *COD* = 1,5-cyclooctadiene) and Ru*Tp*(*py*)$_2$Cl (**14**).

Results and Discussion

Dimerization

As has been shown previously [3], complex **1** catalyzes the coupling of terminal alkynes to give butenynes. The catalytic cycle is initiated by loss of a PPh_3 ligand and formation of the coordinatively unsaturated species Ru*Tp*(PPh_3)Cl as monitored by $^{31}P\{^1H\}$ NMR spectroscopy in benzene-d_6 at 80°C. Upon adding HC≡CPh (10 equiv), the neutral vinylidene complex Ru*Tp*(PPh_3)(Cl)(=C=CHPh) (**2**) is formed as an intermediate; no other intermediate could be detected by NMR spectroscopy in addition to the reaction products **1a** and **1b** in the further course of the reaction (Table 1). The use of isolated compound **2** in an independent reaction catalyzes the coupling of HC≡CPh in a fashion nearly identical to **1** (Table 1). A possible reaction scheme could involve the coordinatively unsaturated alkyne complex Ru*Tp*(PPh_3)(–C≡CPh) formed by the liberation of HCl (Scheme 1), a proposal in accordance with other investigations [6, 9a, 9b]. In order to establish the mechanism of this process, complexes **3**–**12** have been tested as possible catalyst precursors for the dimerization of HC≡CPh.

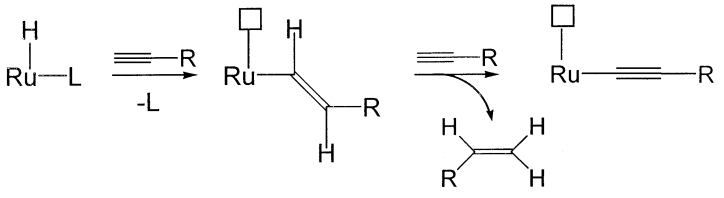


Scheme 1

Complex **3** is slightly less reactive than **1** affording about 80% conversion. The selectivity, however, remains unchanged (Table 1). In the course of the reaction, release of *py* rather than of PPh_3 is observed by ^1H NMR spectroscopy. The catalytically active species should thus be the same alkynyl complex as that originating from **1**. Complexes **4**, **6**, and **7**, on the other hand, are both less reactive and selective, the conversion rate dropping to 10, 14, and 50%, respectively. Complex **5** is catalytically inactive. Likewise, complex **8**, containing the chelating ligand *dppe*, does not show any catalytic activity. Complex **9**, featuring the hemilabile phosphino-amine ligand $Ph_2PCH_2CH_2NMe_2$ which is able to provide temporarily a coordination site due to reversible Ru-N bond cleavage, exhibits some although modest reactivity. The conversion is merely 13% (Table 1), the main outcome being the unusual coupling product Ru*Tp*(Cl)(κ^3(P, C, C)-$Ph_2PCH{=}CHC(Ph){=}CH_2$) reported previously [7]. The isoelectronic Ru*Cp** complex **10** turned out to be more reactive than **9** but shows no selectivity, yielding a 1:1 mixture of the *E* and *Z* isomers **1a** and **1b**. In the case of **11**, the selectivity of the reaction is reversed giving predominantly the head-to-head dimer (*Z*)-1,4-diphenyl-1-buten-3-yne (**Ib**) with about 70% conversion.

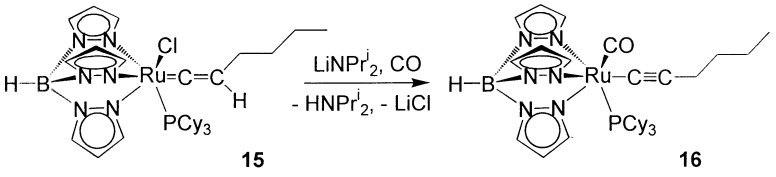
The poor reactivity of most of these complexes can be attributed to the lack of substitutive reactivity. Whereas ligands forming weak metal–ligand bonds (weak bases such as PPh_3, *py*) and/or sterically demanding ligands (*e.g.* PPh_3, PCy_3) facilitate the formation of a $16e^-$ intermediate, π acceptor ligands such as CO suppress ligand dissociation. Furthermore, the presence of bulky and/or hemilabile ligands promotes the subsequent formation of vinylidene complexes.

The most efficient catalyst precursor both in terms of reactivity and selectivity is complex **12**. As the primary step, a release of PPh_3 can be observed by means of $^{31}P\{^1H\}$ NMR spectroscopy. The conversion is essentially quantitative, and the head-to-head dimer (*E*)-1,4-diphenyl-1-buten-3-yne (**Ia**) is formed selectively (Table 1). The catalytically active species is expected to be the same alkynyl complex Ru*Tp*(PPh_3)(–C≡CHPh) as that arising from **1**, but presumably originating from insertion of the alkyne into the Ru–H bond [1, 2] giving first a vinyl intermediate which then undergoes σ-bond metathesis with another alkyne molecule releasing an olefine and the catalytically active $16e^-$ alkynyl species (Scheme 2). This process appears to be more facile than that described in Scheme 1, as becomes apparent in the case of aliphatic alkynes which are generally less reactive than the aromatic ones. Thus, the dimerization of $HC{\equiv}CBu^t$ catalyzed by **1** yields exclusively the respective *Z*-enyne. The conversion, however, is low (10%) even after 68 h at reflux in toluene. Complex **12** exhibits the same selectivity as **1**, but the conversion is increased to 16% already after 20 h under the same reaction condition.



Scheme 2

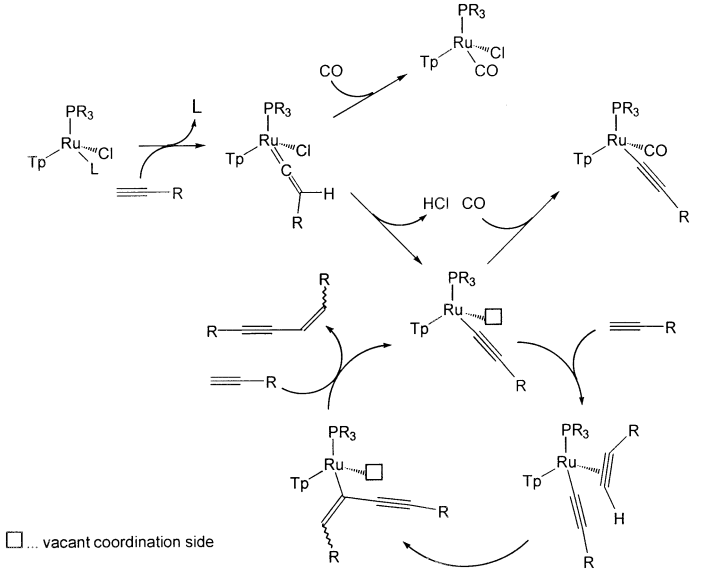
In order to provide further evidence for a 16e$^-$ akynyl complex as a reactive intermediate in the catalytic cycle, Ru*Tp*(P*Cy*$_3$)(=C=CHBu^n)Cl (**15**) has been treated with the strong base LiNPr$^i_2$ (1 equiv) at $-80°$C under a CO atmosphere. Under this condition, the coordinatively unsaturated intermediate Ru*Tp*(P*Cy*$_3$)-(–C≡C–Bu^n) is initially formed and subsequently trapped as Ru*Tp*(P*Cy*$_3$)(–C≡C–Bu^n)(CO) (**16**). Which has been isolated in 69% yield (Scheme 3) and was characterized by elemental analysis as well as ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy.



Scheme 3

In the ^{1}H NMR spectrum of **16**, the characteristic peak of the vinylidene proton at 4.06 ppm [8] is missing now, and in the ^{13}C{^{1}H} NMR spectrum of **16**, characteristic resonances for the C_α and C_β atoms of the alkyne moiety are found at 95.9 ($J_{CP} = 15.2$ Hz) and 105.9 ppm, respectively. The CO ligand gives rise to a doublet centered at 207.3 ppm ($J_{CP} = 15.3$ Hz). The resonances of the *Tp* and P*Cy*$_3$ ligands are in the expected ranges.

After liberation of HCl in the absence of a potential ligand such as CO, a second alkyne molecule is readily added to the alkynyl intermediate followed by a selectivity determining C–C coupling step as depicted in Scheme 4. Accordingly, the C_4 unsaturated product is eventually liberated from an intermediate σ-organyl metal species by σ-bond metathesis with an additional alkyne molecule.

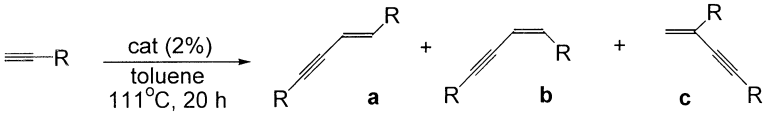


Scheme 4

The majority of all hitherto known catalytic dimerizations of terminal alkynes to C_4 units are migratory insertions of acetylenes into σ metal–carbon bonds proceeding, for instance, *via* alkynyl–vinylidene or alkynyl–vinyl coupling (*Bianchini* mechanism) [9]. In the case of late transition metals, enynyl intermediates could be isolated occasionally giving predominantly (*Z*) head-to-head coupling products [10]. A somewhat other mechanism appears to operate in the case of early transition metals, lanthanides, and actinides, where preferentially (*E*) head-to-head and head-to-tail dimers together with trimeric and even oligomeric coupling products are obtained. The catalytically active species in all these cases is a metal alkynyl complex generated by the intervention of strongly basic ligands such as hydride and alkyl groups.

Thus, the stereo- and regioselectivity of the dimerization should vary with the substituent on the alkyne. This indeed has been shown by us and others [1, 2, 3]. Similar results have been found in this work while studying the catalytic dimerization of HC≡C*R* ($R = SiMe_3$ (**II**), Bu^n (**III**), Bu^t (**IV**), CH_2Ph (**V**), C_6H_{11} (**VI**), COOEt (**VII**)) with **12** as precatalyst. As can be seen from Table 2, terminal alkynes which are able to form a conjugated system with the intermediate vinylidene or vinyl complexes appear to yield exclusively 1,4-enynes (*E* and/or *Z*), suggesting the operation of the *Bianchini* mechanism. Whether an *E* or *Z* isomer is formed depends on the ligand environment of the ruthenium complex (cf. Table 1, complexes **11** and **12**) as well as on the size of the substituent of the alkyne. For smaller alkynes, the insertion of another alkyne is often faster than the elimination of enynes; thus, also trimeric [11] or even oligomeric products are generated. Indeed, with **VII** and **12** as the catalyst, the main product is an oligomeric species

Table 1. Conversion and product distribution of the catalytic dimerization of HC≡CPh



Catalyst	Conversion (%)[a]	**Ia** (%)	**Ib** (%)	**Ic** (%)
Ru*Tp*(PPh_3)$_2$Cl (**1**)	98[b]	91	6	–
Ru*Tp*(PPh_3)(=C=CHPh)Cl (**2**)	98[b]	91	5	–
Ru*Tp*(PPh_3)(*py*)Cl (**3**)	80[b]	92	6	–
Ru*Tp*(PPh_3)(PMe_3)Cl (**4**)	10	59	41	–
Ru*Tp*(PPh_3)(CO)Cl (**5**)	–	–	–	–
Ru*Tp*(PBu^n_3)$_2$Cl (**6**)	14	75	25	–
Ru*Tp*(PCy_3)(OMe)Cl (**7**)	50	65	35	–
Ru*Tp*(*pn*)Cl (**8**)	13[b]	75	21	–
Ru*Tp*(*dppe*)Cl (**9**)	–	–	–	–
Ru*Cp**(PPh_3)H_3 [2a]	85	33	67	–
Ru*Cp**(*pn*)Cl (**10**)	63	50	50	–
Ru(*pn*)$_2Cl_2$ (**11**)	70	10	90	–
Ru*Tp*(PPh_3)$_2$H (**12**)	99	92	8	–

[a] Conversions are for isolated products; [b] oligo- or polymeric byproduct

Table 2. Conversion and product distribution of the catalytic dimerization of acetylenes with Ru*Tp*$(PPh_3)_2$H (**2**) as pre-catalyst

H-C≡C-*R*	Conversion (%)[a]	**a** (%)	**b** (%)	**c** (%)
R = Ph (**I**)	99	92	8	–
R = $SiMe_3$ (**II**)	67	–	69	29
R = n-Bu (**III**)	34	32	21	47
R = t-Bu (**IV**)	16		100	
R = CH_2Ph (**V**)	65	30	26	44
R = C_6H_{11} (**VI**)	86	85	15	–
R = COOEt (**VII**)	17[b]	100	–	–

[a] Conversions are for isolated products; [b] yield of dimeric species

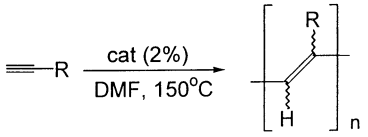
obtained in 83% yield (cf. Table 3). On the other hand, acetylene to vinylidene isomerizations are known to be sluggish for aliphatic alkynes [2, 12]. Therefore, the direct insertion of η^2-alkynes into the Ru-alkynyl σ-bond produces preferentially 1,3-enynes in a fashion similar to early transition metal catalyzed dimerizations of alkynes.

Oligo- and Polymerization

In order to study the oligo- or polymeric by-products formed in the catalytic dimerizations of terminal alkynes, we focused on those complexes affording high yields of polymeric products. Prerequisite for such a catalyst is the availability of two vacant coordination sites. Here we report on the ability of Ru*Tp*(*COD*)Cl (**13**) and Ru*Tp*$(py)_2$Cl (**14**) to promote oligo -and polymerizations of some terminal alkynes. As is known from our recent studies [4], in boiling *DMF* the *COD* ligand in **13** is labile and can be readily replaced by a variety of ligands. An intermediate in this reaction, although neither isolated nor spectroscopically detected, might be Ru*Tp*$(DMF)_2$Cl. Likewise, the *py* ligands in **14** are labile and are readily replaced by other potential ligands in *DMF* as the solvent. In a typical procedure, HC≡C*R* (0.3 *M*, *R* = Ph, Bu^n, COOEt) was added to a suspension of the catalyst (**13**-**14**, 2 mol%) in *DMF* (5 ml). The sealed *Schlenk* tube was heated in an oil bath at 150°C. Some experimental results are listed in Table 3. Noteworthy, in toluene or benzene **13** did not react at all, whereas **14** reacted only with great reluctance. In fact, **13** is stable in refluxing toluene even in the presence of potential ligands [4].

In the presence of **13**, HC≡CPh gave after 30 min a polymer with $\bar{M}_n$ = 7056 g/mol and *PDI* = 1.48. This process is a non-living polymerization, since prolongation of the reaction time to 20 h led to polymer degradation, resulting in a polymer of half the size of that in entry 1 ($\bar{M}_n$ = 3972 g/mol, *PDI* = 1.39). This thermally induced degradation can generally be rationalized in terms of three processes: intrachain backbiting, intramolecular cyclization, and interchain reactions [13]. For a mechanism to be suggested in the present case, the conformation of the poly(phenylacetylene) should be known. The ^{1}H NMR spectrum of entry 1 has a broad peak in the aromatic region (7.6–6.0 ppm) together with some small peaks at 7.84, 7.77, and 7.74 ppm assignable to 1,2,4- and 1,3,5-triphenylbenzene (7.74 ppm) [13, 14]. No resonances of *cis*-backbones could be

Table 3. Catalytic polymerization of some terminal acetylenes



Entry	HC≡C*R*	Catalyst	Time (h)	Yield (%)	$\bar{M}_n$[a]	*PDI*[b]	$\bar{n}$[c]
1	Ph	**13**	0.5	98	7056	1.48	69
2	Ph	**13**	20	99	3972	1.39	39
3	Ph	**14**	20	98	4139	1.42	41
4	Bu^n	**13**	20	77	1109	1.31	15
5	COOEt	**13**	5	60	1062	1.30	10

[a] $\bar{M}_n$ = number average molecular weight; [b] *PDI* = polymerization distribution index; [c] $\bar{n}$ = number average degree of polymerization

observed in the range of 6.3–6.1 ppm [13]. A very small and broad peak was detected within 4.1–3.4 ppm, pointing to the occurrence of some intramolecular cyclization products [15]. In the IR spectrum absorptions of *cis*-backbones are typically observed at 740 cm^{-1}, whereas the less significant peak of *trans*-backbones at 1265 cm^{-1} is not observed [16]. These results point to a *trans*-cisoidal structure with some *cis*-transoidal substructures in line with literature reports on thermally induced double bond isomerization from *cis*-transoidal to *trans*-cisoidal structures above 80°C with concomitant degradation of the polymer chain [14]. This degradation, mostly intrachain backbiting and intramolecular cyclization, is possible only for *cis*-subsequences [13] which may explain the missing resonance at 740 cm^{-1} in entry 2. All *cis*-substructures disappeared and molecular weights decreased upon prolonged heating. In the SEC (size exclusion chromatography) analysis, a second peak with $\bar{M}_p = 535$ g/mol ($\bar{M}_p$ = molecular weight at peak maximum) could be detected which may assigned to 1, 2, 4- and 1, 3, 5-triphenylbenzene. It has to be noted that for the calibration of the SEC analysis, poly(styrene) is used with a macroscopic structure quite different to that of the poly(acetylene)s or triphenylbenzene analyzed. Moreover, SEC is sensitive to the hydrodynamic volume of the compounds, and this may explain the deviation of the experimental $\bar{M}_p$ value from the actual molecular weight of triphenylbenzene (306.42 g/mol). Nevertheless, in the ^1H NMR spectrum signals of the substituted benzenes are present. Similar results were obtained with catalyst **14** (cf. entries 2 and 3).

In the presence of **13**, HC≡CBu^n formed an oligomer with $\bar{M}_n = 1109$ g/mol and *PDI* = 1.31 with only 77% yield after 20 h. The ^1H NMR spectrum shows peaks at 7.28 and 6.81 ppm (in a 1:7 ratio) assignable to the vinylic protons of a *cis* and *trans* backbone. From the integration of the aliphatic region some cyclizations can be concluded. In the $^{13}C\{^1H\}$ NMR spectrum, resonances for the vinylic carbons are observed at 143.3, 142.6, 139.0, and 126.9 ppm, suggesting again a mixture of (at least) *cis* and *trans* substructures. No evidence of cyclotrimerization products was found. The IR spectrum, surprisingly, showed peaks at 2017 cm^{-1}

and 1957 cm^{-1}, which can be assigned to a ν(C≡C) and a ν(C=C=C) vibration, but no corresponding resonances were found by NMR spectroscopy. We assume that these groups act as terminating structures in the oligomer produced *via* a metathesis mechanism.

In the presence of **13**, HC≡C-COOEt formed an oligomer with $\bar{M}_n = 1062$ g/mol and $PDI = 1.30$ in 60% yield after 5 h. The remaining 40% were found to be cyclotrimerization products, with the 1, 2, 4- and 1, 3, 5-derivatives in a 1:3 ratio. The cyclotrimers might also stem from a direct cyclotrimerization reaction in parallel fashion. The oligomer seems to be non ordered in view of the broad resonance of the vinylic protons (6.4–6.1 ppm) and the broadened $^{13}C\{^1H\}$ NMR resonances. Presumably, cycloaddition reactions may have occurred to some extent based on the signals of the allylic protons at 3.1–2.8 ppm.

In summary, the present catalysis presumably proceeds *via* a metathesis mechanism. The stereochemistry of the transition state of the coupling reaction determines the primary structure of the polymer [13, 17]. If bulky substituents (Ph) are involved, a *trans* dominated polymer backbone is generated which is more difficult to degradate. In this case, longer polymer chains are obtained. Small substituents (Bu^n, COOEt), on the other hand, give rise to polymers of a *cis* dominated structure which can be readily degradated. Therefore, and also because of the high temperature needed for pre-catalyst activation, short oligomers are afforded.

Experimental

General

All manipulations were performed under an inert atmosphere of argon using *Schlenk* techniques. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures [18]. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. Ru*Tp*$(PPh_3)_2$Cl (**1**) [19], Ru*Tp*(PPh_3)(=C=CHPh)Cl (**2**) [3], Ru*Tp*(PPh_3)(*py*)Cl (**3**) [3], Ru*Tp*$(PPh_3)(PMe_3)$Cl (**4**) [20], Ru*Tp*(PPh_3)(CO)Cl (**5**) [3], Ru*Tp*(PCy_3)(OMe)Cl (**7**) [8], Ru*Tp*(*pn*)Cl (**8**) [4], Ru*Tp*(*dppe*)Cl (**9**) [4], Ru*Cp**(*pn*)Cl (**10**) [11], Ru$(pn)_2Cl_2$ (**11**) [21], Ru*Tp*$(PPh_3)_2$H (**12**) [22], Ru*Tp*(*COD*)Cl (**13**) [4], Ru*Tp*$(py)_2$Cl (**14**) [4], and Ru*Tp*(PCy_3)(=C=CHBu^n)Cl (**15**) [8] were prepared according to the literature. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC-250 spectrometer operating at 250.13, 62.86 and 101.26 MHz, respectively, and were referenced to $SiMe_4$ and H_3PO_4 (85%). Microanalysis were done by the Microanalytical Laboratories of the University of Vienna. FT-IR spectra were taken on a Bomem FT-IR M 100; samples were cast from dichloromethane solutions on NaCl plates. For molecular weight determination by size exclusion chromatographie (SEC) at $T = 25°C$ the following arrangement was used: *THF* as solvent, a Merck-Hitachi L6200 intelligent pump combined with a degasser and pulse dampener, Polymer Standard Service seperation columns (10^6, 10^5, and 10^3 Å) and a Viscotek model 200 differential refractometer-viscometer. Poly(styrene) standards ($M_p = 685 - 1.8 \times 10^6$, $PDI < 1.1$) by Polymer Standard Service were used for calibration.

RuTp(PBu$^n_3$)$_2$Cl (**6**)

13 (315 mg, 0.688 mmol) and PBu^n_3 (348 mg, 1.49 mmol) were combined in *DMF* (4 ml) and refluxed for 2 h. The volume of the solution was reduced to about 0.5 ml, and the product was precipitated by addition of 4 ml of *n*-hexane. The residue was collected on a glass frit, washed with *n*-hexane, and dried *in vacuo*.

Yield: 234 mg (44%); $C_{33}H_{64}BClN_6P_2Ru$ (754.20 g/mol); calcd.: C 52.55, H 8.55, N 11.14; found: C 52.57, H 8.54, N 11.20; ^{1}H NMR (δ, $CDCl_3$, 20°C): 7.92 (2H, *Tp*), 7.68 (1H, *Tp*), 7.57 (2H, *Tp*), 7.33 (1H, *Tp*), 6.09–6.06 (m, 3H, *Tp*), 1.77 (m, 6H), 1.20–0.73 (m, 21H) ppm; ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20°C): 148.0 (1C, *Tp*), 144.6 (2C, *Tp*), 136.6 (1C, *Tp*), 135.3 (2C, *Tp*), 105.8 (1C, *Tp*), 105.7 (2C, *Tp*), 26.8 (t, $J_{PC} = 17.6$ Hz, 3C), 26.2 (bs, 3C), 25.3 (t, $J_{PC} = 8.8$ Hz, 3C), 14.4 (s, 3C) ppm; ^{31}P{^{1}H} NMR (δ, $CDCl_3$, 20°C): 22.4 ppm.

RuTp(PCy$_3$)(-C≡C-Bu^n)(CO) (**16**)

Ru*Tp*(P*Cy*$_3$)(=C=CHBu^n)Cl (**15**) (100 mg, 0.141 mmol) and *LDA* (15.1 mg, 0.141 mmol) were combined at −80°C in 4 ml of *THF* under a CO atmosphere and allowed to warm to room temperature. The solvent was removed *in vacuo*, the resulting solid was redissolved in CH_2Cl_2, the remaining solid was filtered off, the volume of the solution was reduced to about 0.5 ml and the product was precipitated by addition of 4 ml *n*-hexane. The residue was collected on a glass frit, washed with *n*-hexane, and dried *in vacuo*.

Yield: 68 mg (69%); $C_{34}H_{49}BN_6OPRu$ (700.66 g/mol); C 58.29, H 7.05, N 11.99; found: C 58.50, H 7.25, N 11.76; ^{1}H NMR (δ, Acetone-d_6, 20°C): 8.04 (1H, *Tp*), 7.86 (2H, *Tp*), 7.80 (1H, *Tp*), 7.64 (1H, *Tp*), 7.53 (1H, *Tp*), 6.29 (1H, *Tp*), 6.27 (1H, *Tp*), 6.15 (1H, *Tp*), 2.27−1.23 (m, 32H), 0.90−0.82 (m, 8H) ^{13}C{^{1}H} NMR (δ, Acetone-d_6, 20°C): 207.3 (d, $J_{PC} = 15.3$ Hz, CO), 146.5 (*Tp*), 145.7 (*Tp*), 144.3 (*Tp*), 137.6 (*Tp*), 136.7 (*Tp*), 135.6 (*Tp*), 107.3 (*Tp*), 106.5 (*Tp*), 106.4 (*Tp*), 105.9 (Ru-C≡*C*-Bu), 95.9 (d, $J_{PC} = 15.2$ Hz, Ru-*C*≡C-Bu), 36.2, 35.9, 34.9, 31.4–28.9, 27.6, 23.3, 14.8 ppm; ^{31}P{^{1}H} NMR (δ, Acetone-d_6, 20°C): 50.0 ppm.

Catalytic dimerization of terminal alkynes

In a typical procedure, alkynes H-C≡C-*R* (0.3 *M*, *R* = Ph, $SiMe_3$, Bu^n, Bu^t, CH_2Ph, C_6H_{11}, COOEt) were added to a suspension of the catalyst (**1**–**12**, 2 mol%) in toluene (5 ml), and the sealed *Schlenk* tube was heated in an oil bath for 20 h at 111°C. After that time the reaction mixture was evaporated to dryness under vacuum, and the coupling products were extracted with *n*-hexane. The solvent was again removed under vacuum affording isomeric mixtures of coupling products. The product distribution was determined by ^{1}H NMR spectroscopy. Where necessary for identification, separation of isomers was performed by column chromatography (silica gel, Merck, grade 60, 70–230 mesh, 60 Å).

(E)-1,4-Diphenylbut-3-en-1-yne (**Ia**)

^{1}H NMR (δ, $CDCl_3$, 20°C): 7.57−7.37 (m, 10 H, Ph), 7.12 (d, 1H, $J = 16.3$ Hz, H^3), 6.45 (d, 1H, $J = 16.3$ Hz, H^4) ppm; ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20°C): 141.7 (1C, C^4), 136.7 (1C, Ph), 132.0 (2C, Ph), 129.1 (2C, Ph), 129.0 (1C, Ph), 128.8 (2C, Ph), 128.6 (1C, Ph), 126.7 (2C, Ph), 123.8 (1C, Ph), 108.6 (1C, C^3), 92.2 (1C, C^1), 89.4 (1C, C^2) ppm.

(Z)-1,4-Diphenylbut-3-en-1-yne (**Ib**)

^{1}H NMR (δ, $CDCl_3$, 20°C): 8.07−7.97 (m, 2 H, Ph), 7.63−7.38 (m, 8H,Ph), 6.77 (d, 1H, $J = 11.8$ Hz, H^4), 6.02 (d, 1H, $J = 11.8$ Hz, H^3) ppm; ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20°C): 138.7 (1C, C^4), 136.6 (1C, Ph), 131.5 (1C, Ph), 128.9−123.4 (10C, Ph), 107.0 (1C, C^3), 95.9 (1C, C^1), 88.3 (1C, C^2) ppm.

(Z)-1,4-Di(trimethylsilyl)but-3-en-1-yne (**IIb**)

^{1}H NMR (δ, $CDCl_3$, 20°C): 6.26 (d, 1 H, $J = 15.2$ Hz), 6.16 (d, 1H, $J = 15.2$ Hz), 0.19 (s, 18H, $SiMe_3$) ppm; ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20°C): 146.8 (1C, C^3), 125.4 (1C, C^4), 105.8 (1C, C^1), 99.2 (1C, C^2), 0.3 (3C), −0.5 (3C) ppm.

1,3-Di(trimethylsilyl)but-3-en-1-yne (**IIc**)

^{1}H NMR (δ, $CDCl_3$, 20°C): 6.12 (d, 1 H, $J = 3.5$ Hz), 5.70 (d, 1H, $J = 3.5$ Hz), 0.16 (s, 18H) ppm; $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 135.6 (1C, C^3), 135.4 (1C, C^4), 125.4 (1C, C^4), 107.2 (1C, C^1), 99.1 (1C, C^2), 0.7 (3C), −1.6 (3C) ppm.

(E)-Dodec-7-en-5-yne (**IIIa**)

^{1}H NMR (δ, $CDCl_3$, 20°C): 6.04 (dt, 1 H, $J = 16.1$ Hz, $J = 7.0$ Hz, H^8), 5.45 (dt, 1H, $J = 16.1$ Hz, $J = 2.3$ Hz, H^7), 2.35−2.05 (m, 4H), 1.70−1.24 (m, 8H), 0.91 (t, 6H) ppm; $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 132.9 (C^8), 110.9 (C^7), 90.1 (C^6), 81.7 (C^5), 31.3, 31.0, 30.1, 22.3, 19.2, 17.7, 14.0, 13.6 ppm.

(Z)-Dodec-7-en-5-yne (**IIIb**)

^{1}H NMR (δ, $CDCl_3$, 20°C): 5.82 (dt, 1 H, $J = 11.0$ Hz, $J = 7.0$ Hz, H^8), 5.48 (dt, 1H, $J = 11.0$ Hz, $J = 2.2$ Hz, H^7), 2.34−2.07 (m, 4H), 1.72−1.24 (m, 8H), 0.93 (t, 6H) ppm; $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 142.1 (C^8), 110.3 (C^7), 88.7 (C^6), 80.0 (C^5), 31.3, 31.0, 30.1, 22.6, 19.5, 17.8, 14.1, 13.6 ppm.

2-Butyloct-1-en-3-yne (**IIIc**)

^{1}H NMR (δ, $CDCl_3$, 20°C): 5.20 (d, 1 H, $J = 2.4$ Hz, H^1), 5.12 (d, 1H, $J = 2.4$ Hz, H^1), 2.44−2.37 (m, 4H), 1.77−1.26 (m, 8H), 0.94 (t, 6H) ppm; $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 142.9 (C^2), 119.5 (C^1), 91.6 (C^4), 84.3 (C^3), 31.2, 30.8, 26.4, 22.0, 18.3, 17.9, 14.1, 13.6 ppm.

(Z)-2,2,7,7-(Tetramethyl)oct-5-en-3-yne (**IVb**)

^{1}H NMR (δ, $CDCl_3$, 20°C): 5.72 (d, 1 H, $J = 12.0$ Hz, H^6), 5.38 (d, 1H, $J = 12.0$ Hz, H^5), 1.28 (s, 9H), 1.22 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 152.9 (C^6), 118.5 (C^5), 106.4 (C^4), 67.3 (C^3), 29.8, 29.7, 27.5 (Me), 27.3 (Me) ppm.

(E)-1,6-Diphenylhex-4-en-2-yne (**Va**)

^{1}H NMR (δ, C_6D_6, 20°C): 7.80−6.90 (m, 10 H, Ph), 6.20 (dt, 1H, $J = 16.2$, 6.6 Hz, H^5), 5.51 (d, 1H, $J = 16.2$ Hz, H^4), 3.46 (s, 2H, H^1), 3.04 (2H, d, $J = 6.6$ Hz, H^6) ppm; $^{13}C\{^1H\}$ NMR (δ, C_6D_6, 20°C): 139.0 (C^4), 128.9 (Ph), 128.7 (Ph), 128.6 (Ph), 128.1 (Ph), 126.5 (Ph), 111.6 (C^5), 88.5 (C^3), 83.6 (C^2), 39.3 (C^6), 25.6 (C^1) ppm.

(Z)-1,6-Diphenylhex-4-en-2-yne (**Vb**)

^{1}H NMR (δ, C_6D_6, 20°C): 7.84−6.85 (m, 10 H, Ph), 6.65 (d, 1H, $J = 11.8$, 5.5 Hz, H^4), 5.80 (d, 1H, $J = 11.8$ Hz, H^4), 3.76 (s, 2H, H^1), 3.14 (2H, d, $J = 5.5$ Hz, H^6) ppm; $^{13}C\{^1H\}$ NMR (δ, C_6D_6, 20°C): 139.8 (C^4), 128.9 (Ph), 128.7 (Ph), 128.6 (Ph), 128.1 (Ph), 126.5 (Ph), 112.6 (C^5), 88.6 (C^3), 83.6 (C^2), 39.2 (C^6), 25.6 (C^1) ppm.

5-Phenyl-2-(phenylmethyl)-pent-1-en-3-yne (**Vc**)

^{1}H NMR (δ, C_6D_6, 20°C): 7.82−6.90 (m, 10 H, Ph), 5.41 (d, 1H, $J = 1.5$ Hz, H^1), 5.05 (d, 1H, $J = 1.5$ Hz, H^1), 3.36 (s, 2H, CH_2), 3.33 (s, 2H, CH_2), ppm; $^{13}C\{^1H\}$ NMR (δ, C_6D_6, 20°C): 142.2 (C^2), 129.4 (Ph), 128.7 (Ph), 128.6 (Ph), 128.2 (Ph), 126.6 (Ph), 121.3 (C^1), 91.6 (C^3), 87.2 (C^4), 44.1 (CH_2Ph), 25.8 (C^5) ppm.

(E)-1,4-Di(1-cyclohexenyl)but-3-en-1-yne (**VIa**)

^{1}H NMR (δ, $CDCl_3$, 20°C): 6.57 (d, 1H, $J = 15.9$ Hz, H^4), 6.01 (m, 1H, *c*Hex), 5.84 (m, 1H, *c*Hex), 5.61 (d, $J = 15.9$ Hz, H^3), 2.16−2.13 (6H), 1.69−1.60 (6H) ppm; $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 144.6 (1C, C^4), 134.7 (*c*Hex^2), 133.2 (*c*Hex^1), 132.6 (*c*Hex^1), 133.2 (*c*Hex^2), 104.9 (1C, C^3), 93.1 (1C, C^1), 87.5 (1C, C^2), 29.9, 24.5, 23.3, 23.1, 22.94, 22.90, 22.88, 22.2 ppm.

(Z)-1,4-Di(1-cyclohexenyl)but-3-en-1-yne (**VIb**)

^{1}H NMR (δ, $CDCl_3$, 20°C): 6.10 (m, 1H, *c*Hex), 6.05 (d, 1H, $J = 11.8$ Hz, H^4), 5.97 (m, 1H, *c*Hex), 5.42 (d, $J = 11.8$ Hz, H^3), 2.17−2.13 (6H), 1.69−1.60 (6H) ppm; $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 142.1 (1C, C^4), 136.2 (*c*Hex^2), 135.3 (*c*Hex^1), 132.7 (*c*Hex^2), 133.2 (*c*Hex^1), 104.5 (1C, C^3), 96.7 (1C, C^1), 85.4 (1C, C^2), 29.5, 26.7, 23.3, 23.1, 22.94, 22.90, 22.88, 22.2 ppm.

(E)-But-3-en-1-yne-1,4-dicarboxylic acid, diethylester (**VIIa**)

^{1}H NMR (δ, $CDCl_3$, 20°C): 6.77 (d, 1H, $J = 16.0$ Hz, H^4), 6.45 (d, 1H, $J = 16.0$ Hz, H^3), 4.28 (m, 2H, CH_2), 4.25 (q, 2H, CH_2), 1.32 (t, 3H, CH_3), 1.30 (t, 3H, CH_3) ppm; $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 165.0 (COOEt), 160.0 (COOEt), 136.0 (C^4), 122.1 (C^3), 87.6 (C^2), 82.0 (C^1), 63.0 (OCH_2CH_3), 61.9 (OCH_2CH_3), 14.7 (2C, OCH_2CH_3) ppm.

1,3,5-Benzenetricarboxylic acid, triethylester (**VIId**)

^{1}H NMR (δ, $CDCl_3$, 20°C): 8.81 (s, 3H, $Ph^{2,4,6}$), 4.40 (q, 6H, CH_2CH_3), 1.42 (t, 9H, CH_2CH_3) ppm; $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 165.5 (3C, $COOCH_2CH_3$), 134.9 (3C, $Ph^{2,4,6}$), 132.0 (3C, $Ph^{1,3,5}$), 62.2 (3C, $COOCH_2CH_3$), 14.9 (3C, $COOCH_2CH_3$) ppm.

1,2,4-Benzenetricarboxylic acid, triethylester (**VIIe**)

^{1}H NMR (δ, $CDCl_3$, 20°C): 8.37 (d, $J = 1.9$ Hz, 1H, Ph^3), 8.17 (dd, $J = 1.9$ Hz, $J = 7.8$ Hz, 1H, Ph^5), 7.75 (d, $J = 7.8$ Hz, 1H, Ph^6), 4.38 (m, 6H, CH_2CH_3), 1.38 (m, 9H, CH_2CH_3) ppm; $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 167.9 (1C, $COOCH_2CH_3$), 167.1 (1C, $COOCH_2CH_3$), 165.6 (1C, $COOCH_2CH_3$), 136.8 (1C, Ph^1), 133.2 (1C, Ph), 132.6 (1C, Ph), 132.5 (1C, Ph), 130.6 (1C, Ph^3), 129.4 (1C, Ph^6), 62.5 (1C, $COOCH_2CH_3$), 62.4 (2C, $COOCH_2CH_3$), 14.6 (s, 3C, $COOCH_2CH_3$) ppm.

Catalytic oligo- and polymerization of terminal alkynes

In a typical procedure, alkynes (0.3 *M*, $R = Ph$, COOEt, Bu^n) were added to a suspension of the catalyst (**13**, **14**; 2 mol%) in *DMF* (5 ml), and the sealed *Schlenk* tube was heated in an oil bath at 150°C. After the time given below, the reaction mixture was evaporated to dryness, volatiles were removed under vacuum, and the product was analyzed.

Poly(phenylacetylene)

(a) Reaction time: 30 min; catalyst: **13**; yield: 98%; SEC: $\bar{M}_n = 7056$, $\bar{M}_w = 10440$, $\bar{M}_p = 9180$, $PDI = 1.48$; ^{1}H NMR (δ, $CDCl_3$, 20°): 7.84 (s) 7.77 (s), 7.74 (s), 7.6−6.0 (bm), 4.1−3.4 (bs) ppm; $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 128.0−123.2 ppm; IR: 3075 (w), 3053 (w), 3022 (w), 2919 (w), 1964 (w), 1598 (m), 1492 (m), 1448 (m), 1314 (w), 1217 (w), 1031 (w), 740 (m), 757 (s), 698 (s) cm^{-1}.

(b) Reaction time: 20 h; catalyst: **13**; yield: 99 %; SEC: $\bar{M}_n = 3972$, $\bar{M}_w = 5503$, $\bar{M}_p = 4986$, $PDI = 1.39$; additional byproduct: $\bar{M}_p = 535$; ^{1}H NMR (δ, $CDCl_3$, 20°C): 7.84, 7.77 (s), 7.74 (s), 7.6–6.0 (bm), 4.1–3.4 (bs) ppm; $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 142.3–130.6, 128.0–123.2 ppm; IR: 3075 (w), 3053 (w), 3022 (w), 2919 (w), 1964 (w), 1598 (m), 1492 (m), 1448 (m), 1314 (w), 1217 (w), 1031 (w), 757 (s), 698 (s) cm^{-1}.

(c) Reaction time: 20 h; catalyst: **14**; yield: 98%; SEC: $\bar{M}_n = 4138$, $\bar{M}_w = 5854$, $\bar{M}_p = 4778$, $PDI = 1.42$; additional byproduct: $\bar{M}_p = 607$; NMR and IR spectra as above.

Oligo(n-hexyne)

Reaction time: 20 h; catalyst: **13**; yield: 77%; SEC: $\bar{M}_n = 1109$, $\bar{M}_w = 1461$, $\bar{M}_p = 1014$, $PDI = 1.31$; ^{1}H NMR (δ, $CDCl_3$, 20°C): 7.28 (s, 0.15H), 6.81 (s, 1H), 2.58–2.52 (m), 2.23–1.89 (bm), 1.61–2.36 (bm), 0.95–0.88 (m) ppm; $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 143.3, 142.6, 139.0, 126.9, 126.5, 36.3, 24.2, 32.8–31.0, 23.8–23.5, 23.2, 14.6 ppm; IR: 2981 (s), 2925 (2), 2856 (s), 2027 (m), 1957 (m), 1726 (m), 1605 (m), 1463 (s), 1381 (s), 1314 (m), 1221 (m), 1117 (m), 1050 (m), 900 (w), 863 (w), 758 (w), 721 (w) cm^{-1}.

Oligo(ethylpropionate)

Reaction time: 5 h; catalyst: **13**; yield: 60%; SEC: $\bar{M}_n = 1062$, $\bar{M}_w = 1384$, $\bar{M}_p = 921$, $PDI = 1.30$; oligomers were seperated by precipitation on addition of methanol; ^{1}H NMR (δ, $CDCl_3$, 20°C): 6.41–6.07 (bm) 4.30–4.21 (bm), 3.1–2.8 (bm), 1.42–1.21 (bm) ppm; $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 165.8–165.5, 135.0–132.1, 61.7–61.2, 14.9–14.7 ppm; IR: 2983 (m), 2936 (w), 2090 (w), 2081 (w), 2069 (w), 2003 (w), 1963 (w), 1725 (s), 1472 (w), 1450 (w), 1391 (w), 1370 (m), 1304 (m), 1249 (s), 1187 (m), 1114 (m), 1029 (m), 935 (w), 863 (w), 767 (w) cm^{-1}.

Acknowledgements

Financial support by the *Fonds zur Förderung der Wissenschaftlichen Forschung* is gratefully acknowledged (Project No. 11896).

References

[1] For an overview of literature concerning catalytic dimerization of terminal alkynes see: Trost BM, Sorum MT, Chan C, Harms AE, Rühter G (1997) J Am Chem Soc **119**: 698

[2] (a) Yi CS, Liu N (1996) Organometallics **15**: 3968; (b) Straub T, Haskel A, Eisen MS (1995) J Am Chem Soc **117**: 6364; (c) Wakatsuki Y, Yamazaki H, Kumegawa N, Satoh T, Satoh JY (1991) J Am Chem Soc **113**: 9604 and references [9]

[3] Slugovc C, Mereiter K, Zobetz E, Schmid R, Kirchner K (1996) Organometallics **15**: 5275

[4] Gemel C, Trimmel G, Slugovc C, Mereiter K, Kremel S, Schmid R, Kirchner K (1996) Organometallics **15**: 3998

[5] For leading references see: (a) Wegner G (1981) Angew Chem **93**: 352; (b) Chien JCW (1984) Polyacetylene. In: Chemistry, Physics and Material Sciences. Academic Press, New York; (c) Gibson HW, Skotheim TJ (ed) (1986) Handbook of Conducting Polymers. Marcel Dekker, New York; (d) Fox HH, Wolf MO, O'Dell R, Lin BL, Schrock RR, Wrighton MS (1994) J Am Chem Soc **116**: 2827; (e) Rasmussen SC, Ronco SE, Misna DA, Billadeau MA, Pennington WT, Kolis JW, Petersen JD (1995) Inorg Chem **34**: 821; (f) Ginsburg EJ, Gorman CB, Grubbs RH (1995) Polyacetylenes. In: Stang PJ, Diederich F (ed) Modern Acetylene Chemistry. VCH Weinheim, p 353

[6] Bruce MI, Hall BC, Zaitseva NN, Skelton BW, White AH (1996) J Organomet Chem **552**: 307

[7] Slugovc C, Wiede P, Mereiter K, Schmid R, Kirchner K (1997) Organometallics **16**: 2768
[8] Gemel C, Kickelpick G, Schmid R, Kirchner K (1997) J Chem Soc Dalton Trans 2119
[9] (a) Bianchini C, Innocenti P, Peruzzini M, Romerosa A, Zanobini F (1996) Organometallics **15**: 272; (b) Bianchini C, Peruzzini M, Zanobini F, Frediani P, Albatini A (1991) J Am Chem Soc **113**: 5433; (c) Barbaro P, Bianchini C, Peruzzini M, Polo A, Zanobini F, Frediani P (1994) Inorg Chim Acta **220**: 5
[10] For crystal structures of coordinated enynes see: (a) Alcock NW, Hill AF, Melling RP (1991) Organometallics **10**: 3898; (b) Liles DC, Verhoeven PFM (1996) J Organomet Chem **522**: 33; (c) Yang SM, Chan MCW, Cheung KK, Che CM, Peng SM (1997) Organometallics **16**: 2819 and references [9]
[11] Mauthner K, Slugovc C, Mereiter K, Schmid R, Kirchner K (1997) Organometallics **16**: 1956
[12] Bruce MI (1991) Chem Rev **91**: 197
[13] Kunzler J, Percec V (1990) J Polym Sci Polym Chem Ed **28**: 1221 and references therein
[14] Simionescu CI, Percec V, Dumitrescu S (1977) J Polym Sci Polym Chem Ed **15**: 2497
[15] (a) Mayo FR (1968) J Am Chem Soc **90**: 1289; (b) Kirchner K, Riederle K (1983) Angew Makromol Chem **111**: 1; (c) Chong YK, Rizzardo E, Solomon DH (1983) J Am Chem Soc **105**: 7761
[16] Tsonis CP, Farona MF (1979) J Polym Sci Polym Chem Ed **17**: 1779
[17] Percec V (1983) Polym Bull **10**: 1
[18] Perrin DD, Armarego WLF (1988) Purification of Laboratory Chemicals, 3rd edn. Pergamon, New York
[19] Alcock NW, Burns ID, Claire KS, Hill AF (1992) Inorg Chem **31**: 2906
[20] Slugovc C, Sapunov VN, Wiede P, Merieter K, Schmid R, Kirchner K (1997) J Chem Soc Dalton Trans 4209
[21] Shen JY, Slugovc C, Wiede P, Mereiter K, Schmid R, Kirchner K (1998) Inorg Chim Acta **268**: 69
[22] Tenorio MJ, Tenorio MAJ, Puerta MC, Valerga P (1997) Inorg Chim Acta **259**: 77

Received July 10, 1997. Accepted September 26, 1997