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Journal of Organometallic Chemistry 593–594 (2000) 292–298

Journal of Organometallic Chemistry

Dimerization of terminal alkynes catalyzed by indenyl ruthenium(II) complexes

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Received 9 June 1999; accepted 22 September 1999

Dedicated to Professor Fausto Calderazzo, on the occasion of his 70th birthday.

Abstract

The indenyl ruthenium complexes [Ru(η^5-C_9H_7)X(dppm)] (X = H, **1**; C≡CPh, **2**; (*E*)-CH=CHPh, **3**), [Ru(η^5-C_9H_7)X(PPh_3)$_2$] (X = H, **4**; C≡CPh, **5**), [Ru(η^5-C_9H_7)X(dppe)] (X = H, **6**; C≡CPh, **7**), [Ru(η^5-C_9H_7)Cl(COD)] (**8**), (dppm = bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane; COD = 1,5-cyclooctadiene) catalyze the dimerization of phenylacetylene to (*E*)- and (*Z*)-1,4-diphenylbut-1-en-3-yne. The cyclopentadienyl complex [Ru(η^5-C_5H_5)H(dppm)] (**9**) is inactive. The activity of the complexes depending on phosphine follows the order dppm > bis-PPh_3 > dppe, after 13 h. The catalysis is less efficient for the aliphatic 1-octyne than for phenylacetylene. Addition of PPh_3 to complexes **5** and **8** enhances the conversion to the dimerization products. The isomeric distribution of *E* and *Z* enynes is dependent on different factors, such as temperature, reaction time, substrate to catalyst molar ratio, nature of σ-ligand. The isomers (*E*) and (*Z*)-1,4-diphenylbut-1-en-3-yne are synthesized on a semipreparative scale by catalysis of either complex **4** or **5**, and can be separated from the isomeric mixture by standard methods. The procedure represents a one pot preparation of the two isomers starting from one terminal alkyne by C–H activation.

Keywords: Indenyl; Ruthenium; Dimerization; Catalysis; Enynes

1. Introduction

Carbon–carbon coupling of alkynes is catalyzed by a variety of transition metal complexes and represents a convenient entry to unsaturated dimeric species, in particular 1,3- and 1,4-disubstituted enynes, as well as cycloisomeric products [1,2]. Among the complexes which perform the catalysis, those of ruthenium(II) have shown efficiency and selectivity in the dimerization of terminal alkynes (Scheme 1) [2].

$$2RC{\equiv}CH \rightarrow RC{\equiv}C{-}CH{=}CHR \quad (E+Z)$$

Scheme 1.

Active ruthenium complexes are characterized by the presence of various ancillary ligands, for instance the pentamethylcyclopentadienyl (C_5Me_5) group [3,4], the chelating anionic trispyrazolylborate [5] or maltolato ligands [6], multidentate phosphorus donors [7,8], or monodentate phosphine ligands [9]. The ancillary ligands affect the catalytic as well as the regio- and stereo-chemical features of the dimerization process. For instance, the reactions of pentamethylcyclopentadienyl ruthenium hydride complexes [Ru(η^5-C_5Me_5)H_3(L)] with terminal alkynes RC≡CH depend on the nature of the R group for the 1,3/1,4 disubstitution pattern of the enyne, while on the nature of L (PPh_3, PCy_3, PMe_3) for the relative formation of the *E* and *Z* isomers [3].

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0022-328X/00/$ - see front matter
PII: S0022-328X(99)00553-7

Table 1
Conversion of phenylacetylene in the presence of indenyl ruthenium complexes and regioselectivity (E/Z) for 1,4-diphenylbut-1-en-3-ynes [a,b]

Complex		Overall conversion of PhC≡CH (%)			Conversion of PhCCH into (E,Z)-enyne (%)			E/Z		
		13h	18h	42h	13h	18h	42h	13h	18h	42h
1	[Ru(η^5-C_9H_7)H(dppm)]	47			20			1.3		
2	[Ru(η^5-C_9H_7)(C≡CPh)(dppm)]	52		57	32 [c]		18 [d]	6.3		2.7
3	[Ru(η^5-C_9H_7){(*E*)-CH=CHPh}(dppm)]	43			28			10.2		
4	[Ru(η^5-C_9H_7)H(PPh_3)$_2$]	52		88	16		68	0.3		0.5
5	[Ru(η^5-C_9H_7)(C≡CPh)(PPh_3)$_2$]	68		97	21		27	2.4		1.8
5	[Ru(η^5-C_9H_7)(C≡CPh)(PPh_3)$_2$] + PPh_3 [e]		86			51			3.2	
6	[Ru(η^5-C_9H_7)H(dppe)]	44			10			2.0		
7	[Ru(η^5-C_9H_7)(C≡CPh)(dppe)]	42			12			8.3		
8	[Ru(η^5-C_9H_7)Cl(COD)] [f]		78			Traces			0.3	
8	[Ru(η^5-C_9H_7)Cl(COD)] + PPh_3 [f,g]		98			37			0.1	
9	[Ru(η^5-C_5H_5)H(dppm)]	10			0					
10	No complex	13								

[a] PhC≡CH (0.89 mmol), complex (0.025 mmol), toluene or toluene-d_8 (0.50 ml), $T = 110$°C.
[b] By GLC, bibenzyl as internal standard.
[c] (*E*, 28%; *Z*, 4%).
[d] (*E*, 13%; *Z*, 5%).
[e] PPh_3, 0.28 mmol.
[f] By ^{1}H-NMR.
[g] PPh_3, 0.25 mmol.

With regard to the mechanism, there is general agreement that the fundamental step of carbon–carbon bond formation involves intramolecular coupling between a coordinated acetylide and an alkyne–vinylidene ligand, to form a metal bound butenynyl species [3,7,10]. Therefore, the catalyst precursor is expected to allow the formation of an acetylide complex and of a free coordination site for π-alkyne–vinylidene isomerization [11].

We have studied extensively the stoichiometric activation of terminal alkynes and alkynols by indenyl ruthenium complexes, which has allowed the synthesis of a series of alkynyl and unsaturated carbene derivatives, mainly vinylidene and allenylidene complexes [12]. In a kinetic study on the mechanism of the insertion of phenylacetylene into the Ru–H bond of [Ru(η^5-C_9H_7)H(dppm)] (dppm = bis(diphenylphosphino)methane), we have also observed the formation of (*E*) and (*Z*)-PhCH=CHC≡CPh, in the presence of excess phenylacetylene [13]. Indenyl complexes are known to exhibit higher reactivity than the corresponding cyclopentadienyl analogues in different reactions of transition metal complexes [13–16]. With regard to catalysis, the higher activity of indenyl complexes has been described for the trimerization of alkynes in rhodium(I) systems [17].

We describe here the dimerization reaction of terminal alkynes catalyzed by the indenyl ruthenium complexes [Ru(η^5-C_9H_7)X(dppm)] (X = H, **1**; C≡CPh, **2**; (*E*)-CH=CHPh, **3**), [Ru(η^5-C_9H_7)X(PPh_3)$_2$] (X = H, **4**; C≡CPh, **5**), [Ru(η^5-C_9H_7)X(dppe)] (X = H, **6**; C≡CPh, **7**), [Ru(η^5-C_9H_7)Cl(COD)] (**8**), and by the cyclopentadienyl complex [Ru(η^5-C_5H_5)H(dppm)] (**9**) (dppe = 1,2-bis(diphenylphosphino)ethane; COD = 1,5-cyclooctadiene) (Fig. 1).

We report on the effect of the σ-ligand X, of the phosphine and of the pentahapto ligand on the catalytic activity. These complexes either contain or offer access to an acetylide species as well as allow formation of 16 electron species, through indenyl ring slippage (η^5 to η^3 isomerization) [14], ring opening of the bidentate dppm ligand [18,19], or triphenylphosphine dissociation [20]. The experimental procedures for the preparation and isolation of pure (*E*) and (*Z*)-1,4-diphenylbut-1-en-3-yne are also described.

2. Results

2.1. Product analyses

Phenylacetylene, ring substituted arylacetylenes, and 1-octyne have been reacted in the presence of the ruthenium complexes in toluene. The reaction of phenylacetylene, which has been studied in more detail, proceeds toward the formation of the products of homocoupling, (*E*) and (*Z*)-1,4-diphenylbut-1-en-3-yne (Scheme 1, R = Ph).

In a typical experiment, a catalytic amount of indenyl complex (15–20 mg, 0.025 mmol, 3%) in 0.50 ml of

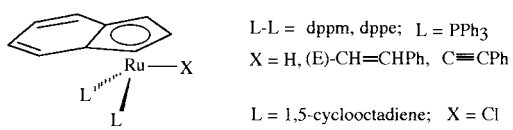


Fig. 1. Structure of ruthenium(II) precatalysts.

toluene and a 35 molar excess of phenylacetylene (100 μl, 0.90 mmol) were heated in a sealed vial. Table 1 reports the overall conversion of phenylacetylene, the conversion into the enyne products, and the isomeric composition as molar ratio of the *E* and *Z* species. These data have been obtained at 13 h of reaction or longer, by GLC or ^{1}H-NMR experiments. Detailed gas chromatography/mass spectrometry (GC-MS) analyses of the volatile products indicate that (*E*,*Z*)-1,4-diphenylbut-1-en-3-yne are the dominant components, accompanied by traces of styrene, of the dimer 1,4-diphenylbuta-1,3-diyne, and of trimeric species. A FAB analysis of the crude reaction mixture from complex [Ru(η^5-C_9H_7)(C≡CPh)(PPh_3)$_2$] (**5**) shows the presence of oligomers of phenylacetylene, from the trimer up to the undecamer ($M^+ = 1122$). Blank experiments, in the absence of metal complex, show that about 13% of PhC≡CH converts into polymeric species after 13 h at 110°C and this conversion increases at longer reaction times.

Product analyses for the reactions of phenylacetylene, *p*-chlorophenylacetylene, *o*-methylphenylacetylene, and 1-octyne in the presence of complex **5**, [Ru(η^5-C_9H_7)(C≡CPh)(PPh_3)$_2$], are reported in Table 2.

2.2. Stereoselectivity

With regard to the isomeric composition of (*E*) and (*Z*)-1,4-diphenylbut-1-en-3-yne, we have found that it is dependent on different factors, such as temperature, reaction time, concentration of reactants, and often scarcely reproducible. With increasing reaction times, the molar ratio [*E*]/[*Z*] decreases. This change is due to consumption of the *E* isomer, most likely involved in the formation of oligomeric products, and not to isomerization. In fact, by comparison of the reaction at 13 and 42 h, catalyzed by [Ru(η^5-C_9H_7)(C≡CPh)(dppm)], the moles of the *E* isomer are less at longer reaction time (Table 1). Isomerization into the *Z* isomer does not take place when a sample of the *E* species is heated for 48 h in the presence of complex **2**, and in the absence of phenylacetylene. At a temperature as low as 50°C, the conversion of phenylacetylene proceeds slowly, although with higher selectivity favoring the *E* isomer ($E/Z = 10/1$), in the reaction of complex **1**, [Ru(η^5-C_9H_7)H(dppm)]. Except for complexes **4** and **8**, the formation of the *E* isomer is dominant for the alkyne–complex molar ratio 35, used in most experiments.

2.3. Synthesis of (E) and (Z)-1,4-diphenylbut-1-en-3-yne

The reaction of phenylacetylene in the presence of complex [Ru(η^5-C_9H_7)(C≡CPh)(PPh_3)$_2$] was carried out under preparative conditions, starting from 0.97 g of the alkyne and 270 mg of **5**, for two days at 120°C. After separation of the organic products from the organometallic species, an isomeric mixture of 1,4-diphenylbut-1-en-3-yne (245 mg, yield 25%, $E/Z = 1.6$) was isolated by column chromatography (silica–petroleum ether). The *E* isomer can be separated from the *Z* isomer by consecutive crystallizations, from diethylether–hexane (−30°C) or by slow evaporation of hexane at room temperature, to obtain samples of 95–98% of isomeric excess. Separation of the two isomers can also be achieved by column chromatography.

The analogous reaction was carried out using complex **4**, [Ru(η^5-C_9H_7)H(PPh_3)$_2$], for 24 h at 120°C. Column chromatography of the extracted organic products ($E/Z = 0.34$) yields a first fraction containing (*Z*)-1,4-diphenylbut-1-en-3-yne (yield 25%, purity 97%) and a second one containing both isomers (total yield 44%). The yields of isolated enyne products are in agreement with the values calculated by NMR on smaller reaction scales.

2.4. Spectroscopic analysis of the ruthenium complexes

The transformations of the ruthenium complexes during the progress of the reaction have been observed by ^{31}P-NMR. Chemical shifts of the starting complexes and of the species observed during the catalytic cycle are reported in Table 3. The dppm hydride complex **1** is transformed into the vinyl complex **3** by insertion of phenylacetylene into the Ru–H bond [13]. This process

Table 2
Product analyses of the reactions of different alkynes in the presence of complex [Ru(η^5-C_9H_7)(C≡CPh)(PPh_3)$_2$] (**5**) [a,b]

Alkyne	Alkyne (%)	*E* isomer (%)	*Z* isomer (%)	*E*/*Z*	PPh_3 (%) [c]
PhC≡CH	14	48	30	1.6	9
*p*Cl–C_6H_4–C≡CH	–	42	48	0.9	10
*o*Me–C_6H_4–C≡CH	–	21	71	0.3	8
C_6H_{13}–C≡CH [d]	43	19	6	3.5	8

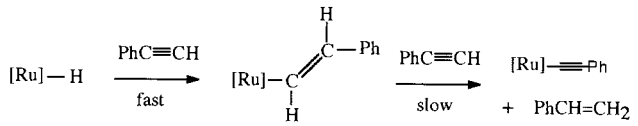
[a] Alkyne (0.84–0.92 mmol), ruthenium complex (0.025–0.028 mmol), toluene (0.50 ml), 120°C, 48 h, in sealed ampules.
[b] By gas chromatography.
[c] From complex decomposition.
[d] C_6H_{13}–CH=C=C=CH–C_6H_{13} (15%), and trimeric species (8%).

Table 3
^{31}P-NMR data of the indenyl ruthenium complexes **1**–**5**, during the dimerization of phenylacetylene [a]

Complex		Reaction start [b]	48 h
1	[Ru(η^5-C_9H_7)H(dppm)]	20.89 (d) [c] 22.97 [d]	22.89 traces 19.84
2	[Ru(η^5-C_9H_7)(C≡CPh)(dppm)]	19.84	19.84 22.80 traces
3	[Ru(η^5-C_9H_7){(*E*)-CH=CHPh}(dppm)]	22.97	19.84 (abundant precipitate)
4	[Ru(η^5-C_9H_7)H(PPh_3)$_2$]	65.13 (d) [e]	65.13 24.98 −3.00
5	[Ru(η^5-C_9H_7)(C≡CPh)(PPh_3)$_2$]	52.5	55.5 traces 53.7 24.98 −3.0

[a] Spectra taken at 80°C, in toluene-d_8, chemical shifts in ppm versus H_3PO_4 as internal standard.
[b] Before addition of alkyne.
[c] Doublet, $J_{P-H} = 12.0$ Hz.
[d] After addition of PhC≡CH.
[e] Doublet, $J_{P-H} = 3.6$ Hz.

is very fast at high temperature. Then, the vinyl complex reacts slowly with excess alkyne to form the acetylide complex **2** and styrene, and remains the stable organometallic species during catalysis ($\delta = 19.8$ ppm) (Scheme 2).



[Ru] = [Ru(η^5-C_9H_7)(dppm)]

Scheme 2.

The alkyne does not insert into the bis-phosphine hydride complex **4** [13], which changes slowly into a new complex ($\delta = 24.98$ ppm in toluene-d_8) by loss of ligands. This species, which is equally formed starting from the bis-phosphine acetylide complex **5**, shows an infrared band at 1945 cm^{-1} (CCl_4) and no NMR peaks of the indenyl group, except for a broad absorption centered at 7 ppm (^{1}H) and one in the range 125–130 ppm (^{13}C). Since an isolated sample of this complex does not exhibit any catalytic activity in the presence of phenylacetylene, it can be regarded as an inactive by-product of the bis-triphenylphosphine complexes.

The acetylide complex **2** does not show any reactivity in the presence of an equimolar amount of phenylacetylene, from room temperature to about 90°C, in toluene. Upon addition of a twenty-fold excess of the alkyne, the onset of reaction is observed at that temperature, as shown by the appearance of the doublet of (*E*)-1,4-diphenylbut-1-en-3-yne at 6.23 ppm ($J_{H-H} = 16.3$ Hz).

3. Discussion

3.1. General features

Phenylacetylene reacts in the presence of different indenyl ruthenium complexes to yield the products of head to head dimerization, (*E*) and (*Z*)-1,4-diphenylbut-1-en-3-yne. Although these ruthenium complexes do not promote high catalytic conversions into the dimerization products, this feature offers the possibility to evaluate the effects of complex structure, in particular ligand effects, on the activity and on the stereoselectivity. We have found that the indenyl complexes studied in this work exhibit more involved reaction features than those reported for the dimerization process catalyzed by other ruthenium complexes [3–9]. The complexity regards essentially the dependence of the isomeric composition of the enynes on different effects, and the formation of oligomeric products. In this respect, the *E* isomer is consumed during reaction. This accounts for both the formation of oligomers and the change of isomeric composition with reaction time. Related to this may be the reported finding that the *E* isomer is involved in the formation of a trimeric η^3-butadienyl complex by reaction with complex [Ru(η^5-C_5Me_5)(C≡CPh)(PPh_3)], and not the *Z* isomer. In general, *E*/*Z* stereoselectivity is higher at lower temperatures and shorter reaction times. Independently of the phosphine ligands, the *E* isomer is favored starting from the acetylide than from the hydride complexes. The formation of oligomers, accounting for the difference between the overall conversion and that into enynes, is due to the thermal polymerization of the alkyne,

and to the catalyst. For instance, complex **8**, [Ru(η^5-C_9H_7)Cl(COD)], characterized by the presence of the very labile ligand 1,5-cyclooctadiene, converts about 80% of phenylacetylene into oligomeric products and traces of enynes, which can be compared to the extent of conversion (13%) in the absence of metal complex (Table 1).

The addition of free PPh_3 to the reaction of complex **8** increases (i) overall conversion of the alkyne; (ii) formation of the dimerization products (from traces to 37%); and (iii) selectivity in *Z* isomer. This is similar to the effect observed on addition of tertiary phosphines to the [Ru(COD)(COT)] (COT = cyclooctatriene) complex, which led to selective formation of *Z*-butatrienes [21]. It suggests that ligation by phosphines is fundamental for selectivity of dimerization versus oligomerization and for geometric stereoselectivity. Obviously, a more naked metal center favors further couplings of the dimeric species.

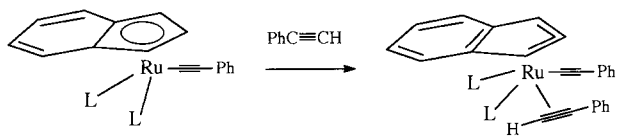
3.2. Synthesis

Since previous works on ruthenium catalyzed dimerizations of alkynes were limited to experiments at an analytical level, we have carried out the reaction of phenylacetylene on a semipreparative scale and have observed that the procedure represents an alternative method for the preparation of (*E*) and (*Z*)-1,4-diphenylbut-1-en-3-yne. The reported syntheses involve the palladium catalyzed cross coupling reaction of phenylacetylene with either *E* or *Z* styryl bromide [22,23], known as the Heck reaction, or with an alkenyl(phenyl)iodonium salt, [(*E*)-PhCH=CHIPh]BF_4 [24], obtained in turn from the corresponding alkenyltrimethylsilane [25]. In this work we have described that after isolation of the enyne products, the two isomers can be separated by further chromatography or by crystallization of the *E* isomer. It is remarkable that the procedure represents a one pot synthesis starting from one terminal alkyne by C–H activation, and the contemporary preparation of the two isomers, by turning into an advantage a lack of geometric stereoselectivity.

3.3. Ligand effects

The cyclopentadienyl complex [Ru(η^5-C_5H_5)H(dppm)] does not allow insertion of phenylacetylene into the Ru–H bond [13] neither does catalytic dimerization. This report represents another case of indenyl effect in catalysis involving alkynes, after the work on the trimerization reaction to benzene derivatives by rhodium(I) complexes [17]. Substitution on the benzene ring of the alkyne does not seem to affect significantly the ease of conversion (Table 2). Arylacetylenes are converted more readily than the aliphatic 1-octyne, which suggests the occurrence of vinylidene species in the cycle, known to be unfavored in aliphatic alkynes [11].

The activity is higher for the dppm **1**, **2** and **3**, and the bis-triphenylphosphine **4** and **5** complexes than for the dppe complexes **6** and **7**. The stereoselectivity changes in the order dppe > dppm. Both effects may be due to the larger steric hindrance of dppe than of dppm. Addition of free PPh_3 to the reaction catalyzed by [Ru(η^5-C_9H_7)(C≡CPh)(PPh_3)$_2$] (**5**) enhances both the conversion into the enynes and the stereoselectivity, in analogy to what described for complex **8**. These facts suggest that the role of triphenylphosphine is not that of promoting the reaction by formation of a free coordination site, through dissociation. In agreement with this proposal, we have observed that triphenylphosphine in **4**, [Ru(η^5-C_9H_7)H(PPh_3)$_2$], and **5**, [Ru(η^5-C_9H_7)(C≡CPh)(PPh_3)$_2$], is tightly bound. In fact, complex **4** remained unchanged upon treatment with a tenfold excess of PPh_2Me in refluxing toluene for 18 h, whereas complex **5** did not exchange phosphine after 48 h at 80°C, and underwent only partial substitution after reflux for 18 h. This behavior contrasts with that of the chloride complex [Ru(η^5-C_9H_7)Cl(PPh_3)$_2$] which exchanges triphenylphosphine for $PPhMe_2$ or PPh_2Me, quantitatively in a few hours at 50°C, in both toluene or thf [20]. If access of the alkyne to the metal center is not at the expense of a coordinated phosphine, one possibility is that this occurs through the classical η^5 to η^3 shift of the indenyl ligand, as depicted in Scheme 3 [13,14].



Scheme 3.

Direct observation by ^{31}P-NMR of the ruthenium complexes during the catalytic process indicate the sequence from **1** (hydride) to **3** (styryl) to **2** (acetylide), for the dppm complexes (Scheme 2), which appear quite robust, and from either **4** (hydride) or **5** (acetylide) to a decomposition product, for the bis-triphenylphosphine complexes. The exchange from hydride to acetylide upon reaction with an alkyne to form an active dimerization precatalyst is common in ruthenium complexes [3,5,8,21,26].

According to mechanistic studies on the subject, the most likely reaction sequence of enyne formation, in which a Ru–acetylide species is the catalyst precursor, may involve the following steps: (i) generation of a free coordination site and coordination of the alkyne; (ii) rearrangement of the π-complexed molecule to a vinylidene species; (iii) intramolecular acetylide migration to the α-vinylidene carbon to form a labile η^3 or η^1-

butenynyl complex; (iv) formal σ-bond metathesis at the Ru–alkenyl bond with a molecule of free alkyne to form the enyne product and regenerate the catalytic acetylide species [3,7,10]. Any of these possible species from the ruthenium complexes of this study are evidently highly reactive and escape direct observation. More simple pictures, implying insertion of the alkyne into the Ru–acetylide bond [4] or direct attack of a free alkyne molecule to the acetylide fragment, followed by reductive coupling of the butenynyl complex, would be consistent with the lack of observable intermediates, as it is often the case. These matters will be addressed through more specific mechanistic experiments.

4. Conclusions

The activity of indenyl ruthenium complexes in the dimerization and polimerization of terminal alkynes is reported, as well as another case of indenyl effect in catalysis. The role of phosphine is that of tuning chemioselectivity (dimers–polymers) and stereoselectivity (E/Z) by steric effects and electron donation. The one pot preparation of both geometric isomers of 1,4-diphenylbut-1-en-3-yne is accessible through a process of atom economy.

5. Experimental

The indenyl ruthenium complexes **1**, **3**, **4** [13], **2**, **5**–**7** [27], **8**, [28] and the cyclopentadienyl complex **9** [29] have been prepared as described in the literature. The reactions were carried out in toluene, which was distilled over potassium–benzophenone under nitrogen. Hexane and petroleum ether (40–70°C) were distilled before use. Silica Gel 60 (0.063–0.200 mm) was used for chromatography. In a typical run, the alkyne (0.90 mmol) and the ruthenium complex (0.023–0.025 mmol), in 0.50 ml of toluene, or of toluene-d_8, were sealed in a vial, or in a 5 mm NMR tube, under argon, and heated at the chosen temperature. The vials were opened, the appropriate amount of bibenzyl (ca. 20 mg) was added, and the reaction mixture analyzed by GLC or GC-MS. In the gas chromatographic method, the moles of products were determined by the use a conversion factor for phenylacetylene (0.50) and for the enynes (0.90) with respect to the internal standard bibenzyl. In the NMR method, the conversion was determined by integration of the peaks due to phenylacetylene ($\delta = 2.74$) and to 1,4-diphenylbut-1-en-3-yne (E isomer: $\delta = 6.22$, d, $J_{H-H} = 16.3$ Hz; Z isomer: $\delta = 5.75$, d, $J_{H-H} = 11.9$ Hz) with respect to the multiplet of toluene-δ_8 at δ 2.09 (Ph*Me*), as internal standard.

NMR spectra were recorded on a Bruker AC300 instrument at 300 MHz (^{1}H) or 121.5 MHz (^{31}P) using $SiMe_4$ or 85% H_3PO_4 as standards. GLC Analyses were performed on a Varian 3400 gas chromatograph (OV1 capillary column, 25 m × 0.25 mm). GC-MS analyses were obtained on a HP5890 GC (OV1 capillary column, 12 m × 0.2 mm) coupled with a HP5970 MSD. Low resolution mass spectra (FAB, *m*-nitrobenzyl alcohol) were obtained with a VG-Quattro Instrument, at the Università di Tor Vergata, Roma.

5.1. (E)-1,4-Diphenylbut-1-en-3-yne

A vial containing complex **5**, [Ru(η^5-C_9H_7)(C≡CPh)(PPh_3)$_2$] (0.27 g, 0.32 mmol), phenylacetylene (0.97 g, 9.5 mmol) and toluene (3 ml), was sealed and heated at 120°C for 48 h. After evaporation of the solvent and of unreacted alkyne, the residue was washed with hexane (5 × 3 ml), while crashing the mixture in a ultrasonic bath, in order to separate the organic products from insoluble material. The organic extracts, containing the enyne products and PPh_3, were chromatographed over silica (250 g) using petroleum ether as eluant to obtain a mixture of E (65%) and Z (34%) 1,4-diphenylbut-1-en-3-yne as the first band (0.24 g, 1.21 mmol, 25% yield). The E isomer separates out of the reaction mixture by crystallization from diethylether–hexane (−20°C), or from hexane at room temperature (98% purity). The isomeric mixture (168 mg) can be chromatographed further (silica, petroleum ether) to yield a band of essentially the Z component (36 mg, 93%), a second band of both isomers, and a third band of essentially the E component (46 mg, 96%).

5.2. (Z)-1,4-Diphenylbut-1-en-3-yne

A vial containing complex **4**, [Ru(η^5-C_9H_7)H(PPh_3)$_2$] (0.15 g, 0.20 mmol), phenylacetylene (0.97 g, 9.5 mmol) and toluene (3 ml), was sealed and heated at 120°C for 24 h. The crude reaction mixture was washed with hexane, and the extracts were chromatographed, as above. The first fraction yields 253 mg of Z enyne (97% by gc, 25% yield). A second band is eluted containing 177 mg of the isomers in comparable quantities (total yield 44%).

Acknowledgements

Financial support for travel from NATO (Collaborative Research Grant 950794), and CNR–CSIC (Program of Scientific Cooperation), are acknowledged.

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