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Stoichiometric cyclotrimerisation of chiral alkynes at a ruthenium centre: preparation of optically active (η^6-arene)(η^4-cycloocta-1,5-diene)ruthenium(0) complexes

Paolo Pertici, Alessandra Verrazzani, Emanuela Pitzalis, Anna Maria Caporusso, Giovanni Vitulli *

Centro di Studio del CNR per le Macromolecole Stereordinate ed Otticamente Attive, Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Risorgimento 35, 56126 Pisa, Italy

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Abstract

The chiral alkynes (*S*)-MeCH(*R*)–C≡CH, **2** (R = Et, 3-methyl-1-pentyne, **a**; ^{i}Pr, 3,4-dimethyl-1-pentyne, **b**; ^{t}Bu, 3,4,4-trimethyl-1-pentyne, **c**), containing a stereogenic centre in α position to the triple bond, react at room temperature with the complex Ru(η^6-naphthalene)(η^4-COD), **1**, to give the corresponding optically active complexes Ru{η^6-(*S*)-1,3,5-C_6H_3[CH(Me)R]$_3$}(η^4-COD), **6**, and Ru{η^6-(*S*)-1,2,4-C_6H_3[CH(Me)R]$_3$}(η^4-COD), **7**, the η^6-1,3,5-arene regioisomer being the prevalent product. With (*S*)-**2a**, a mixture of **6a** and **7a** (**6a**/**7a** = 90:10) is obtained and, with the more sterically demanding alkynes (*S*)-**2b** and (*S*)-**2c**, the regioselectivity to the corresponding complexes **6b** and **6c** is almost complete. This synthetic procedure does not involve the stereogenic centres on the alkynes and it proceeds with complete stereoselectivity.

Keywords: Optically active complexes; Ruthenium; Alkyne cyclotrimerisation; Arene complexes; 1,5-Cyclooctadiene complexes

1. Introduction

Arene ruthenium complexes are of great interest in preparative chemistry and catalysis [1,2]. In the presence of additional chiral phosphine ligands, (η^6-arene)Ru(II) species have been found to be excellent enantioselective hydrogen transfer catalysts [3]. In these compounds the arene–metal bond is very stable [4–6] and this makes them attractive for asymmetric synthesis due to the availability of chiral complexes in which the chirality depends on the arene ligand. Chiral (η^6-arene)(η^4-COD)ruthenium(0) complexes (COD = 1,5-cyclooctadiene) have been previously prepared by replacing the η^6-ligand in the complexes Ru(η^6-cycloocta-1,3,5-triene)(η^4-COD) [7–9] or Ru(η^6-naphthalene)(η^4-COD) [10–12] by the suitable arene. The subsequent reaction with hydrochloric acid affords the corresponding [$RuCl_2$(η^6-arene)]$_2$ complex [7,10].

We recently found that the stoichiometric cyclotrimerisation of alkynes promoted by Ru(η^6-naphthalene)(η^4-COD), **1**, allows the preparation of a wide range of Ru(η^6-arene)(η^4-COD) complexes, some of which cannot be obtained by alternative way [13]. We report here that using chiral alkynes such as (*S*)–MeCH(*R*)–C≡CH, **2** (R = Et, 3-methyl-1-pentyne, a; ^{i}Pr, 3,4-dimethyl-1-pentyne, b; ^{t}Bu, 3,4,4-trimethyl-1-pentyne, c), characterised by different steric requirements, the above reaction provides a valuable preparative route to the corresponding new optically active Ru(η^6-arene)(η^4-COD) complexes.

2. Results and discussion

2.1. Preparation of the optically active 1-alkynes (S)-3-methyl-1-pentyne, 2a, (S)-3,4-dimethyl-1-pentyne, 2b and (S)-3,4,4-trimethyl-1-pentyne, 2c

The enantiomerically enriched 1-alkynes **2a**–**c** have been prepared according to Scheme 1. The optically

* Corresponding author. Tel.: +39-050-918224; fax: +39-050-918260.

E-mail address: pervit@dcci.unipi.it (G. Vitulli).

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active propargylic carbinols (*S*)-**4a**–**c**, used as starting materials, have been easily obtained by resolution of their hydrogen phthalates with (−)-brucine in acetone as solvent and subsequent hydrolysis [14–17]. They were converted into the methanesulfonates (*S*)-**5a**–**c** by reaction, at −70°C, with one equivalent of butyllithium followed by treatment with methanesulfonyl chloride. Compounds (*S*)-**5a**–**c** react nicely in situ with a suspension of $LiCu_2Br_3$ in THF at −70°C, to give, after 5 min at room temperature (r.t.), the bromoallenes (*R*)-**3a**–**c** in excellent yields [14,18]. The reaction of compounds (*R*)-**3a**–**c** with two equivalents of lithium aluminium hydride in diethyl carbitol at r.t. [19] gives, after hydrolysis, the 1-alkynes (*S*)-**2a**–**c** with good overall yields and high purity.

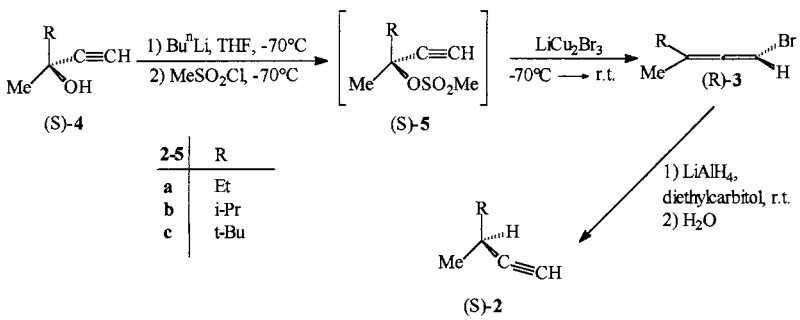
The stereochemical results obtained, reported in Table 1, indicate that the sequence alcohol → alkyne occurs with complete stereoselectivity [14,20]. These reactions can be considered as a suitable pathway to easily obtain optically active α-branched 1-alkynes, most of the other procedures reported in the literature [21–25] lacking in one or more of the fundamental requirements of low racemization, good chemical yields and availability of the chiral reaction intermediates. For instance, the high number of steps in the sequence based on the bromination–dehydrobromination of the corresponding α-olefins dramatically affects the 1-alkyne overall yield [21,22], while methods based on Wittig-type reactions starting from chiral aldehydes are affected by significant racemization phenomena [23].

2.2. Reaction of complex Ru(η^6-naphthalene)(η^4-COD), **1**, with the alkynes (*S*)-**2a**–**c**: synthesis of the optically active Ru(η^6-arene)(η^4-COD) complexes, **6** and **7**

Complex **1** reacts with the chiral alkynes (*S*)-**2a**–**c** at r.t. to give the new optically active Ru(η^6-arene)(η^4-COD) complexes, **6** and **7**, in which the arene is formed by cyclotrimerisation of the acetylenic compound (Scheme 2).

The reactions have been performed in THF as solvent, other solvents (i.e., aliphatic hydrocarbons, acetone, dichloromethane, chloroform) giving rise to partial decomposition. The best yields have been obtained using an excess of alkyne with respect to complex **1** (molar ratio alkyne/complex ≅ 6). The progress of the reaction was examined analysing by ^{1}H-NMR samples withdrawn at different times; the reactions were stopped when the starting complex **1** had completely reacted.

The regiomeric mixture of complexes **6** and **7** was recovered after chromatography on alumina in good to moderate yield [65, 40 and 25% using the alkynes **2a**, **2b** and **2c**, respectively] as a yellow oily material and they have been characterised by elemental analysis, ^{1}H-NMR spectroscopy and EI-MS spectrometry as reported in Tables 2 and 3. In all the reactions small

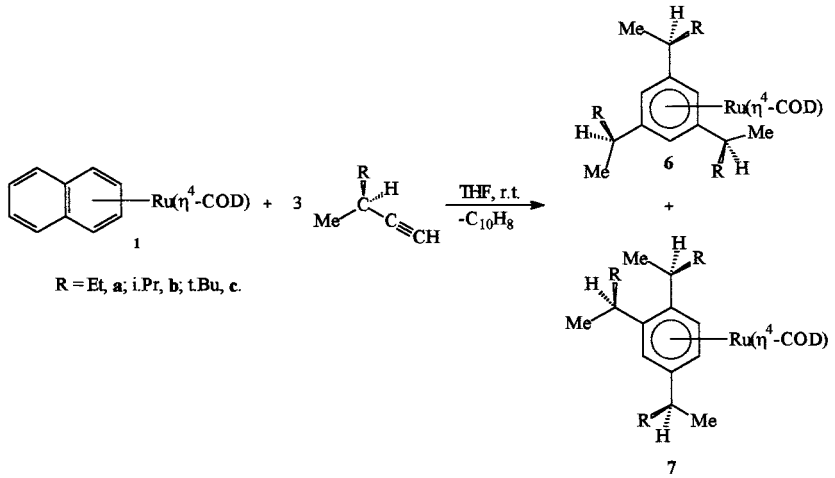


Scheme 1.

Table 1
Synthesis of 1-alkynes (*S*)-**2** via $LiAlH_4$ reduction of the corresponding bromoallenes (*R*)-**5**

Propargyl Carbinol				Bromoallene (*R*)-**5**		1-alkyne (*S*)-**2**			Stereoselectivity
(*S*)-**4**	R	$[\alpha]_D$ [a]	ee% [b]	$[\alpha]_D$ [a]	Yield%	$[\alpha]_D$ [a]	ee% [b]	overall yield%	
(*S*)-**4a**	Et	+2.84 [c]	94	−74.7 [d]	70	+43.40 [c]	93 [e]	63	>99
(*S*)-**4b**	^{i}Pr	+5.20 [d]	86	−87.9 [d]	68	+25.5 [d]	84 [f]	59	99
(*S*)-**4c**	^{t}Bu	+1.02 [c]	89	−86.1 [c]	83	+11.2 [d]	89 [f]	66	100

[a] Rotations were measured on neat liquids.
[b] By complexation GLC analyses on a [Ni-(*S*)-CAM] column.
[c] At 20°C.
[d] At 25°C.
[e] See Ref. [21].
[f] See Ref. [22].



Scheme 2.

Table 2
Ru(η6-arene)(η4-COD) complexes, **6** and **7**, obtained according to Scheme 2 [a]

Alkyne	Time (h)	Yield (%)	Products [b] (%)
(*S*)-3-Methyl-1-pentyne, **2a** [c]	24	65	Ru{η6-1,3,5-tri-[(*S*)-1-methylpropyl]benzene}(η4-COD), **6a** (90) Ru{η6-1,2,4-tri-[(*S*)-1-methylpropyl]benzene}(η4-COD), **7a** (10)
(*S*)-3,4-Dimethyl-1-pentyne, **2b** [d]	31	40	Ru{η6-1,3,5-tri-[(*S*)-1,2-dimethylpropyl]benzene}(η4-COD), **6b** (>95) Ru{η6-1,2,4-tri-[(*S*)-1,2-dimethylpropyl]benzene}(η4-COD), **7b** (just detectable)
(*S*)-3,4,4-Trimethyl-1-pentyne, **2c** [e]	36	25	Ru{η6-1,3,5-tri-[(*S*)-1,2,2-trimethylpropyl]benzene}(η4-COD), **6c** (>95) Ru{η6-1,2,4-tri-[(*S*)-1,2,2-trimethylpropyl]benzene}(η4-COD), **7c** (just detectable)

[a] Reaction conditions: **1** (0.5 g, 1.48 mmol), alkyne (8.9 mmol), THF (5 ml), r.t.
[b] The regioisomeric composition (**6** and **7**%) was determined by ^{1}H-NMR spectroscopy.
[c] 93% ee.
[d] 84% ee.
[e] 89% ee.

amounts of free arenes and linear oligomers have been detected by ^{1}H-NMR and EI-MS analysis.

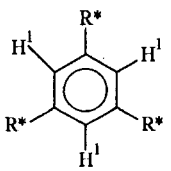
The regiomeric composition (**6** vs **7**) of the resulting mixture of arene-ruthenium complexes can be valued by the intensity of the aromatic proton resonances between δ 4 and 6 ppm in their ^{1}H-NMR spectra. The equivalent protons of the 1,3,5-substituted arene derivative **6** give a singlet while the non-equivalent protons of the 1,2,4-substituted arene derivative **7** furnish three different signals [13]. It was found that the alkyne **2a** gives a mixture of **6a** and **7a**, in which the first regioisomer containing the more stable symmetric 1,3,5-substituted arene is the main product (**6a**/**7a** = 90/10). Similarly, with the bulkier alkynes **2b** and **2c**, the complexes **6b** and **6c** are largely prevalent in the reaction mixture (>95%), the complexes **7b** and **7c** being only just detectable.

This result indicates that the steric hindrance at the stereogenic centre in α position to the triple bond has a considerable influence to determine the regioselectivity of the cyclotrimerisation. Accordingly to the generally accepted mechanism of cyclotrimerisation of alkynes [26], the ruthenacyclopentadienes **8** and **9** are possible intermediates of the reaction (Scheme 3) and the bulky alkynes **2a**–**c** will react preferentially with the intermediate **8** with formation of the less sterically hindered 1,3,5-substituted arene. As indicated by spectroscopic analyses, the stoichiometric cyclotrimerisation of the alkynes **2a**–**c** to the aromatic derivatives with formation of the complexes **6** and **7** does not involve the stereogenic centres on the alkynes and it occurs with almost complete stereoselectivity. Diastereomeric mixtures have not been observed by ^{1}H- and ^{13}C-NMR measurements. The ^{1}H-NMR spectra of the 1,3,5-regioisomers **6** exhibit only one singlet around δ 4.9 ppm, due to the equivalent aromatic protons, hence deriving from only one diastereoisomer present in solution. Similarly, the ^{13}C-NMR spectra of complexes **6** show one

Table 3
Analytical and spectroscopic complexes **6** and **7**

Complex[a]	Analysis (%)[b]		EI-MS	^{1}H NMR data[d]		
				Aromatic ligand		C_8H_{12}
	C	H	m/z[c]	η^6-arene protons	Others	
Ru{η^6-C_6H_3-1,3,5-[CH(Et)Me]$_3$}-(η^4-C_8H_{12}), **6a**[e] (90) Ru{η^6-C_6H_3-1,2,4-[CH(Et)Me]$_3$}-(η^4-C_8H_{12}), **7a**[e] (10)	68.39 (68.52)	9.39 (9.29)	456	5.15 (dd, 1H, H^3, J_{23} = 5.5 Hz, J_{34} = 1.1 Hz, 7a); 4.92 (s, 3H, H^1 6a); 4.56 (d, 1H, H^4, 7a); 4.42 (d, 1H, H^2, 7a)	1.96 (m, 3H, C_6H_3CH); 1.55 (m, 6H, CH_2CH_3); 1.12 (d, 9H, $CHCH_3$, J = 7.4 Hz); 0.79 (t, 9H, CH_2CH_3, J = 7.2 Hz)	3.25 (br s, 4H, =CH), 2.39 (br s, 8H, CH_2)
Ru{η^6-C_6H_3-1,3,5[CH(i.Pr)Me]$_3$}-(η^4-C_8H_{12}), **6b** (>95)	69.86 (69.97)	9.60 (9.72)	498	4.96 (s, 3H, H^1)	2.15 (m, 3H, C_6H_3CH); 1.72 (m, 3H, $CH(CH_3)_2$); 1.12 (d, 9H, $CHCH_3$, J = 7.4 Hz); 0.82 (d, 18H, $CH(CH_3)_2$; J = 7.3 Hz)	3.05 (br s, 4H, =CH), 2.05 (br s, 8H, CH_2)
Ru{η^6-C_6H_3-1,3,5[CH(t.Bu)Me]$_3$}-(η^4-C_8H_{12}), **6c** (>95)	71.30 (71.19)	10.19 (10.08)	540	4.97 (s, 3H, H^1)	2.10 (q, 3H, C_6H_3CH, J = 7.4 Hz); 1.07 (d, 9H, $CHCH_3$); 0.85 (s, 27 H, $C(CH_3)_3$)	3.20 (br s, 4H, =CH), 2.30 (br s, 8H, CH_2)

[a] The regioisomeric composition (%) of the mixtures was calculated by integration of the aromatic protons.
[b] Calculated values are given in parentheses.
[c] Referred to the most intense peak, corresponding to ^{102}Ru, of a cluster of peaks due to parent ion.
[d] Spectra were measured at 200 MHz in C_6D_6 using Me_4Si as internal standard; δ scale; s = singlet, d = doublet, t = triplet, m = multiplet, br = broad.
[e] Proton numbering for 1,3,5- and 1,2,4-substituted arene.



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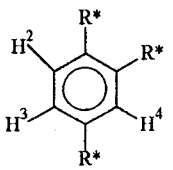

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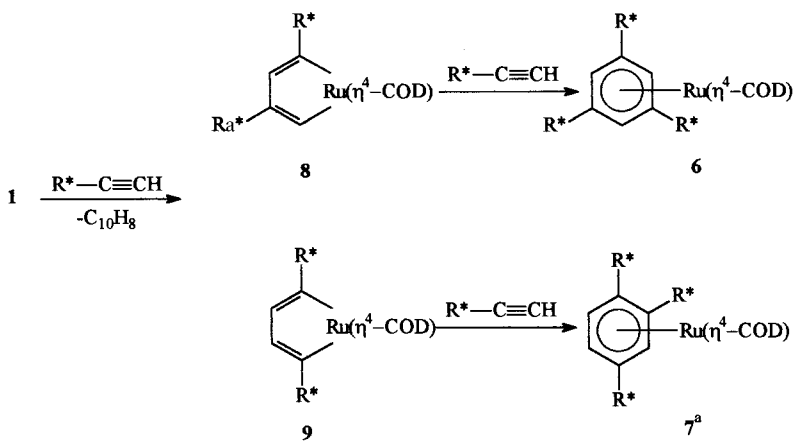

Scheme 3.

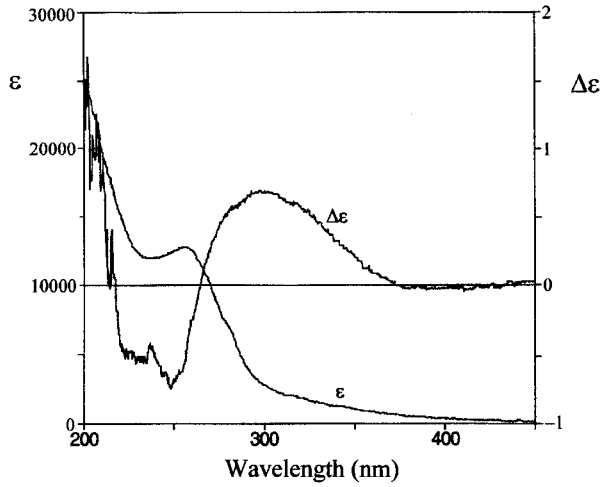

Fig. 1. UV and CD spectra of the complex Ru{η⁶-1,3,5-tri-[(*S*)-1,2-dimethylpropyl]-benzene}(η⁴-COD), **6b** (purity > 95%) ($c = 1.35 \times 10^{-3}$ mol dm^{-3}, hexane).

singlet in the range δ 110–108 ppm and another singlet in the range δ 86–84 ppm, due to the substituted and unsubstituted aromatic carbon atoms, respectively. This result is in agreement with the mechanism of cyclotrimerisation of alkynes [26], which does not involve the carbon atom in α position to the triple bond, as observed, for example, in the catalytic cyclotrimerisation of optically active 1-alkynes to benzene derivatives with nickel- and titanium-based catalysts which proceeds with complete stereoselectivity [27].

The chirooptical properties of complexes **6** and **7**, examined measuring the absorption and circular dichroism (CD) spectra, agree also with the stereoselectivity in their formation. In Fig. 1 the UV and CD spectra of the complex **6b**, obtained with very high chemoselectivity (> 95%) in the reaction of complex **1** with the alkyne **2b**, are reported. The UV-Vis spectrum, measured between 450 and 200 nm, shows a maximum at $\lambda = 260$ nm ($\varepsilon = 12.000$–13.000). At $\lambda > 260$ nm a long tail is observed till to 450 nm while at $\lambda < 260$ nm the absorption increases rapidly (i.e. at $\lambda = 200$ nm, $\varepsilon = 25.000$). As far as the maximum at 260 nm is concerned, its high intensity strongly indicates that this absorption is due to an electrically allowed transition making unlikely the assignment to the ^1L_b transition, typical of the substituted arenes, which generally exhibits an $\varepsilon \cong 500$ [28]. The 260 nm band is probably due to a charge transfer transition involving the orbital of the metal and the π-electrons of the ligand. This is supported with the comparable values of both the position and the intensity of this band observed also for the other complexes (mixture **6a** + **7a** and **6c**) which present a very similar structure of the transition metal–arene 'core'. The CD spectrum of **6b** shows the following sequence of the signals: negative Cotton effect at 400 nm with $\Delta\varepsilon = -0.03$, positive one at 300 nm with $\Delta\varepsilon = +0.7$ and negative one at 250 nm with $\Delta\varepsilon = -0.75$. Similar results have also been obtained with the mixture **6a** + **7a**, resulting from the reaction of **1** with the alkyne (*S*)-**2a**, indicating that the relative position of the stereogenic centres does not affect the chirooptical properties of the complexes.

It is worthy to note that the title synthetic route appears as the only method to prepare the complexes **6** and **7**, different procedures to get such kind of complexes, which employ preformed arenes [7,29,30], being unsuccessful. The reactions of the (*R*)(*S*)-1,3,5-tri-(1-methylpropyl)benzene with the complex **1**, in the presence of acetonitrile [29,30], and with the complex Ru(η⁶-cycloocta-1,3,5-triene)(η⁴-COD), under hydrogen atmosphere [7], were examined but in no case the formation of the complex **6a** was observed.

3. Concluding remarks

The results reported here show that the complex Ru(η⁶-naphthalene)(η⁴-COD), **1**, containing the naphthalene weakly bonded to the metal, is a very useful starting material to get with a simple procedure optically active arene ruthenium complexes, Ru(η⁶-arene)(η⁴-COD), by cyclotrimerisation of chiral 1-alkynes with a stereogenic centre in α position to the triple bond. This method appears as the only synthetic procedure to prepare complexes **6** and **7** and, probably, other similar complexes in which the arene contains bulky substituents. The starting alkynes **2a**–**c** have been conveniently obtained from the corresponding propargylic alcohols utilising a simple pathway which occurs with complete stereoselectivity and which represents a suitable and general synthetic procedure. It has been observed that the steric hindrance of the substituent at the stereogenic centre determines the regiochemistry of the cyclotrimerisation with formation of the thermodinamically more stable 1,3,5-trisubstituted isomer.

Finally, it is worth noting that the arene-ruthenium(0) complexes **6** can be converted in good yield to the corresponding arene-ruthenium(II) dichloride compounds by reaction with hydrocloric acid [7,10] and, hence, they are the starting material to get a wide range of other optically active η⁶-arene ruthenium complexes.

4. Experimental

All the operations regarding the manipulation of the ruthenium complexes were performed under argon atmosphere using conventional Schlenk-tube techniques. Solvents were purified by conventional methods. The complexes Ru(η⁶-naphthalene)(η⁴-COD), **1**, [30] and Ru(η⁶-cycloocta-1,3,5-triene)(η⁴-COD) [31–33] were obtained as previously reported. The (*R*)(*S*)-1,3,5-tri-

(1-methylpropyl)benzene [27] and the racemic propargylic alcohols (*R*)(*S*)-**4a**–**c** [34] were prepared and purified according to literature methods.

^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Gemini 200 instrument at 200 and 50.3 MHz, respectively. Chemical shifts were determined relative to internal $Si(CH_3)_4$ ($\delta = 0$ ppm); coupling constants J are in Hz. Mass spectra (EI) were recorded on a VG 7070E spectrometer. GC-MS analyses were performed on a Perkin–Elmer Q-Mass 910 spectrometer connected with a Perkin–Elmer gas chromatograph, equipped with a 'split-splitless' injector, using a SiO_2 capillary column and helium as carrier gas. GLC analyses were performed on a Perkin–Elmer 8600 gas chromatograph, equipped with an 'in column' injector and a flame ionisation detector (FID), using an SiO_2 'Wide Bore' column (DB1, 30m × 0.53mm, 5 μm) and helium as carrier gas. Complexation GLC analyses were performed using a glass capillary column (25 m × 0.25 mm) with 0.1% nickel bis [3-(heptafluorobutyryl)-1-(*S*)-camphorate] in OV-1 [Ni-(*S*)-CAM column] [35]. Optical rotations were measured with a Perkin–Elmer 142 automatic polarimeter using standard cuvettes (l = 0.1 and 1 dm). Microanalyses were carried out by the Laboratorio di Microanalisi, Facoltà di Farmacia, Università di Pisa, Italy.

4.1. Optical resolution of propargylic alcohols (R)(S)-4a–c. General procedure

The hydrogen phthalate of racemic carbinols (*R*)(*S*)-**4a**–**c** (0.7–0.8 mol), obtained by a published procedure [15,16] in 80–90% yield, was dissolved with stoichiometric amount of anhydrous (−)-brucine in ca. 4 l of boiling acetone. After the mixture was cooled to r.t. the brucine salt was filtered off, recrystallised from acetone several times, and decomposed with dilute HCl solution (6 N). The obtained (+)-hydrogen phthalate was treated with 10 M KOH solution and the (+)(*S*)-carbinol [20] was recovered by steam distillation. The enantiomeric excesses (ee%) of the recovered samples were evaluated by complexation GLC analysis on [Ni–(*S*)–CAM] column; samples from the racemic alcohols gave baseline-separated chromatographic peaks to allow the accurate estimation of the ee.

4.1.1. (S)-3-Methyl-1-pentyn-3-ol, (S)-4a

From two recrystallizations of the hydrogen phthalate brucine salt: b.p. 66°C/760 torr; d_4^{20} 0.8688; $[\alpha]_D^{20}$ + 2.84 (94% ee); ^{1}H-NMR (20%, $CDCl_3$), δ 1.02 (t, 3H, $J = 7$ Hz, CH_3); 1.46 (s, 3H, CH_3); 1.70 (q, 2H, $J = 7$ Hz, CH_2); 2.43 (s, 1H, ≡CH); 3.18 (s, 1H, OH).

4.1.2. (S)-3,4-Dimethyl-1-pentyn-3-ol, (S)-4b

From one recrystallization of the hydrogen phthalate brucine salt: b.p. 68°C/60 torr; d_4^{25} 0.8658; $[\alpha]_D^{25}$ + 5.20 (86% ee); ^{1}H-NMR (20%, $CDCl_3$), δ 0.95 (d, 3H, J = 7 Hz, CH_3); 0.99 (d, 3H, $J = 7$ Hz, CH_3); 1.39 (s, 3H, CH_3); 1.76 (m, 1H, CH); 2.22 (s, 1H, ≡CH); 2.37 (s, 1H, OH).

4.1.3. (S)-3,4,4-trimethyl-1-pentyn-3-ol, (S)-4c

From five recrystallizations of the hydrogen phthalate brucine salt: b.p. 50°C/17 torr; d_4^{20} 0.8664; $[\alpha]_D^{20}$ + 1.02 (89% ee); ^{1}H-NMR (20%, $CDCl_3$), δ 1.03 (s, 9H, CH_3); 1.40 (s, 3H, CH_3); 2.43 (s, 1H, ≡CH); 3.23 (s, 1H, OH).

4.2. Preparation of (R)-1-bromo-1,2-dienes, (R)-5a–c. General procedure

To a stirred solution of the appropriate optically active carbinol (*S*)-**4** (100 mmol) in THF (200 ml) were successively added, at −70°C, 100 mmol of buthyllithium in hexane and 110 mmol of methanesulfonyl cloride. After 5 min at −70°C, a suspension of $LiCu_2Br_3$ (from 120 mmol of LiBr and 240 mmol of CuBr in 200 ml of anhydrous THF) was added and the mixture was allowed to warm to r.t. within 30 min. The reaction mixture was quenched with saturated ammonium chloride and the organic materials were extracted with ether. The combined extracts were washed with additional ammonium chloride and water, dried (Na_2SO_4) and concentrated in vacuo (15–20 torr). The pure bromoallene was obtained by fractional distillation as a colorless liquid.

4.2.1. (R)-1-Bromo-3-methyl-1,2-pentadiene, (R)-5a

70% yield; b.p. 42°C/17 torr; d_4^{25} 1.2546; $[\alpha]_D^{25}$ −74.7; ^{1}H-NMR ($CDCl_3$), δ 1.05 (t, 3H, $J = 7$ Hz, CH_3); 1.83 (d, 3H, $J = 2$ Hz, CH_3C=); 2.10 (m, 2H, CH_2C=); 5.85 (m, 1H, =C=CHBr).

4.2.2. (R)-1-Bromo-3,4-dimethyl-1,2-pentadiene, (R)-5b

68% yield; b.p. 58°C/17 torr; d_4^{25} 1.1949; $[\alpha]_D^{25}$ −87.9; ^{1}H-NMR ($CDCl_3$), δ 1.08 (d, 6H, $J = 7$ Hz, CH_3); 1.85 (d, 3H, $J = 2.3$ Hz, CH_3C=); 2.27 (m, 1H, CHC=); 5.87 (m, 1H, =C=CHBr).

4.2.3. (R)-1-Bromo-3,4,4-trimethyl-1,2-pentadiene, (R)-5c

83% yield; b.p. 66°C/17 torr; d_4^{20} 1.1612; $[\alpha]_D^{20}$ −86.1; ^{1}H-NMR ($CDCl_3$), δ 1.08 (s, 9H, CH_3); 1.79 (d, 3H, $J = 2.2$ Hz, $CH_3C=$); 5.88 (q, 1H, $J = 2.2$ Hz, =C=CHBr).

4.3. $LiAlH_4$ reduction of (R)-1-Bromo-1,2-dienes, (R)-5, to (S)-1-alkynes, (S)-2. General procedure

A solution of the appropriate (*R*)-1-bromo-1,2-diene, (*R*)-**5** (60–70 mmol), in anhydrous diethylcarbitol (5–10 ml) was added dropwise, at 0°C, to a suspension of two equivalents of $LiAlH_4$ (30–40 mmol) in the same

solvent (30–50 ml). The reaction mixture was stirred for 20–24 h at r.t. and then hydrolysed with water. The crude product was recovered at 17 torr in a liquid nitrogen trap. Subsequent careful distillation yielded pure products.

*4.3.1. (S)-3-Methyl-1-pentyne, (S)-**2a***

90% yield; b.p. 58°C/760 torr; $[\alpha]_D^{20}$ +43.40 (93% ee) [21]; ^{1}H-NMR, δ 1.00 (t, 3H, $J = 7.3$ Hz, CH_3); 1.17 (d, 3H, $J = 6.9$ Hz, CH_3); 1.47 (m, 2H, CH_2); 2.02 (d, 1H, $J = 2.4$ Hz, ≡CH); 2.36 (m, 1H, CH); ^{13}C-NMR, δ 11.5, 20.5, 27.3, 29.7, 68.1, 88.9.

*4.3.2. (S)-3,4-Dimethyl-1-pentyne, (S)-**2b***

87% yield; b.p. 81°C/760 torr; $[\alpha]_D^{25}$ +25.5 (84% ee) [22]; ^{1}H-NMR, δ 0.97 (d, 6H, $J = 6.6$ Hz, CH_3); 1.15 (d, 3H, $J = 7$ Hz, CH_3); 1.55–1.74 (m, 1H, CH); 2.02 (d, 1H, $J = 2.4$ Hz, ≡CH); 2.25–2.42 (m, 1H, CHC≡); ^{13}C-NMR, δ 18.4, 18.5, 20.4, 32.6, 32.8, 68.9, 87.5.

*4.3.3. (S)-3,4,4-Trimethyl-1-pentyne, (S)-**2c***

80% yield; b.p. 100°C/760 torr; $[\alpha]_D^{25}$ +11.2 (89% ee) [22]; ^{1}H-NMR, δ 0.97 (s, 9H, CH_3); 1.15 (d, 3H, $J = 7$ Hz, CH_3); 2.05 (d, 1H, $J = 2.4$ Hz, ≡CH); 2.25 (dq, 1H, $J = 2.4$ and 7 Hz, CH); ^{13}C-NMR, δ 15.9, 27.0, 33.0, 37.1, 69.2, 88.0.

*4.4. Reaction of Ru(η^6-naphthalene)(η^4-COD), **1**, with the alkynes (S)-**2a–c**: synthesis of Ru(η^6-arene)(η^4-COD) complexes **6** and **7**. General procedure*

Complex **1** (0.5 g, 1.48 mmol) was dissolved in THF (5 ml) and the alkyne (8.9 mmol) was added. The solution was stirred at r.t. The progress of the reaction was checked by removing liquid samples of the solution and analysing the residue, obtained after evaporation of the solvent, by ^{1}H-NMR spectroscopy (C_6D_6); the reaction was stopped when the spectrum showed the disappearence of the signals of **1**. The solvent was removed under vacuum and the residue was dissolved in pentane (5 ml). The yellow–brown solution was chromatographed on an alumina column (20 cm, activity grade III) using pentane as eluent. Two fractions were collected.

The first colourless fraction was concentrated and analysed by GC-MS showing presence of dimers and cyclotrimers (arenes). From **2a**: dimer, $m/z = 164$; cyclotrimer, $m/z = 246$. From **2b**: dimer, $m/z = 192$; cyclotrimer, $m/z = 246$. From **2c**: dimer, $m/z = 220$; cyclotrimer, $m/z = 330$. The second yellow fraction was evaporated to dryness giving the Ru(η^6-arene)(η^4-COD) complex as an oily yellow material. The yield of the reactions together with elemental analyses, ^{1}H-NMR and mass data for the complexes **6** and **7** are reported in Tables 2 and 3.

*4.5. Reaction of Ru(η^6-naphthalene)(η^4-COD), **1**, with (R)(S)-1,3,5-tri-(1-methylpropyl)benzene in the presence of acetonitrile*

Complex **1** (0.1 g, 0.29 mmol) and (*R*)(*S*)-1,3,5-tri-(1-methylpropyl)benzene (0.714 g, 2.9 mmol) were treated with THF (5 ml) and acetonitrile (0.3 ml, 5.8 mmol). The red–orange mixture was stirred for 48 h at r.t. The resulting pale red–orange solution was separated from the solid material by filtration and then evaporated to dryness (0.1 torr). The ^{1}H-NMR (C_6D_6) of the residue showed presence of complex **1**, arene and free naphthalene.

4.6. Reaction of Ru(η^6-cycloocta-1,3,5-triene)(η^4-COD) with (R)(S)-1,3,5-tri-(1-methylpropyl)benzene under hydrogen atmosphere

(*R*)(*S*)-1,3,5-Tri-(1-methylpropyl)benzene (0.78 g, 3.2 mmol) was added to a solution of Ru(η^6-cycloocta-1,3,5-triene)(η^4-COD) (0.1 g, 0.32 mmol) in THF (5 ml) and the yellow solution was stirred under hydrogen (1 atm) at r.t. After ca. 3 h the solution became colourless and metallic ruthenium precipitated. The solution was separated from the solid by filtration and then evaporated to dryness (0.1 torr). The ^{1}H-NMR (C_6D_6) of the residue showed presence of the unreacted arene.

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