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Stoichiometric alkyne cyclotrimerization at a ruthenium centre: A new synthetic route to Ru(η^6-arene)(η^4-cycloocta-1,5-diene) complexes [1]

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Abstract

Alkynes RC_2R' [R = H, R′ = Bu^n, CH_2CMeEt, $(CH_2)_5C_2H$; R = R′ = Me, Ph; R = Me, R′ = Pr^n] undergo stoichiometric cyclotrimerization on reaction with the naphthalene–ruthenium(0) complex Ru(η^6-$C_{10}H_8$)(η^4-C_8H_{12}), **1**, at room temperature to give the corresponding Ru(η^6-arene)(η^4-C_8H_{12}) complexes in moderate to excellent yield. Unsymmetrical alkynes give a mixture of the isomeric η^6-1,3,5- (**a**) and η^6-1,2,4-arene (**b**) complexes, the ratio **a**:**b** being dependent on the electronic and steric effects of R and R′. In the presence of **1**, 1-hexyne and 4-methyl-1-hexyne cocyclotrimerize with acetonitrile to give substituted pyridines, which are formed in addition to the Ru(η^6-arene)(η^4-C_8H_{12}) complexes. © 1998 Elsevier Science S.A.

Keywords: Ruthenium; Alkyne cyclotrimerization; Arene complexes; 1,5-cyclooctadiene complexes; Pyridines

1. Introduction

The cyclotrimerization of alkynes to benzene derivatives catalysed by organotransition metal complexes is a well-known reaction [1–6]. In some cases the reaction occurs stoichiometrically to give a π-arene metal complex rather than the free arene, thus providing a route to η^6-arene transition metal compounds that has found occasional application [7]. For example, η^6- η^4-bis(arene) compounds of zero-valent ruthenium have been obtained by UV irradiation of Ru(η^6-C_6H_6)(η^4-1,3-C_6H_8) in the presence of an excess of alkyne [8]. Sterically hindered hexasubstituted arene cations [Ru(η^6-arene)(η^5-C_5H_5)]$^+$ have been prepared by reaction of η^4-cyclobutadiene ruthenium complexes and acetylenes [9,10]. Masuda et al. [11] have recently reported the synthesis of [Ru(η^6-arene)(η^5-C_5R_5)]$^+$ (R = H, Me) cations by cycloaddition of conjugated dienes and acetylene mediated by [CpRu]$^+$ or [Cp*Ru]$^+$ at low temperature.

In continuation of our studies [12–15] on the reactivity of the complex Ru(η^6-$C_{10}H_8$)(η^4-C_8H_{12}), **1** ($C_{10}H_8$ = naphthalene; C_8H_{12} = cycloocta-1,5-diene), we found that 3-hexyne displaces naphthalene from **1** and undergoes [2 + 2 + 2] cycloaddition to give the complex Ru(η^6-hexaethylbenzene)(η^4-C_8H_{12}), whose stereochemistry in solution at different temperatures and in the solid state was established [16]. This reaction obviously offers a new general route to Ru(η^6-arene)(η^4-C_8H_{12}) complexes containing variously substituted arenes. Zero-valent ruthenium compounds containing hexasubstituted arenes C_6R_6 are not easily accessible by the methods described in the literature except when R = H or Me [17,18].

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[1] Dedicated to Professor Peter Maitlis on the occasion of his 65th birthday.

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In this article we report the results obtained in the reaction of **1** with terminal and internal alkynes containing groups of varying steric bulk and electronic properties. The same reaction in the presence of acetonitrile has been found to provide a new synthetic entry to substituted pyridines.

2. Results and discussion

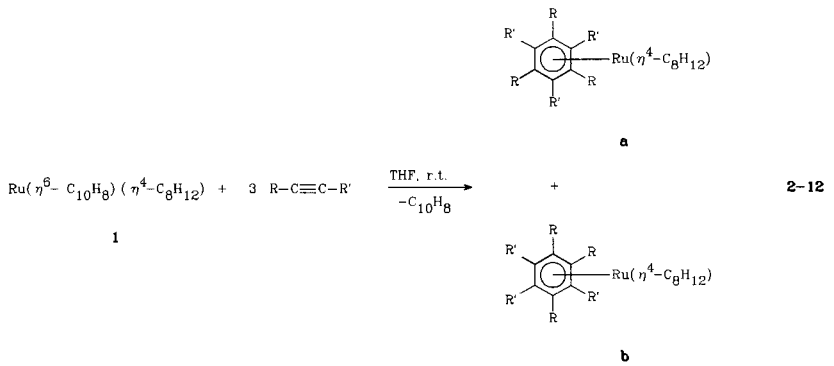
2.1. Reaction of complex 1 with alkynes

Complex **1** reacts at room temperature with internal and terminal alkynes giving the complexes Ru(η^6-arene)(η^4-C_8H_{12}), the arene being generated by cyclotrimerization of the acetylenic compound (Scheme 1).

The reactions are best carried out in THF, other solvents (i.e., aliphatic hydrocarbons, acetone, dichloromethane) giving rise to more decomposition. After chromatography (Al_2O_3) of the mother liquor, complexes **2**–**12** are recovered in moderate to high yield (20–90%) as yellow materials. However, the diphenylacetylene complex **11** is best isolated by slow crystallization from the reaction mixture without chromatography. At room temperature, complexes **2**, **3**, **5**, **6**, **7** and **10** are oils and complexes **4**, **9**, **11** and **12** are solids. The results obtained from reaction between **1** and alkynes are summarized in Table 1. Complex **1** reacts with either terminal or internal aliphatic alkynes containing a C≡CCH_2R group to give the mononuclear arene–ruthenium complexes within 1–4 h (runs 1, 2, 4, 8, 9, 11). The sterically hindered alkynes isopropylacetylene and *t*-butylacetylene (runs 5 and 6) react more slowly (15 h) and yields are lower (ca. 30%) owing to competitive decomposition. Trimethylsilylacetylene (run 7) reacts rapidly (3.5 h), but the isolated arene complexes were accompanied by $SiMe_3$-containing impurities that could not be separated by chromatography. Diisopropylacetylene and bis(trimethylsilyl)acetylene did not form Ru(η^6-arene)(η^4-C_8H_{12}) under the reaction conditions. Phenylacetylene (run 3) and diphenylacetylene (run 10) are less reactive than the aliphatic acetylenes (reaction time 5 and 10 h, respectively), probably because they contain deactivated triple bonds that coordinate with more difficulty to the metal. Interestingly, with 1,8-nonadiyne (run 4), only one of the acetylenic groups reacts, furnishing selectively complexes **5a** and **5b** containing free triple bonds.

Complexes **2**–**12** have been characterized by ^{1}H NMR spectroscopy, EI-MS spectrometry, and, in most cases, by elemental analysis, as reported in Table 2 and in Section 3. The regioisomeric composition (**a**% and **b**%) of the mixtures resulting from the cyclotrimerization of unsymmetrically substituted alkynes was calculated from the ^{1}H NMR spectra. For example, Fig. 1 displays the aromatic proton resonances of the mixture of Ru(η^6-1,3,5-tri-*n*-butylbenzene)(η^4-C_8H_{12}), **2a**, and Ru(η^6-1,2,4-tri-*n*-butylbenzene)(η^4-C_8H_{12}), **2b**, formed in the reaction between **1** and 1-hexyne (run 1). It shows a singlet at δ 4.83 ppm, attributed to the three equivalent protons of the 1,3,5-trisubstituted arene, and a doublet at δ 4.98 ppm, a singlet at δ 4.53 ppm and a doublet at δ 4.51 ppm due to the H_1, H_2 and H_3 protons of the 1,2,4-trisubstituted arene, respectively. The intensities of the signals establish that the regioisomers **2a** and **2b** are present in relative amounts of 70% and 30%, respectively.

VPC analysis of the mother liquor, performed after separation of the η^6-arene–ruthenium complex, shows that free mononuclear arene is not present in solution. Thus the arene, once formed by cyclotrimerization of the acetylenic compound, remains attached to the metal. Similar results are obtained also in the presence of an excess of alkyne (molar ratio of alkyne:**1** = 100), either at room temperature or under reflux, indicating the stability of the mononuclear arene–ruthenium bond [20]. In this case the excess of alkyne is recovered unchanged because the Ru(η^6-arene)(η^4-



Scheme 1. **2**: R = H, R′ = $(CH_2)_3CH_3$; **3**: R = H, R′ = $CH_2CH(CH_3)C_2H_5$; **4**: R = H, R′ = C_6H_5; **5**: R = H, R′ = $(CH_2)_5C{\equiv}CH$; **6**: R = H, R′ = $CH(CH_3)_2$; **7**: R = H, R′ = $C(CH_3)_3$; **8**: R = H, R′ = $Si(CH_3)_3$; **9**: R = R′ = CH_3; **10**: R = R′ = $(CH_2)_2CH_3$; **11**: R = R′ = C_6H_5; **12**: R = CH_3, R′ = $(CH_2)_2CH_3$.

Table 1
Ru(η^6-arene)(η^4-C_8H_{12}) complexes, **2**–**12**, obtained according to Scheme 1[a]

Run	Alkyne	Time (h)	Yield (%)	Products (%)[b]
1	1-Hexyne	1	95	Ru(η^6-1,3,5-tri-*n*-butylbenzene) (η^4-C_8H_{12}), **2a** (70) Ru(η^6-1,2,4-tri-*n*-butylbenzene) (η^4-C_8H_{12}), **2b** (30)
2	4-Methyl-1-hexyne	2	95	Ru[η^6-1,3,5-tri(2-methylbutyl)-benzene](η^4-C_8H_{12}), **3a** (75) Ru[η^6-1,2,4-tri(2-methylbutyl)-benzene](η^4-C_8H_{12}), **3b** (25)
3	Phenylacetylene	5	95	Ru(η^6-1,3,5-triphenylbenzene) (η^4-C_8H_{12}), **4a** (20) Ru(η^6-1,2,4-triphenylbenzene) (η^4-C_8H_{12}), **4b** (80)
4	1,8-Nonadiyne	3	90	Ru[η^6-1,3,5-tri(6-heptynyl)-benzene](η^4-C_8H_{12}), **5a** (70) Ru[η^6-1,2,4-tri(6-heptynyl)-benzene](η^4-C_8H_{12}), **5b** (30)
5	Isopropylacetylene[c]	15	28	Ru(η^6-1,3,5-triisopropylbenzene)(η^4-C_8H_{12}), **6a** (88) Ru(η^6-1,2,4-triisopropylbenzene)(η^4-C_8H_{12}), **6b** (12)
6	*t*-Butylacetylene[d]	15	33	Ru(η^6-1,3,5-tri-*t*-butylbenzene)(η^4-C_8H_{12}), **7a** (> 95) Ru[η^6-1,2,4-tri-*t*-butylbenzene)(η^4-C_8H_{12}), **7b** (just detectable)
7	Trimethylsilylacetylene[e]	3.5	23	Ru[η^6-1,3,5-tris(trimethylsilyl)benzene](η^4-C_8H_{12}) **8a** (40) Ru[η^6-1,2,4-tris(trimethylsilyl)benzene](η^4-C_8H_{12}) **8b** (60)
8	2-Butyne	2	95	Ru(η^6-hexamethylbenzene)(η^4-C_8H_{12}), **9**
9	4-Octyne	4	90	Ru(η^6-hexa-*n*-propylbenzene)(η^4-C_8H_{12}), **10**
10	Diphenylacetylene	10	50	Ru(η^6-hexaphenylbenzene)(η^4-C_8H_{12}), **11**
11	2-Hexyne	3	95	Ru(η^6-1,3,5-trimethyl-2,4,6-tri-*n*-propylbenzene)(η^4-C_8H_{12}), **12a** (30) Ru(η^6-1,2,4-trimethyl-3,5,6-tri-*n*-propylbenzene)(η^4-C_8H_{12}), **12b** (70)
12[f]	1-Hexyne	4	–	No reaction

[a]Reaction conditions (except where stated otherwise): **1** (0.196 g, 0.58 mmol), alkyne (3.48 mmol), THF (5 ml), room temperature.
[b]The regioisomeric composition (**a** and **b**%) was determined by ^{1}H-NMR spectroscopy.
[c]Reaction conditions: **1** (0.100 g, 0.29 mmol), alkyne (0.5 ml), THF (5 ml), room temperature.
[d]Reaction conditions: **1** (0.090 g, 0.26 mmol), alkyne (0.5 ml), THF (5 ml), room temperature.
[e]Reaction conditions: **1** (0.086 g, 0.25 mmol), hexane (10 ml), room temperature.
[f]Carried out with the complex Ru(η^6-*p*-cymene)(η^4-C_8H_{12}) (0.200 g, 0.58 mmol), under reflux.

C_8H_{12}) product is not active in the cyclotrimerization; hence reaction stops when no more **1** is present in solution. In agreement, the complex Ru(η^6-*p*-cymene)(η^4-C_8H_{12}), containing a mononuclear arene bonded to ruthenium, does not react with alkynes, even under reflux (run 12, Table 1), again pointing to the importance of the labile arene–ruthenium bond in **1** [21].

In general, the cyclotrimerization yields a mixture of Ru(η^6-arene)(η^4-C_8H_{12}) complexes containing η^6-1,3,5- and η^6-1,2,4-arenes. Terminal aliphatic alkynes form preferentially the 1,3,5-isomer (**a**:**b** ~ 70:30) containing the thermodynamically more stable symmetrical arene (runs 1 and 2), and this tendency is reinforced with the sterically bulkier

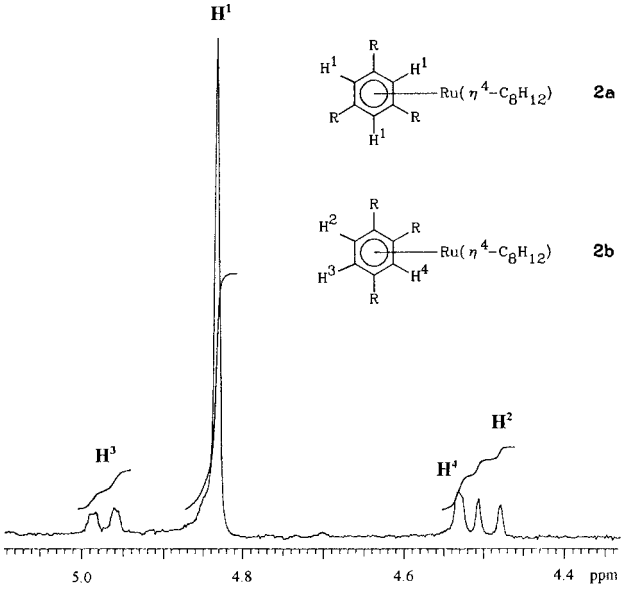


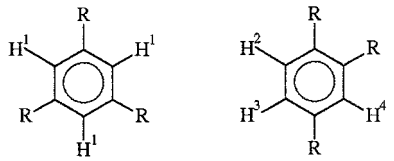
Fig. 1. ^{1}H NMR spectrum (C_6D_6, aromatic protons) of the mixture of complexes **2a** (70%) and **2b** (30%). R = $(CH_2)_3CH_3$.

Table 2
Analytical and spectroscopic data for compounds **2**–**12**

Complex[a]	Analysis (%)[b]		EI-MS	^{1}H NMR data[c]		
	C	H	m/z[d]	Aromatic ligand		C_8H_{12}
				η^6-arene protons[e]	Others	
Ru{η^6-C_6H_3-1,3,5-[$(CH_2)_3Me]_3$} (η^4-C_8H_{12}), **2a** (70); Ru{η^6-C_6H_3-1,2,4-[$(CH_2)_3Me]_3$} (η^4-C_8H_{12}), **2b** (30)	68.64 (68.56)	9.11 (9.23)	446	4.98 (dd, 1H, H^3, J_{23} = 5.5 Hz, J_{34} = 1.2 Hz, **2b**), 4.83 (s, 3H, H^1, **2a**), 4.53 (d, 1H, H^4, **2b**), 4.51 (d, 1H, H^2, **2b**)	2.12 (t, 6H, $C_6H_3CH_2$, J = 7.8 Hz), 1.6–1.2 [m, 12H,$(CH_2)_2$Me], 0.85 (t, 9H, *Me*, J = 7.4 Hz)	3.22 (br s, 4H, =CH), 2.43 (br s, 8H, CH_2)
Ru{η^6-C_6H_3-1,3,5-[$CH_2CH(Me)CH_2Me]_3$} (η^4-C_8H_{12}), **3a** (75); Ru{η^6-C_6H_3-1,2,4-[$CH_2CH(Me)CH_2Me]_3$} (η^4-C_8H_{12}), **3b** (25)	70.09 (70.01)	9.62 (9.66)	498	5.01 (m, 1H, H^3, **3b**), 4.79 (s, 3H, H^1, **3a**), 4.52–4.46 (m, 2H, H^2+H^4, **3b**)	2.15 (m, 3H, ϕCH*H*), 1.90 (m, 3H, ϕCH*H*), 1.6–1.0 (m, 9H, CH*H*CH_2)[f], 0.85 (m, 18H, *Me*)	3.25 (br s, 4H, =CH), 2.40 (br s, 8H, CH_2)
Ru{η^6-C_6H_3-1,3,5-$(C_6H_5)_3$} (η^4-C_8H_{12}), **4a** (20); Ru{η^6-C_6H_3-1,2,4 -$(C_6H_5)_3$} (η^4-C_8H_{12}), **4b** (80)	74.86 (74.55)	6.04 (5.82)	516	5.98 (s, 3H, H^1, **4a**), 5.68 (dd, 1H, H^3, J_{23} = 5.6 Hz, J_{34} = 1.3 Hz, **4b**), 5.19 (d, 1H, H^4, **4b**), 4.68 (d, 1H, H^2, **4b**)	7.6–6.94 (m, 30H, C_6H_5) 3.55 (m, 2H, =CH, **4b**)[a], 3.26 (m, 2H, =CH, **4b**)[a],	3.14 (m, 4H, =CH, **4a**)[a], 2.43–2.05 (m, 8H, CH_2)
Ru{η^6-C_6H_3-1,3,5-[$(CH_2)_5C\equiv CH]_3$} (η^4-C_8H_{12}), **5a** (70); Ru{η^6-C_6H_3-1,2,4-[$(CH_2)_5C\equiv CH]_3$} (η^4-C_8H_{12}), **5b** (30)	73.69 (73.80)	9.51 (8.43)	570	4.96 (d, 1H, H^3, J_{23} = 5.4 Hz, **5b**), 4.78 (s, 3H, H^1, **5a**), 4.44 (d + s, 2H, H^2+H^4, **5b**)	1.98 [m, 12H, $CH_2(CH_2)_3CH_2$], 1.83 (t, 3H, C≡CH, J = 2.7 Hz), 1.35 [br s, 18H, $CH_2(CH_2)_3CH_2$]	3.22 (br s, 4H, =CH), 2.40 (br s, 8H, CH_2)
Ru{η^6-C_6H_3-1,3,5-[$CH(CH_3)_2]_3$} ($\eta^4C_8H_{12}$), **6a** (88); Ru{η^6-C_6H_3-1,2,4-[$CH(CH_3)_2]_3$} (η^4-C_8H_{12}), **6b** (12)			413[g]	5.10 (s, 3H, H^1, **6a**), 4.75–4.60 (m, 3H, H^2, H^3, H^4, **6b**)[h]	2.38 (spt, 1H, J = 6.8 Hz, CH*Me*$_2$, **6a**), 1.25 (d, 6H, J = 6.8 Hz,CH*Me*$_2$, **6a**)	3.0–2.9 (m. 4H, =CH), 2.2-1.8 (m, 8H, CH_2)
Ru{η^6-C_6H_3-1,3,5-[$C(CH_3)_3]_3$} (η^4-C_8H_{12}), (**7a**) (> 95); Ru{η^6-C_6H_3-1,2,4-[$C(CH_3)_3]_3$} (η^4-C_8H_{12}), (**7b**) (< 5)			455[i]	5.46 (s, 3H, H^1, **7a**)[j,k]; 5.31 (m), 4.6 (d) (**7b**)	1.29 (s, CMe_3. **7a**)[j]	3.25 (m, 4H, =CH); 2.1–1.8 (m, 8H, CH_2)[j]
Ru{η^6-C_6H_3-1,3,5-[$Si(CH_3)_3]_3$} (η^4-C_8H_{12}), **8a** (40); Ru{η^6-C_6H_3-1,2,4-[$Si(CH_3)_3]_3$} (η^4-C_8H_{12}), **8b** (80)			504[l]	5.36 (s, 3H, H^1, **8a**), 4.82, 4.75, 4.48 (each m, 1H, H^{2-4}, **8b**)[j]	0.43 (s, $SiMe_3$, **8b**), 0.33 (s, $SiMe_3$, **8b**), 0.22 (s, $SiMe_3$, **8a** + **8b**)[j]	3.54–3.46 (m, 4H, =CH), 2.33–2.14 (m, 8H, CH_2)[j]

Ru{η^6-C_6Me_6}(η^4-C_8H_{12}), **9**[m]	64.73 (64.68)	8.12 (8.08)	372	1.73 (s, 18H, *Me*)	2.57 (m, 4H, =CH), 2.34 (m, 8H, CH_2)
Ru{η^6-$C_6[(CH_2)_2Me]_6$}(η^4-C_8H_{12}), **10**	70.19 (71.23)	10.09 (10.02)	540	2.16 (m, 12H, CH_2CH$_2$Me), 1.72 **(m, 12H, CH_2CH_2Me), 0.95 (t, 18H,** *Me*, *J* = 7.2 Hz)	2.83 (br s, 4H, =CH), **2.39 (m, 8H, CH_2)**
Ru{η^6-$C_6(C_6H_5)_6$}(η^4-C_8H_{12}), **11**	80.63 (80.75)	5.49 (5.65)	744	7.25–6.80 (s, 30H, C_6H_5)	4.18 (br s, 4H, =CH), 2.75 (m, 4H, CH_2), 2.48 (m, 4H, CH_2)
Ru{η^6-C_6-1,3,5-Me_3-2,4,6-$[(CH_2)_2Me]_3$}(η^4-C_8H_{12}), **12a** (30)[n]; Ru{η^6-C_6-1,2,4-Me_3-3,5,6-$[(CH_2)_2Me]_3$}(η^4-C_8H_{12}), **12b** (70)[n]	68.51 (68.56)	9.31 (9.23)	456	2.24 (br m, 6H, C_6CH_2), 1.87 (s, 9H, C_6*Me*, **9a**)[h], 1.77 (s, 3H, C_6*Me*, **9b**)[h], 1.72 (s, 3H, C_6*Me*, **9b**)[h],1.63 (s, 3H, C_6*Me*, **9b**)[h], 1.45 (m, 6H, CH_2Me), 0.91 (m, 9H, CH_2*Me*)	2.69 (br s, 4H, =CH), 2.36 (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]Spectra were measured at 200 MHz in C_6D_6, except where stated otherwise, using Me_4Si as internal standard; δ scale; s = singlet, d = doublet, t = triplet, spt = septet, m = multiplet, br = broad.
[d]Referred to the most intense peak, corresponding to ^{102}Ru, of a cluster of peaks due to parent ion.
[e]Proton numbering for 1,3,5- and 1,2,4-trisubstituted arene:



a **b**

[f]Assigned by double resonance.
[g] High-resolution FAB-MS: found, 412.185194; calc. for $^{12}C^1_{23}H^{101}_{36}$Ru, 412.185919.
[h]$^{13}C\{^1H\}$ NMR of **6a** (*δ*, C_6D_6) 109.8 (arom CH), 84.6 (=CH of COD), 61.5 (CH_2 of COD), 34.0 (*C*HMe$_2$), 23.8 (CH*Me*$_2$); C_3Pr^i and resonances due to **6b** not observed.
[i] High resolution FAB-MS: found, 455.234426; calc. for $^{12}C^1_{26}H^{102}_{42}$Ru, 455.234232.
[j] In CD_2Cl_2.
[k]$^{13}C\{^1H\}$ NMR (*δ*, CD_2Cl_2) 113.2 (arom CH), 81.6 (=CH of COD), 33.2 (*C*Me$_3$), 31.5 (s, C*Me*$_3$).
[l] High resolution FAB-MS: found, 504.1643; calc. for $^{12}C^1_{23}H^{28}_{42}Si_3$, 504.1638.
[m] See also Ref. [19].
[n] The regioisomeric composition (%) of the mixture was calculated by integration of the C_6*Me* protons.

alkynes isopropylacetylene and *t*-butylacetylene (runs 5 and 6). In the latter case, the Ru(η^6-arene)(η^4-C_8H_{12}) complex containing the sterically hindered 1,2,4-isomer is only just detectable. However, the regioisomeric ratio is reversed in the cases of phenylacetylene (**a**:**b** = 20:80, run 3) and trimethylsilylacetylene (**a**:**b** = 40:60, run 7), indicating that electronic effects can also play a role in determining the regioselectivity.

In order to gain some insight into the pathway of this reaction, we have examined the reaction between **1** (1 mol) and 2-butyne (6 mol) by ^{1}H NMR spectroscopy, this alkyne being chosen because of the simplicity of the spectrum of the resulting hexamethylbenzene complex **9**. The reaction was monitored from −80°C in THF-d_8; the spectrum of the starting mixture is shown in Fig. 2a. The reaction starts only at +5°C. At this temperature four new signals appear (Fig. 2b): (i) a singlet at δ 2.14 ppm and a multiplet at δ 8.00 ppm, due to the methyl protons of complex **9** and to four protons of free naphthalene, released from complex **1**, respectively; (ii) two multiplets, at δ 4.82 ppm and 6.12 ppm, attributed to the protons of naphthalene present in the dinuclear bridging naphthalene compound $Ru_2(C_8H_{12})_2(\mu$-$C_{10}H_8)$, **13** [12]. Complex **13** is formed also in the initial steps of the reaction of **1** with mononuclear arenes in the presence of acetonitrile [12] to give Ru(η^6-arene)(η^4-C_8H_{12}) complexes. In this case, the acetonitrile is

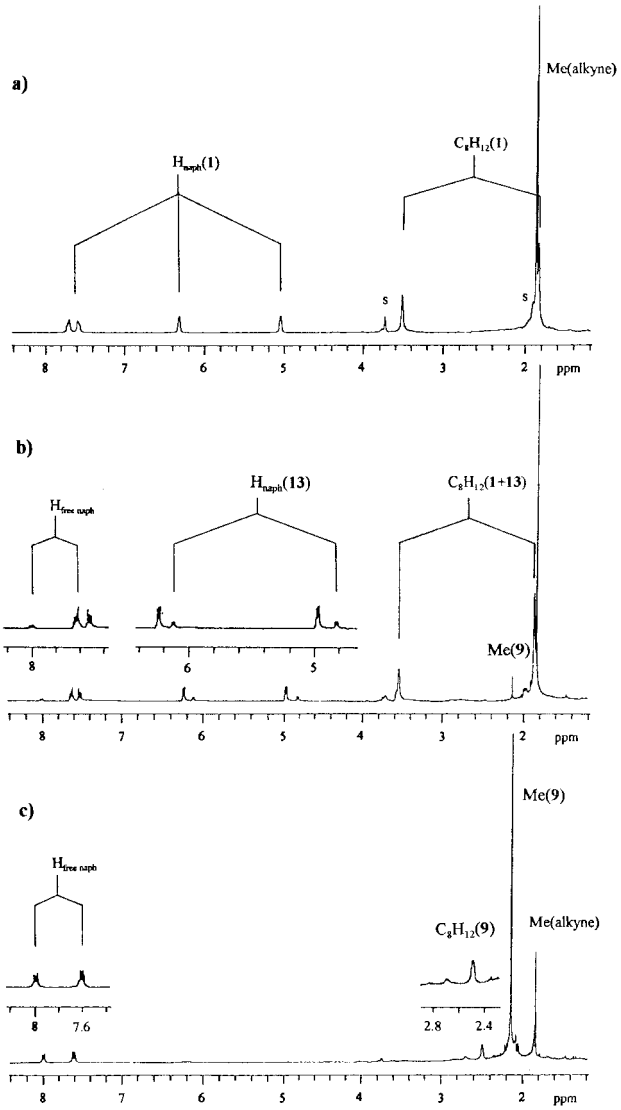
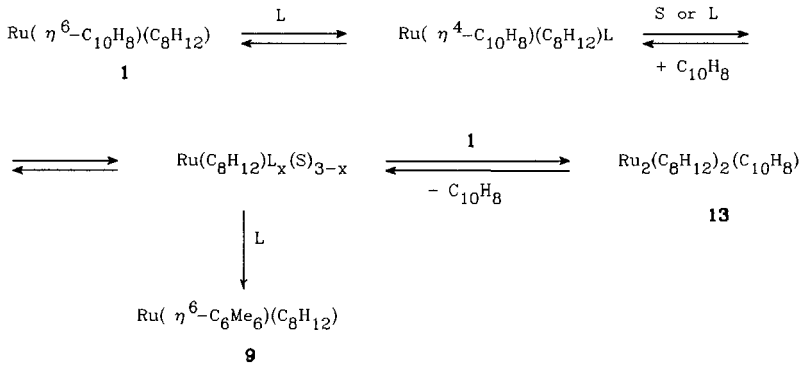


Fig. 2. ^{1}H NMR spectra (THF-d_8, +5°C) of solutions of Ru(η^6-$C_{10}H_8$)(η^4-C_8H_{12}), **1**, and MeC≡CMe (molar ratio 1:6): (a) Starting solution; (b) Reaction mixture containing the complexes $Ru_2(C_8H_{12})_2(\mu$-$C_{10}H_8)$, **13**, and Ru(η^6-C_6Me_6)(η^4-C_8H_{12}), **9**, with unreacted **1** and MeC≡CMe; (c) End of the reaction: the solution contains free $C_{10}H_8$, complex **9** and an excess of MeC≡CMe.



Scheme 2. L = 2-butyne; S = THF.

believed to remove naphthalene from **1** creating a very reactive solvent species $Ru(C_8H_{12})(NCMe)_n$, which reacts with **1** giving the dinuclear complex **13** (Eq. 1).

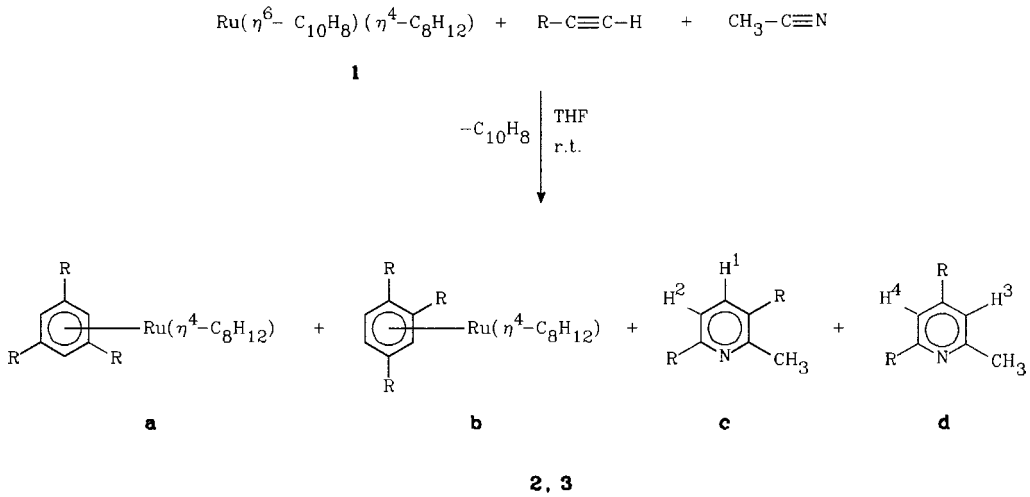
$$\underset{\mathbf{1}}{Ru(C_8H_{12})(C_{10}H_8)} + Ru(C_8H_{12})(\text{solvent})_n \rightleftharpoons \underset{\mathbf{13}}{Ru_2(C_8H_{12})_2(C_{10}H_8)} \quad (1)$$

The reaction is reversible, so **13** acts a source of the coordinatively unsaturated fragment $Ru(C_8H_{12})$ to which the arene binds. The 2-butyne probably behaves similarly to acetonitrile, giving the same compound **13** and forming the species $Ru(C_8H_{12})$ on which the cyclotrimerization occurs to give complex **9**. After 3 h the reaction is complete and the spectrum (Fig. 2c) shows the signals of naphthalene (multiplets at δ 8.00 ppm and 7.60 ppm) and of complex **9** (resonances at δ 2.70 ppm, 2.48 ppm and 2.14 ppm). As shown in Fig. 2b, complexes **9** and **13** are formed simultaneously during the initial steps of the reaction, probably by two independent pathways starting from the same species $Ru(C_8H_{12})$; successively **13** decomposes losing naphthalene and regenerating the $Ru(C_8H_{12})$ fragment that, in the presence of 2-butyne, gives **9**. A possible sequence of events is outlined in Scheme 2.

Complex **9** (and, analogously, the other complexes **2**–**8**, **10**–**12**) are stable 18-electron species in which the arene is strongly bound to ruthenium [20]. Hence, once these compounds are formed and **1** is consumed, no further reaction occurs.

2.2. Reaction of complex 1 with 1-hexyne and 4-methyl-1-hexyne in the presence of acetonitrile

In previous work [12,13,15], it was found that alkane nitriles, especially acetonitrile, promote the removal of naphthalene from ruthenium in **1**, thus creating coordinatively unsaturated species that are useful in catalysis and in preparative chemistry. We therefore investigated the effect of acetonitrile on the reaction between **1** and alkynes, in



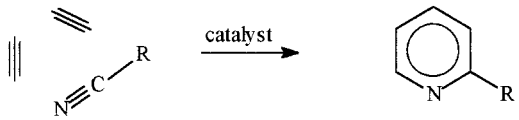
Scheme 3. R = $(CH_2)_3CH_3$, **2**; $CH_2CH(CH_3)C_2H_5$, **3**.

Table 3
Syntheses of Ru(η^6-arene)(η^4-C_8H_{12}) complexes and pyridines according to Scheme 3[a]

Run	Alkyne	Time (h)	Products (%)	Amount (mmol)
10	1-Hexyne	0.5	Ru(η^6-1,3,5-tri-*n*-butylbenzene)(η^4-C_8H_{12}), **2a** (55) Ru(η^6-1,2,4-tri-*n*-butylbenzene)(η^4-C_8H_{12}), **2b** (45) 3,6-Di-*n*-butyl-2-methylpyridine, **2c** (10) 4,6-Di-*n*-butyl-2-methylpyridine, **2d** (90)	0.27 0.40
11	4-Methyl-1-hexyne	1	Ru[η^6-1,3,5-tri(2-methylbutyl)-benzene](η^4-C_8H_{12}), **3a** (30); Ru[η^6-1,2,4-tri(2-methylbutyl)-benzene](η^4-C_8H_{12}), **3b** (70) 3,6-Di(2-methylbutyl)-2-methylpyridine, **3c** (40); 4,6-Di(2-methylbutyl)-2-methylpyridine, **3d** (60)	0.26 0.48
12[b]	1-Hexyne	8	No reaction	

[a] Reaction conditions: **1** (0.098 g, 0.29 mmol), alkyne (5.8 mmol), CH_3CN (0.3 ml, 5.8 mmol), THF (5 ml), room temperature.
[b] Carried out using Ru(η^6-*p*-cymene)(η^4-C_8H_{12}) (0.1 g, 0.29 mmol) as starting complex.

particular to see whether it would undergo cocyclotrimerization with the alkynes to give pyridines (Eq. 2). This type of reaction is known to be catalysed by a range of cyclopentadienylcobalt(I) compounds [22,23].

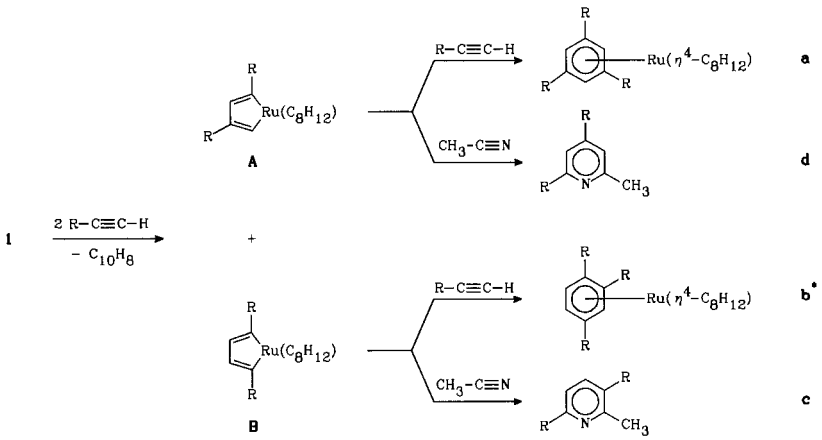


(2)

The acetylenic compounds used were 1-hexyne and 4-methyl-1-hexyne, the first being easily handled and readily available, the second being the precursor to pyridines substituted with chiral groups; these are of considerable interest in organic chemistry and are not easily obtainable by traditional synthetic methods. The reaction of **1** with 1-hexyne or 4-methyl-1-hexyne in the presence of acetonitrile affords Ru(η^6-arene)(η^4-C_8H_{12}) complexes and 2-methylpyridines, 4,6- or 3,6-disubstituted, as shown in Scheme 3.

The reactions were carried out in THF at room temperature with a molar ratio **1**:alkyne:acetonitrile of 1:20:20. Column chromatography (alumina) of the residue furnished the arene ruthenium complexes and the pyridines, the former being eluted with pentane, the latter with toluene. The results, summarized in Table 3, indicate that acetonitrile accelerates the reaction of complex **1** with the alkynes (compare runs 1 and 2 with runs 10 and 11, respectively), probably by assisting the removal of naphthalene from ruthenium. Interestingly, the regioselectivity of formation of the arene–ruthenium complexes **2a**, **2b** and **3a**, **3b** in the presence of acetonitrile differs from that in the absence of acetonitrile, showing that the latter influences the reaction pathway.

The yield of the mononuclear arene–ruthenium complexes, based on complex **1**, is almost quantitative, as found previously in the corresponding reactions without acetonitrile. The pyridines **2c**, **2d** and **3c**, **3d** are formed in slightly larger amount than the arene complexes, but the yield does not increase with prolonged reaction times (24 h), indicating the low catalytic activity of **1** in this reaction. There is no reaction between Ru(η^6-*p*-cymene)(η^4-C_8H_{12}), 1-hexyne and acetonitrile (run 12), the starting ruthenium complex being recovered unchanged after 8 h at room



Scheme 4. * This compound can also arise from intermediate **A**.

temperature. Also the mononuclear arene complexes **2a**, **2b** and **3a**, **3b** formed during the reaction do not catalyse formation of the pyridines.

According to the generally accepted mechanism of cyclotrimerization of alkynes and of formation of pyridines [22,23], we believe that ruthenacyclopentadienes A and B are intermediates in the reaction (Scheme 4). They can react with the alkyne or with the acetonitrile forming the arene–ruthenium complex or the pyridine, respectively. Pyridines are no longer formed once all the ruthenium is present as the catalytically inactive Ru(η^6-arene)(η^4-C_8H_{12}) complex.

However, the yield of pyridines can be increased by use of a large excess of acetonitrile. For example the reaction of **1** with 4-methyl-1-hexyne and acetonitrile (molar ratio **1**:alkyne:nitrile = 1:20:200) furnishes after 1 h ca. 1 mmol of pyridines **3c**, **3d**, compared with 0.48 mmol obtained in run 12 over the same period.

3. Experimental section

All operations were performed under argon using conventional Schlenk-tube techniques. Solvents were purified by conventional methods, distilled and stored under argon. The alkynes were degassed before use and stored under argon. 4-methyl-1-hexyne was prepared by addition of bromine to 4-methyl-1-hexene, obtained by cross-coupling of 2-methylbutylmagnesium chloride and vinyl bromide in the presence of $NiCl_2$(dppe) [24], and subsequent dehydrohalogenation of the resulting 1,2-dibromo-4-methylhexane with sodium amide [25]. The complex Ru(η^6-$C_{10}H_8$)(η^4-C_8H_{12}), **1**, was obtained as previously reported [12]. The complex Ru(η^6-*p*-cymene)(η^4-C_8H_{12}) was made from [$RuCl_2$(η^6-*p*-cymene)]$_2$, 1,5-cyclooctadiene, and Na_2CO_3 in propan-2-ol [19] and identified by comparison of its ^{1}H NMR spectrum with authentic material [26].

^{1}H NMR spectra were recorded on a varion Gemini 200 instrument at 200 MHz and on a Varian VXR-300 at 300 MHz. Chemical shifts were determined relative to internal $Si(CH_3)_4$ ($\delta = 0$ ppm); coupling constants J are in Hz. Mass spectra (EI) of complexes **2**–**9** were carried out on a VG 7070 E spectrometer. Mass spectra of pyridines **2c**, **2d**, **3c** and **3d** were recorded 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. The GLC analyses were performed on a Perkin Elmer 8600 gas chromatograph, equipped with an 'in column' injector and a flame ionization detector (FID), using an SiO_2 'Wide Bore' column (DB1, 30 m × 0.53 mm, 5 μm) and helium as carrier gas. Microanalyses were carried out by the Laboratorio di Microanalisi, Facoltà di Farmacia, Università di Pisa, Italy.

The ^{1}H NMR experiment was performed on a solution of **1** in THF-d_8 in a 5 mm o.d. NMR tube to which 2-butyne was added. The growth in the signals of the product was monitored on a Varian VXR-300 NMR spectrometer at various probe temperatures in the range −80°C to 5°C.

*3.1. Reaction of Ru(η^6-$C_{10}H_8$)(η^4-C_8H_{12}), **1**, with alkynes: Synthesis of Ru(η^6-arene)(η^4-C_8H_{12}) complexes, **2**–**10**, **12***

3.1.1. General procedure

The alkyne (3.48 mmol) was added to a solution of **1** (0.196 g, 0.58 mmol) in THF (5 ml) and the mixture was stirred at room temperature. 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 in C_6D_6; the reaction was stopped when the spectrum showed the disappearance 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). Pentane eluted a yellow fraction from which, after evaporation of the solvent, the Ru(η^6-arene)(η^4-C_8H_{12}) complex was obtained.

The complex Ru(η^6-hexaphenylbenzene)(η^4-C_8H_{12}), **11**, was prepared as described above. On adding pentane (5 ml) to the reaction mixture, at room temperature, light-yellow crystals of **11** were obtained.

The yield of the reactions with the different alkynes and the elemental analyses, ^{1}H NMR and mass data for the complexes **2**–**12** are reported in Tables 1 and 2.

*3.2. Reaction of Ru(η^6-$C_{10}H_8$)(η^4-C_8H_{12}), **1**, with alkynes (1-hexyne and 4-methyl-1-hexyne) in the presence of acetonitrile: Synthesis of Ru(η^6-arene)(η^4-C_8H_{12}) complexes (**2a**, **2b** and **3a**, **3b**) and pyridines (**2c**, **2d** and **3c**, **3d**)*

Only the reaction with 4-methyl-1-hexyne is described in detail, the experimental procedure being the same for 1-hexyne.

4-methyl-1-hexyne (0.557 g, 5.8 mmol) and acetonitrile (0.3 ml, 5.8 mmol) were added to a solution of **1** (0.1 g, 0.29 mmol) in THF (5 ml) and the mixture was stirred at room temperature for 1 h. The volatile materials were

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) eluting first with pentane and then toluene. Pentane eluted a yellow fraction that furnished, on removal of solvent under reduced pressure, a mixture of the complexes Ru[η^6-1,3,5-tri(2-methylbutyl)benzene](η^4-C_8H_{12}), **3a**, and Ru[η^6-1,2,4-tri(2-methylbutyl)benzene](η^4-C_8H_{12}), **3b** (0.129 g, 0.26 mmol, **3a**:**3b** ratio = 30:70) as a yellow oily material. Elution with toluene gave 0.112 g (0.48 mmol) of a mixture of 3,6-di(2-methylbutyl)-2-methylpyridine, **3c**, and 4,6-di(2-methylbutyl)-2-methylpyridine, **3d**, (**3c**:**3d** ratio = 40:60), as a colourless oil.

The characterization of the pyridines **2c**, **2d**, **3c** and **3d** was performed by GC-MS and ^{1}H NMR techniques and by comparison with authentic samples prepared according to literature procedures [27]. (For the aromatic proton numbering see Scheme 3).

*3.2.1. 3,6-di-n-butyl-2-methylpyridine, **2c***

GC-MS (m/z): 205. ^{1}H NMR ($CDCl_3$): δ 7.1 and 6.75 (d, 2H, H^1 and H^2, $J_{12} = 8$ Hz); 2.82 (t, 4H, ArCH_2CH$_2$, $J = 7.8$ Hz); 2.48 (s, 3H, ArCH_3); 1.6–1.2 (br m, 8H, CH$_2$CH_2CH_2CH$_3$); 0.85 (t, 6H, CH$_2$CH_3, $J = 6.8$ Hz).

*3.2.2. 4,6-di-n-butyl-2-methylpyridine, **2d***

GC-MS (m/z): 205. ^{1}H NMR ($CDCl_3$): δ 6.6 and 6.54 (s, 2H, H^3 and H^4); 2.82 (t, 4H, ArCH_2CH$_2$, $J = 7.8$ Hz); 2.48 (s, 3H, ArCH_3); 1.6–1.2 (br m, 8H, CH$_2$CH_2CH_2CH$_3$); 0.85 (t, 6H, CH$_2$CH_3, $J = 6.8$ Hz).

*3.2.3. 3,6-di(2-methylbutyl)-2-methylpyridine, **3c***

GC-MS (m/z): 233. ^{1}H NMR ($CDCl_3$): δ 7.2 and 6.85 (d, 2H, H^1 and H^2, $J_{12} = 7.7$ Hz); 2.78 (m, 4H, ArCHH and ArCHH); 2.52 (s, 3H, ArCH_3); 2.3 (m, 2H, CH$_2$CH); 1.9–1.2 (br m, 4H, CHHCH$_3$ and CHHCH$_3$); 0.85 (m, 12H, CHCH_3 and CH$_2$CH_3).

*3.2.4. 4,6-di(2-methylbutyl)-2-methylpyridine, **3d***

GC-MS (m/z): 233. ^{1}H NMR ($CDCl_3$): δ 6.75 and 6.70 (s, 2H, H^3 and H^4); 2.78 (m, 4H, ArCHH and ArCHH); 2.52 (s, 3H, ArCH_3); 2.3 (m, 2H, CH$_2$CH); 1.9–1.2 (br m, 4H, CHHCH$_3$ and CHHCH$_3$); 0.85 (m, 12H, CHCH_3 and CH$_2$CH_3).

*3.3. Reaction of 4-methyl-1-hexyne and acetonitrile, in excess, in the presence of Ru(η^6-$C_{10}H_8$)(η^4-C_8H_{12}), **1***

4-methyl-1-hexyne (0.557 g, 5.8 mmol) and acetonitrile (3 ml, 58 mmol) were added to a solution of **1** (0.1 g, 0.29 mmol) in THF (5 ml) and the mixture was stirred at room temperature for 1 h. The volatile materials were removed under vacuum and the residue was treated with diethyl ether and, successively, with aqueous HCl (10%). The acidic washings were separated from the organic phase and made alkaline with NaOH (10%). The aqueous solution was then extracted with diethyl ether and the organic phase was dried ($MgSO_4$). The solvent was removed under vacuum giving the mixture of **3c** and **3d** (0.233 g, 1 mmol) as a colourless oil.

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