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Synthesis and characterization of new difunctional alkynylated (η^6-arene)(η^4-cycloocta-1,5-diene)ruthenium(0) complexes as molecular models for organometallic polymers

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Abstract

The new dialkynylated complexes Ru(η^6-DEB-Si)(η^4-COD), **4a**, Ru(η^6-DEBP-Si)(η^4-COD), **4b1**, Ru_2(η^6,η^6-DEBP)(η^4-COD)$_2$, **4b2** [COD = 1,5-cyclooctadiene; DEB-Si = 1,4-bis(trimethylsilylethynyl)benzene; DEBP-Si = 4,4′-bis(trimethylsilylethynyl)biphenyl] have been synthesized by the arene exchange reaction with the complex Ru(η^6-naphthalene)(η^4-COD). The complexes Ru(η^6-DEB)(η^4-COD), **5a**, and Ru(η^6-DEBP)(η^4-COD), **5b1**, have been prepared by desilylation of the corresponding compounds **4a** and **4b1**. All the complexes have been fully characterized by means of spectroscopic techniques.
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Keywords: Dialkynes; Ruthenium; Arene complexes; 1,5-Cyclooctadiene complexes; Molecular models

1. Introduction

Organometallic polymers and model molecules containing transition metals are an interesting class of materials that can manifest unique chemico-physical properties [1]. In particular, when the metal is bridged into a π-conjugated organic fragment, the interactions between the metal sites through the conjugated chain can tune the optical, magnetic and electrical properties [2]. Moreover, the simultaneous presence of different metals such as in the case of heterobimetallic complexes might magnify or modify these properties by means of cooperative effects [3]. In this framework the synthesis of highly ethynylated heterobimetallic complexes and polymers fits well the goal of the tuning of the electronic and chemical interactions and make these complexes good candidates for the development of advanced opto-electronic devices. On these bases our attempt was oriented to the synthesis of Ru-containing monomers, that is the first step for the future synthesis of heterobimetallic polymers containing Pt or Pd centers, schematically depicted in Scheme 1.

The proximity of the metal centers, in our case Pt or Pd with Ru, is expected to influence a cooperative reactivity between the differently coordinated metal sites considering that the alkynyl and arene moieties span the two metals through σ and π coordination. In this way access to readily available building blocks with well-defined structures and properties suitable for nano-architecture, is possible.

Six-membered ring building blocks for organometallic arrays, i.e., arene–chromium complexes [4] and polymers [5] were synthesized, opening a pathway to soluble organometallic π-conjugated polymers. In this framework, the introduction of ruthenium sites is expected to have an active role in gas sensor applications, considering previous results obtained by using homo-metallic (Pt or Pd based)

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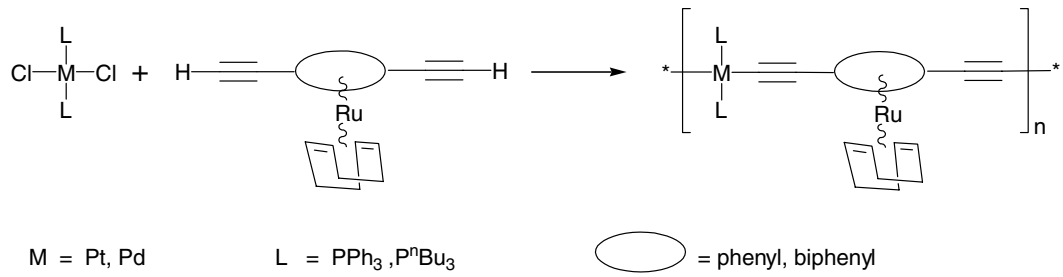


Scheme 1.

rod-like polymers [6] and recent results on sensing behaviour of Ru-containing polymers towards small gas molecules (NO, O_2, CO) [7].

In this paper results on the synthesis and characterization of new difunctional alkynylated arene–ruthenium-complexes, as precursors for organometallic polyynes, are reported.

2. Results and discussion

Several aspects of arene–metal chemistry have hampered the development of this class of compounds. One of the major handicaps is that the direct complexation of alkynylated arenes is very inefficient due to the electron withdrawing nature of the alkynyl substituents and the competitive cyclotrimerization reaction. Another disadvantage is usually the low regioselectivity if more than one benzene ring is present in an alkynyl bridged substrate.

In this work we developed a synthetic methodology for the easy access to ruthenium-containing model molecules, starting from the complex Ru(η^6-naphthalene)(η^4-COD), **1**, [COD = 1,5-cyclooctadiene] [8], and 1,4-bis(trimethylsilylethynyl)benzene (DEB-Si, **3a**) or 4,4′-bis(trimethylsilylethynyl)biphenyl (DEBP-Si, **3b**) molecules, reported in Scheme 2. In this way it was possible to isolate ruthenium containing protected dialkynes (**4a**, **4b1**, **4b2**), avoiding cyclotrimerization products, which would be obtained by direct use of **2a** or **2b** in the same reaction conditions [9]. With a successive removal of the –$SiMe_3$ functionalities, the complexes **5a** and **5b1** were isolated.

*2.1. Preparation of the complexes Ru(η^6-arene)(η^4-COD), **4a** [arene = 1,4-bis(trimethylsilylethynyl)benzene] and **4b1** [arene = 4,4′-bis(trimethylsilylethynyl)biphenyl], and of the complex $Ru_2(\eta^4\text{-COD})_2(\eta^6,\eta^6\text{-arene})$, **4b2** [arene = 4,4′-bis(trimethylsilylethynyl)biphenyl], by naphthalene–arene exchange reaction*

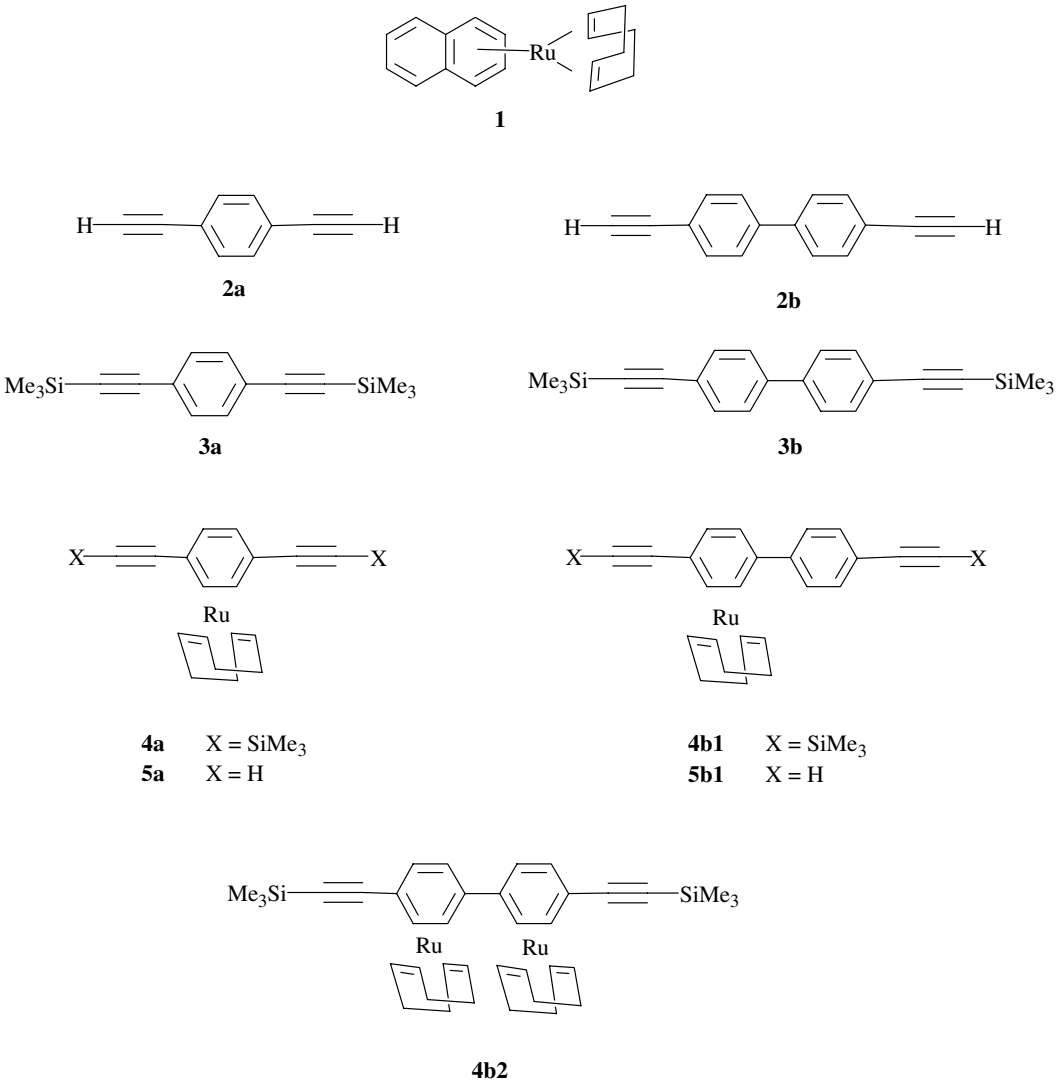
*2.1.1. Reaction of complex **1** with 1,4-bis(trimethylsilylethynyl)benzene, DEB-Si, **3a***

It is now well-established [8,10] that Ru(η^6-arene)-(η^4-COD) complexes can be conveniently prepared by replacing the η^6-naphthalene ligand in the complex Ru(η^6-naphthalene)(η^4-COD), **1**, with a suitable mononuclear arene in the presence of acetonitrile. On the other hand, it is known that complex **1** reacts easily with terminal alkynes furnishing the corresponding benzene derivatives by stoichiometric cyclotrimerization of the triple bond [9]. In this context, experiments by us done on the reaction between **1** and 1,4-diethynylbenzene, **2a**, which contains the arene ring as well as the acetylenic groups, indicate that the cyclotrimerization of **2a** by **1** to benzene derivatives prevails on the arene displacement reaction (Scheme 3, step a) [11]. On the basis of literature reports [9], the cyclotrimerization reaction could be hindered by substituting the acetylenic hydrogens with bulky groups and the trimethylsilyl group seems of relevance considering that it is able to give rise to a considerable steric hindrance around the triple bond. In addition, by simple hydrolysis reaction, the trimethylsilyl group could be removed from the triple bond, restoring the acetylenic moieties. Hence the reaction between **1** and the 1,4-bis(trimethylsilylethynyl)benzene, **3a**, has been examined. According to the literature **3a** has been prepared by reaction of 1,4-diiodobenzene with trimethylsilylacetylene [12]. By reaction with **1**, in the presence of acetonitrile, the naphthalene is replaced by the arene ligand with formation of the new complex Ru(η^6-DEB-Si)(η^4-COD), **4a**, in excellent yield (85%) (Scheme 3, step b).

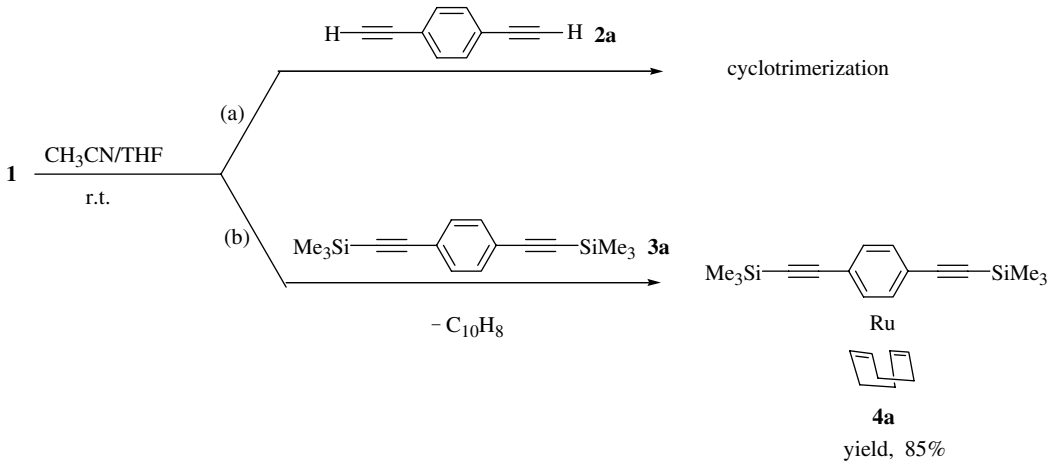
The reaction has been performed in THF as solvent, other solvents (i.e., aliphatic hydrocarbons, acetone, chloroform, dichloromethane) giving rise to partial decomposition. The progress of the reaction was monitored by analysing ^{1}H NMR spectra of samples withdrawn at different times: the reaction was stopped after 6 h when the starting complex **1** had completely disappeared. Complex **4a** was characterized by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry (Table 1). The ^{1}H NMR spectrum shows, as expected, the singlet at 5.84 ppm, due to the arene protons η^6-bonded to ruthenium, shifted upfield as observed for similar arene–ruthenium complexes [13].

*2.1.2. Reaction of complex **1** with 4,4′-bis(trimethylsilylethynyl)biphenyl, DEBP-Si, **3b***

The reaction of **1** with 1,4-bis(trimethylsilylethynyl)-4,4′-biphenyl, **3b**, obtained from the 4,4′-dibromine precursor, has been also examined. The use of this alkyne is of particular interest on the basis of our previous work on polymeric platinum containing materials with sensing properties [14].



Scheme 2.



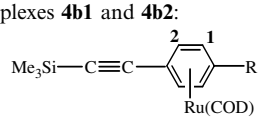
Scheme 3.

Since compound **3b** contains two aromatic rings, in principle, each one can bind a "Ru(η^4-COD)" moiety. In order to avoid the formation of mixtures of arene ruthenium complexes the reaction with complex **1** in presence of acetonitrile has been tested using a molar ratio **1/3b** = 1. The complex Ru(η^6-DEBP-Si)(η^4-COD), **4b1**, is

Table 1
Spectroscopic data for compounds **4a**, **4b1** and **4b2**

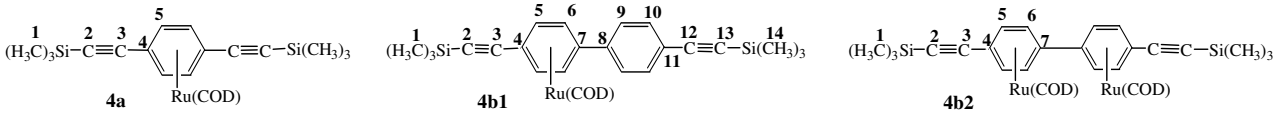
Complex	MS m/z[a]	^{1}H NMR data[b]			^{13}C NMR data[b]		
		Aromatic ligand		η^4-COD	Aromatic ligand[d]		η^4-COD
		η^6-Arene protons[c]	Others		η^6-Arene carbons	Others	
Ru(η^6-DEB-Si)(η^4-COD) **4a**	481.2	5.84 (s,4H)	0.33 (s,18H,$SiMe_3$)	3.36 (m,4H,=CH) 2.24 (m,8H,CH_2)	91.4 (C5) 75.4 (C4)	102.7 (C3) 92.8 (C2) 0.31(C1)	66.8 (CH) 33.9 (CH_2)
Ru(η^6-DEBP-Si)(η^4-COD) **4b1**	556.2	5.72 (d,2H,H_1, $J_{12} = 5.8$); 5.60 (d,2H,H_2)	7.54 (s,4H,H_{ar}) 0.34 (s,9H,$SiMe_3$) 0.32 (s,9H,$SiMe_3$)	3.24 (m,4H,=CH) 2.12 (m,8H,CH_2)	93.2 (C7) 88.6 (C6) 84.7 (C5) 82.5 (C4)	138.2 (C8) 132.4 (C9) 127.1 (C10) 122.2 (C11) 103.2 (C12) 100.1 (C13) 97.3 (C3) 93.7 (C2) 0.33 (C1, C14)	66.6 (CH) 33.6 (CH_2)
$Ru_2(\eta^4\text{-COD})_2[\eta^6,\eta^6\text{-}(C_6H_4)_2\text{-}1,4\text{-}(C_2SiMe_3)_2]$ **4b2**	766.1	5.64 (d,4H,H_1, $J_{12} = 6.4$); 5.55 (d,4H,H_2)	0.30 (s,18H,$SiMe_3$)	3.28 (m,4H,=CH) 2.14 (m,8H,CH_2)	82.5 (C4) 88.5 (C6) 84.9 (C5) 92.7 (C7)	93.6 (C2) 97.5 (C3) 0.32 (C1)	66.5 (CH) 33.6 (CH_2)

[a] Referred to the most intense peak, corresponding to ^{102}Ru, of a cluster of peaks due to parent ion.
[b] Spectra were measured at 300 and 75 MHz for ^{1}H and ^{13}C NMR, respectively, in $CDCl_3$ using Me_4Si as internal standard; δ scale; s, singlet; d, doublet; m, multiplet.
[c] Aromatic proton numbering in complexes **4b1** and **4b2**:

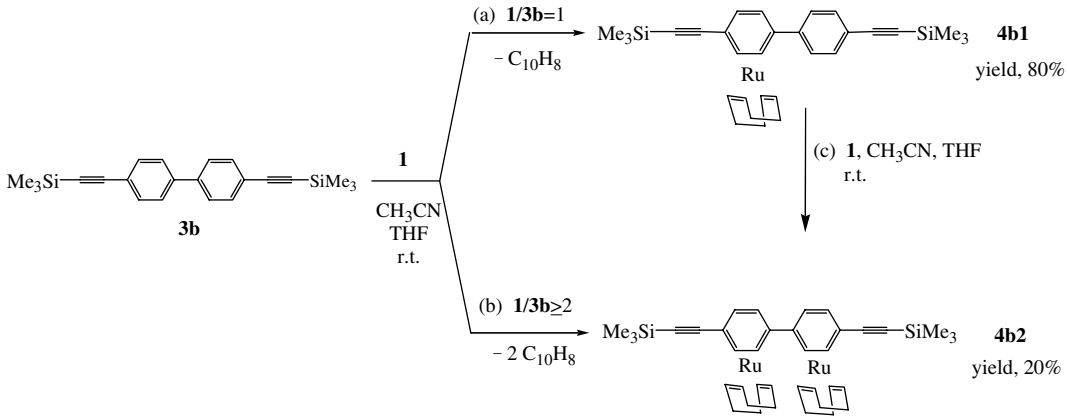


R = C_6H_4-C_2-$SiMe_3$ (**4b1**)
R = C_6H_4-(RuCOD)-C_2-$SiMe_3$ (**4b2**)

[d] Carbon numbering in complexes **4a**, **4b1** and **4b2**:



obtained in high yield (80%) after 6 h (Scheme 4, step a). The reaction was performed as previously reported for the **3a** ligand (see Section 2.1.2). The characterization of **4b1** by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry is reported in Table 1. Its ^{1}H NMR spectrum shows the expected singlet at 7.54 ppm, of relative intensity four,



Scheme 4.

attributed to the protons of the uncoordinated aromatic ring, and two doublets at 5.72 and 5.6 ppm, due to the protons of the aromatic ring bonded to ruthenium.

The reaction between complex **1** and **3b** in presence of acetonitrile was examined also using a molar ratio **1/3b** $\geqslant 2$ (Scheme 4, step b). The dinuclear ruthenium complex $Ru_2(\eta^4\text{-COD})_2(\eta^6,\eta^6\text{-arene})$, **4b2**, is formed in low yield (20%), probably because, being the reaction very slow (complete conversion of the reagents after four days), a lot of decomposition is observed. Complex **4b2** was characterized by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry, as reported in Table 1. Of relevance, the presence in the ^{1}H NMR spectrum of the two doublets at 5.64 and 5.55 ppm, due to the protons of the two equivalent aromatic rings bonded to the metal, has been observed. Interestingly, in the first stages of the reaction, complex **4b1** is also present, as shown by the ^{1}H NMR analysis of the residue of the reaction mixture. Successively **4b1** slowly disappears, indicating that it is an intermediate step in the formation of **4b2**. For this reason the reaction between the complexes **1** and **4b1** in presence of acetonitrile was attempted (Scheme 4, step c), but no improvement in the reaction rate was observed and **4b2** was obtained in low yields ($\leqslant$20%). It is worth noting that the difficulty to bind a second "Ru(η^4-COD)" unit to the uncoordinated ring present in diaryl Ru(η^6-arene)(η^4-COD) complexes has been previously observed [8]. For example, the complex Ru(η^6-PhCH=CHPh)(η^4-COD) is obtained by reaction of **1** and *trans*-stilbene in 12 h while the attachment of the second "Ru(η^4-COD)" unit to the uncoordinated ring requires ca. 5 days.

*2.2. Preparation of the complexes Ru(η^6-arene)(η^4-COD), **5a** [arene = 1,4-diethynylbenzene] and **5b1** [arene = 4,4′-bis(ethynyl)biphenyl], by removal of the trimethylsilyl groups from complexes **4a** and **4b1**, respectively*

The removal of the trimethylsilyl group from the triple bond to restore the acetylenic functionality is a well known reaction in organic chemistry and several methods have been set up to perform this reaction with high efficiency [15]. Recently, Müller and co-workers [4] have selectively desilylated alkynylated (η^6-arene)Cr(CO)$_3$ complexes to the corresponding ethynyl compounds in high yield using sodium hydroxide in methanol or tetrabutyl ammonium fluoride (TBAF) in THF.

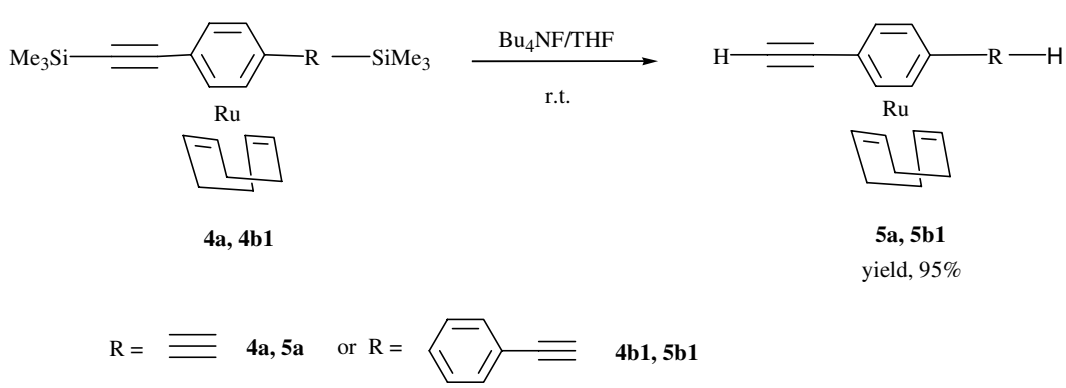
We have examined the desilylation reaction of the compounds **4a** and **4b1**. These compounds, in contrast to **4b2**, are easily available from the reactions reported above; hence, they can be useful sources for the corresponding diacetylenic compounds. The desilylation reaction has been tested with sodium hydroxide in methanol and with TBAF in THF and the better yield has been obtained with the system TBAF/THF. The trimethylsilyl groups have been removed from the triple bond and the corresponding diacetylenic arene–cyclooctadiene ruthenium complexes **5a** and **5b1** have been formed in almost quantitative yield (Scheme 5).

The new complexes have been characterized by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry (Table 2). Their ^{1}H NMR spectra show, in addition to the signals of the arene bonded to ruthenium in the range 5.65–5.90 ppm, singlets around 3.20–3.24 ppm due to the protons of the acetylenic group. Attempts to get crystals, suitable for X-ray characterization, of the complexes **5a** and **5b1** as well as of the trimethylsilyl derivatives **4a**, **4b1** and **4b2**, was unsuccessful.

3. Electronic and structural characterization

The chemical and electronic structure of precursors **1**, **3a**, **3b** and of Ru organometallic complexes **4a**, **4b1** and **4b2** was further investigated by means of FTIR, UV–Vis and XPS spectroscopies, with the aim of evaluating the effect of the chemical structure of the ligands on the electronic character of Ru based organometallic complexes.

FTIR spectra were collected on thin film samples to verify whether any difference with respect to the precursors **3a** and **3b** could be detected. The coordination of Ru to arene moieties was verified by the presence of a series of bands in the region 700–1000 cm^{-1}. In particular, the δ(CH) bending mode of the complex **1** at 782 cm^{-1}, is shifted at 804 cm^{-1} in **4a**, **4b1** and **4b2**, partially overlapped to the DEBP bending of aromatic CH bands. Coordination of

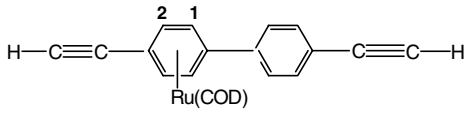


Scheme 5.

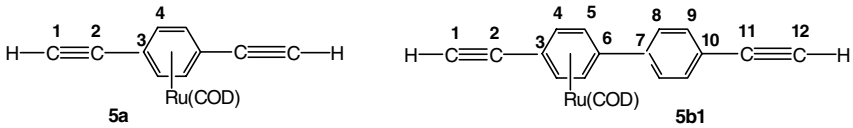
Table 2
Spectroscopic data for compounds **5a** and **5b1**

Complex	MS m/z[a]	^{1}H NMR data[b]			^{13}C NMR data[b]		
		Aromatic ligand		η^4-COD	Aromatic ligand[d]		η^4-COD
		η^6-Arene protons[c]	Others		η^6-Arene carbons	Others	
Ru(η^6-DEB) (η^4-COD) **5a**	335.1	5.90 (s,4H)	3.20 (s,H,alkyne)	3.41 (m,4H,=CH) 2.23 (m,8H,CH_2)	91.5 (C4) 90.4 (C3)	82.9 (C2) 78.1 (C1)	66.8 (CH) 33.8 (CH_2)
Ru(η^6-DEBP) (η^4-COD) **5b1**	411.2	5.75 (d,2H,H_1, $J_{12} = 5.9$) 5.64 (d,2H,H_2)	7.56 (m,4H,H_{ar}) 3.24 (s,H,alkyne) 3.21 (s,H,alkyne)	3.28 (m,4H,=CH) 2.14 (m,8H,CH_2)	91.1 (C6) 87.8 (C5) 85.1 (C4) 83.3 (C3)	141.1 (C7) 132.6 (C8) 127.3 (C9) 125.6 (C10) 83.6 (C11) 78.3 (C12) 79.1 (C1) 72.1 (C2)	66.5 (CH) 33.6 (CH_2)

[a] Referred to the most intense peak, corresponding to ^{102}Ru, of a cluster of peaks due to parent ion.
[b] Spectra were measured at 300 and 75 MHz for ^{1}H and ^{13}C NMR, respectively, in $CDCl_3$ using Me_4Si as internal standard; δ scale; s, singlet; d, doublet; m, multiplet.
[c] Aromatic proton numbering in complexes **5b1**:



[d] Carbon numbering in complexes **5a** and **5b1**:



Ru to **3a** and **3b** did not affect the C≡C stretching frequency, found in DEBP based samples **4b1** and **4b2** at about 2158 cm^{-1} and in **4a** at 2156 cm^{-1}.

The UV–Vis absorption spectra have been also carried out. The optical absorption maxima of the Ru containing complexes **4a**, **4b1** and **4b2** (centered at about 278–292, 289 and 282 nm, respectively), are *blue-shifted* in comparison with the organic precursors **3a** and **3b** (whose absorption maxima were found at 280–294 and 302 nm, respectively). This shift towards lower wave length is indicative of a decreased degree of electronic delocalization along the arene–acetylene backbone, due to the coordination effect with the metal center, more pronounced in the case of DEBP based complexes (about 20 nm) with respect to the Ru-DEB derivative (about 2 nm, see experimental). In Fig. 1 the UV–Vis absorption spectra of complexes **4b1** and **4b2**, as well as the spectra of the compounds **1** and **3b**, are presented.

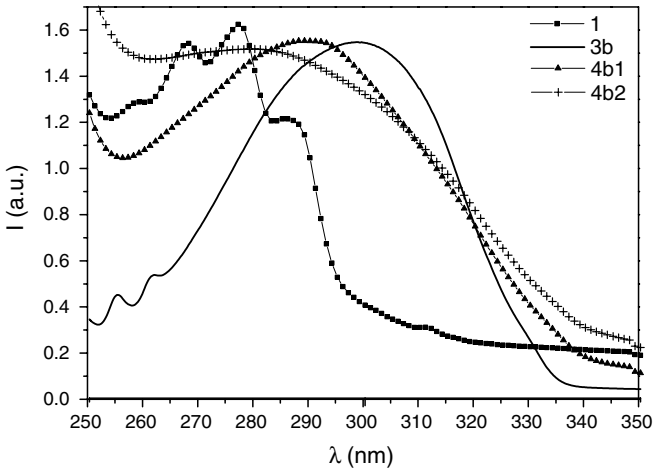


Fig. 1. UV–Vis spectra ($CHCl_3$) of compounds **1**, **3b**, **4b1** and **4b2**.

XPS measurements were also carried out in order to better investigate the electronic structure of the organometallic complexes. The main peaks characterizing the structures were C1s, Ru3d and Si2p for **4a**, **4b1** and **4b2** while the complexes **5a** and **5b1** could not be examined because of their unstability. However, the results of the former complexes can be likely transferred to the latter ones because of their structural analogy. Table 3 lists the C1s, Ru3d 5/2 and Si2p binding energies (B.E.) and full width half maxima (FWHM) values referred to the C1s signal of aromatic carbons at 284.70 eV, for compounds **1**, **4a**, **4b1** and **4b2**.

The spectra of all our samples in the range 280–290 eV appeared structured and despite the difficulty arising from the partial overlapping of the C1s and Ru3d 5/2 and 3/2 peaks, they were deconvoluted by curve fitting into three

Table 3
XPS data for compounds **1**, **4a**, **4b1** and **4b2**

	Ru3d 5/2		C1s		Si2p 3/2	
	B. E.	(FWHM)	B. E.	(FWHM)	B. E.	(FWHM)
	eV		eV		eV	
1	281.55	(1.91)	284.70	(1.91)	–	
4a	281.12	(1.99)	284.70	(1.91)	102.03	(3.85)
4b1	281.00	(1.70)	284.70	(1.96)	102.10	(2.25)
4b2	281.10	(1.93)	284.70	(1.93)	102.16	(2.11)

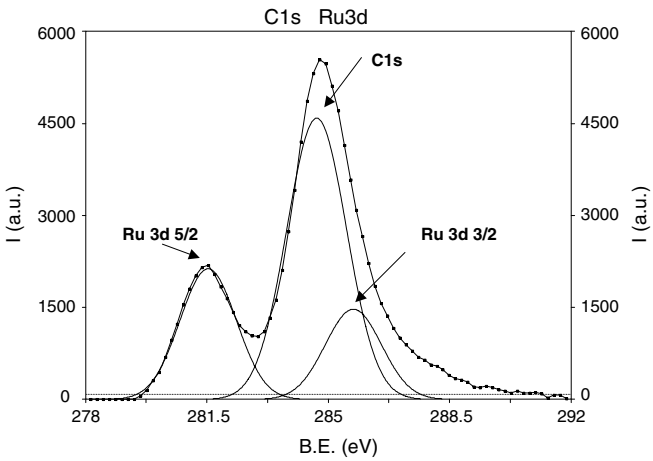


Fig. 2. XPS spectrum (dots) and fitting (line) in the range 278–292 eV for compound **1**.

individual peaks. The main feature at B.E. = 284.70 eV was assigned to the aromatic carbons, the second component at about 281 eV to the Ru3d 5/2 signal and the third one (with Δ(BE) equal to 4.17 eV) at about 285 eV to the Ru 3/2 spin orbit coupling. As example, the fitting of the components is reported in Fig. 2 for complex **1**.

The Ru 3d 5/2 signal of the complex **1** is shifted towards higher B.E. values (281.5 eV), with respect to Ru(0) line, found in the literature at about 280.2 eV for Ruthenocene derivatives [16]. This shift suggests the occurring of charge-transfer from the organic ligand to the coordinated metal center. By comparison of the Ru 3d 5/2 line of complex **1** with those of compounds **4a**, **4b1** and **4b2** (see Table 3), a shift towards lower B.E. was observed, thus suggesting an enhancement of the charge density around the metal centre. A reasonable explanation for this phenomenon can be envisaged in a higher charge mobility due to delocalization effects of the conjugated organic spacer which is reflected in a more negative Ru centre upon formation of the organometallic complexes **4a**, **4b1** and **4b1**. A relatively low intensity in the Ru signals in the samples **4a**, **4b1** and **4b2** was observed, probably due to minor desorption effects arising from the Ru-COD fragment.

4. Concluding remarks

The difunctional alkynylated Ru(η^6-arene)(η^4-COD) complexes **5a** and **5b1**, useful organo-ruthenium monomers as building blocks to prepare new organometallic conjugated polymers, have been synthesized in high yield with a very simple and efficient procedure starting from the complex Ru(η^6-naphthalene)(η^4-COD), **1**. Owing to the lability of the η^6-naphthalene–ruthenium bond in **1**, the arene-exchange reaction between **1** and the trimethylsylyl dialkynylated compounds **3a** and **3b** occurs easily with formation of the corresponding η^6-arene–ruthenium complexes **4a** and **4b1**. The dinuclear ruthenium complex **4b2** is obtained in low yield for the difficulty to bind the second "Ru(η^4-COD)" unit to the uncoordinated ring of **3b**. The trimethylsylyl groups in complexes **4a** and **4b1** can be removed, furnishing quantitatively the corresponding diacetylenic complexes **5a** and **5b1**. Optical and electronic characterizations showed that a charge-transfer occurs from the conjugated organic ligand to the coordinated Ru centres in complex **1**. This effect is less pronounced in complexes **4a**, **4b1** and **4b2** where the Ru centres appeared more negative as a consequence of the electronic density of the conjugated ligand.

Further studies are in progress to develop poly(alkynyl) homo and heterobimetallic polymers.

5. Experimental

All manipulations of the ruthenium complexes were performed under argon with use of standard Schlenk techniques. Solvents were purified by conventional methods and saturated with argon before use. 1,4-Diethynylbenzene (DEB, **2a**), 1,4-bis(trimethylsilylethynyl)benzene (DEB-Si, **3a**), 4,4′-bis(ethynyl)biphenyl (DEBP, **2b**) and 4,4′-bis(trimethylsilylethynyl)biphenyl (DEBP-Si, **3b**) were prepared by following the literature methods [12] The complex Ru(η^6-naphthalene)(η^4-1,5-cyclooctadiene), **1**, was carried out as previously reported [8]. Chromatographic separations of the Ru(η^6-arene)(η^4-1,5-cyclooctadiene) complexes were obtained with 70–230 mesh alumina (Merck), by using the appropriate eluents.

^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 and 75 MHz, respectively. Chemical shifts were determined relative to internal $Si(CH_3)_4$ ($\delta = 0$ ppm); coupling constants J are in Hz. Mass spectra were performed on an Applied Biosystems Sciex API 4000 MDS (Sciex, Concord, Ont., Canada) triple quadrupole mass spectrometer equipped with a Turbo-V Ionspray source under the following experimental

conditions: infusion at 20 μl/min (Syringe Pump Harvard mod. 22); CUR, 10; GS1, 25; GS2, 25; IS Voltage, 5 kV; Turbo T, 300 °C; DP, 20 V; the samples were prepared dissolving the complex in a toluene–methanol mixture.

FTIR spectra were recorded as nujol mulls or as films deposited by $CHCl_3$ solutions by using CsI cells, on a Perkin–Elmer 1700X Fourier Transform spectrometer. UV–Vis spectra were recorded on Perkin–Elmer Lambda 16 instrument. XPS spectra were obtained using a custom designed spectrometer. A non monochromatised Mg Kα X-rays source (1253.6 eV) was used and the pressure in the instrument was maintained at 1×10^{-9} Torr throughout the analysis. The experimental apparatus consists of an analysis chamber and a preparation chamber separated by a gate valve. An electrostatic hemispherical analyser (radius 150 mm) operating in the fixed analyser transmission (FAT) mode and a 16-channel detector were used. The film samples were prepared by dissolving our materials in $CHCl_3$ and spinning the solutions onto polished stainless steel substrates. The samples showed sufficient stability during the XPS analysis, preserving the same spectral features and chemical composition; the sampling of the thin film was carried out in Ar atmosphere. Binding energies (B.E.) were corrected by adjusting the position of the C1s peak to 284.70 eV of the aromatic carbons, in agreement with literature data [17]. The C1s, Ru3d, Si2p spectra were deconvoluted into their individual peaks using the *Peak Fit* curve fitting program for PC. Quantitative evaluation of the atomic ratios was obtained by analysis of the XPS signal intensity, employing Scofield's atomic cross section values [18] and experimentally determined sensitivity factors.

Microanalyses were carried out by the Laboratorio di Microanalisi, Facoltà di Farmacia, Università di Pisa, Italy.

5.1. Preparation of Ru[η^6-1,4-bis(trimethylsilylethynyl)-benzene](η^4-COD), **4a**

1,4-Bis(trimethylsilylethynyl)benzene (DEB-Si) (0.2 g, 0.74 mmol), **3a**, was added to a solution of **1** (0.25 g, 0.74 mmol) in THF (5 ml). Acetonitrile (0.77 ml, 14.8 mmol) was then added and the mixture was stirred at room temperature. The progress of the reaction was checked by removing a liquid sample of the solution and analysing the residue, obtained after evaporation of the reaction solvent, by ^{1}H NMR spectroscopy. The reaction was stopped after 6 h when the spectrum showed the disappearance of the signals of **1**. The solvent was removed under vacuum and the residue was dissolved in toluene (5 ml). The yellow-brown solution was chromatographed on an alumina column (20 cm, activity grade III). Pentane eluted naphthalene and unreacted **3a**; toluene eluted a yellow fraction that was evaporated to dryness. The solid so obtained was purified by crystallization at −78 °C from a mixture of THF (10 ml) and pentane (2 ml). Complex **4a** was obtained as yellow crystals (0.3 g, yield 85%). Anal. Calc. for $C_{24}H_{34}Si_2Ru$: C, 60.12; H, 7.1. Found: C, 59.75; H, 6.71%. IR ν(C≡C): 2156, 804 cm^{-1}; UV ($CHCl_3$): 278.0, 292.1 nm. ^{1}H and ^{13}C NMR and mass data are reported in Table 1.

5.2. Preparation of Ru[η^6-4,4′-bis(trimethylsilylethynyl)-biphenyl](η^4-COD), **4b1**

The reaction was performed as reported in Section 5.1. 4,4′-Bis(trimethylsilylethynyl)biphenyl (DEBP-Si) (0.26 g, 0.74 mmol), **3b**, was added to a solution of **1** (0.25 g, 0.74 mmol) and acetonitrile (0.77 ml, 14.8 mmol) in THF (5 ml). The mixture was stirred at r.t. for 5 h and chromatographed on alumina. Toluene eluted a yellow-brown fraction from which, by crystallization with a toluene/pentane mixture, complex **4b1** was obtained (0.33 g, yield 80%). Anal. Calc. for $C_{30}H_{38}Si_2Ru$: C, 64.85; H, 6.85. Found: C, 64.13; H, 6.54%. IR ν(C≡C): 2158, 804 cm^{-1}; UV ($CHCl_3$): 289.0 nm. ^{1}H and ^{13}C NMR and mass data are reported in Table 1.

5.3. Preparation of Ru_2 (η^4-COD)$_2$ [η^6,η^6-4,4′-bis-(trimethylsilylethynyl)biphenyl], **4b2**

The reaction was performed as reported in Section 5.1. 4,4′-Bis(trimethylsilylethynyl)biphenyl (DEBP-Si) (0.13 g, 0.37 mmol), **3b**, was added to a solution of **1** (0.25 g, 0.74 mmol) and acetonitrile (0.77 ml, 14.8 mmol) in THF (5 ml). The mixture was stirred at r.t. for 4 days. A large amount of solid materials was formed. The solvent was removed under vacuum and the residue was extracted with toluene (5 ml). The yellow-brown solution was chromatographed on an alumina column (20 cm, activity grade III). Toluene eluted a yellow-brown fraction which was evaporated to dryness. The solid was purified by crystallization at −78 °C from THF-pentane, furnishing complex **4b2** as yellow-brown crystals (0.056 g, yield 20%). Anal. Calc. for $C_{38}H_{50}Si_2Ru_2$: C, 59.65; H, 6.59. Found: C, 59.22; H, 6.34%. IR ν(C≡C): 2158, 804 cm^{-1}; UV ($CHCl_3$): 282.1 nm. ^{1}H and ^{13}C NMR and mass data are reported in Table 1.

5.4. Preparation of the complexes Ru(η^6-arene)(η^4-COD), **5a** [arene = 1,4-diethynylbenzene] and **5b1** [arene = 4,4′-bis(ethynyl)biphenyl]. General procedure

A solution of Ru(η^6-arene)(η^4-COD) [arene = 1,4-bis(trimethylsilylethynyl)benzene, **4a**; arene = 4,4′-bis-(ethynyl)biphenyl, **4b1**] (1.0 mmol) and tetrabutylammonium fluoride trihydrate (TBAF) (4 ml, 4.0 mmol) in THF (5 ml) was stirred at room temperature for 5 h. The progress of the reaction was checked by removing a liquid sample of the solution and analysing the residue, obtained after evaporation of the solvent, by ^{1}H NMR spectroscopy. The reaction mixture was then poured into water (15 ml) and extracted with toluene (3 × 10 ml). The organic extract was dried and the solvent was evaporated in vacuo. The residue was purified by chromatography on

alumina using toluene as eluent. The solid, obtained after removal of the solvent, was dissolved in toluene (5 ml) and the solution was treated with pentane (2 ml). The mixture deposited at −78 °C red-brown crystals of Ru(η^6-arene)(η^4-COD).

Arene = 1,4-diethynylbenzene, **5a** (0.32 g, yield = 95%). Anal. Calc. for $C_{18}H_{18}Ru$: C, 64.45; H, 5.41. Found: C, 65.02; H, 5.75%.

Arene = 4,4′-bis(ethynyl)biphenyl, **5b1** (0.39 g, yield = 95%). Anal. Calc. for $C_{24}H_{22}Ru$: C, 70.05; H, 5.38. Found: C, 70.94; H, 5.86%.

^{1}H and ^{13}C NMR and mass data of the complexes are reported in Table 2.

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References

[1] (a) R.P. Kingsborough, T.M. Swager, Transition metal coordination in polymeric π-conjugated organic frameworks, in: K.D. Karlin (Ed.), Progress in Inorganic Chemistry, vol. 48, Wiley, New York, 1999, p. 123;
(b) J.N. Long, C.K. Williams, Angew. Chem., Int. Ed. Engl. 42 (2003) 2586.

[2] (a) J. Lewis, M.S. Khan, S.J. Davies, A.K. Kakkar, B.F. Johnson, T.B. Marder, H.B. Fyfe, F. Wittmann, R.H. Friend, A.E. Dray, J. Organomet. Chem. 425 (1992) 165;
(b) D.L. Lichtenberger, S.K. Renshaw, R.M. Bullock, J. Am. Chem. Soc. 115 (1993) 3276;
(c) M. Sprinsbourg, J. Solid State Chem. 176 (2003) 311.

[3] Y. Yang, K.A. Abboud, L. McElwee-White, J. Chem. Soc., Dalton Trans. (2003) 4288.

[4] T.J.J. Müller, M. Ansorge, K. Polborn, J. Organomet. Chem. 578 (1999) 252.

[5] Y. Morisaki, H. Chen, Y. Chujo, J. Organomet. Chem. 689 (2004) 1271.

[6] C. Caliendo, I. Fratoddi, C. Lo Sterzo, M.V. Russo, J. Appl. Phys. 93 (2003) 10071.

[7] (a) Y. Amao, I. Okura, Sens. Act. B 88 (2003) 162;
(b) N. Egashira, H. Kumasako, T. Uda, K. Ohga, Electroanalysis 14 (2002) 871.

[8] M.A. Bennett, H. Neumann, M. Thomas, X.-qi Wang, P. Pertici, P. Salvadori, G. Vitulli, Organometallics 10 (1991) 3237.

[9] (a) P. Pertici, A. Verrazzani, E. Pitzalis, A.M. Caporusso, G. Vitulli, J. Organomet. Chem. 621 (2001) 246;
(b) R. Baldwin, M.A. Bennett, D.C.R. Hockless, P. Pertici, A. Verrazzani, G. Uccello Barretta, F. Marchetti, P. Salvadori, J. Chem. Soc., Dalton Trans. 23 (2002) 4488.

[10] (a) M.A. Bennett, Coord. Chem. Rev. 166 (1997) 225;
(b) G. Bodes, F.W. Heinemann, G. Jobi, J. Klodwig, S. Neumann, U. Zenneck, Eur. J. Inorg. Chem. (2003) 281.

[11] P. Pertici et al. (manuscript in preparation).

[12] S. Takahashi, Y. Kuroyama, K. Sonogashira, N. Hagihara, Synthesis 627 (1980).

[13] P. Pertici, G. Vitulli, Comments Inorg. Chem. 11 (1991) 175, and references therein.

[14] (a) I. Fratoddi, C. Battocchio, G. Polzonetti, P. Mataloni, M.V. Russo, A. Furlani, J. Organomet. Chem. 674 (2003) 10;
(b) G. Polzonetti, C. Battocchio, I. Fratoddi, M.V. Russo, Chem. Phys. Lett. 400 (2004) 290.

[15] (a) See, as examples of different procedures, E.J. Corey, H.A. Kirst, J.A. Katzenellenbogen, J. Am. Chem. Soc. 92 (1970) 6314;
(b) R.L. Hillard III, C.A. Parnell, K.P.C. Vollhardt, Tetrahedron 39 (1983) 905;
(c) R. Rossi, A. Carpita, M. Ciofalo, V. Lippolis, Tetrahedron 47 (1991) 8443;
(d) G. Balme, D. Bouyssi, Tetrahedron 50 (1994) 403;
(e) C. Meyer, I. Marek, G. Courtemanche, J.F. Normant, J. Org. Chem. 60 (1995) 863.

[16] P.G. Gassman, C.H. Winter, J. Am. Chem. Soc. 110 (1988) 6130.

[17] G. Beamson, D. Briggs, High Resolution XPS of Organic Polymers, the Scienta ESCA300 Database, Wiley, New York, 1992.

[18] J.M. Scofield, J. Electron. Spectrosc. Relat. Phenom. 8 (1976) 129.