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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.

Keywords: Dialkynes; Ruthenium; Arene complexes; 1,5-Cyclooctadiene complexes; Molecular models

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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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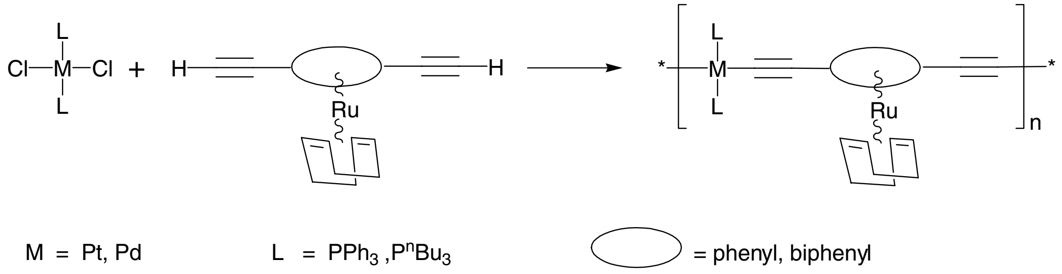

Scheme 1.

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(η⁶-arene)(η⁴-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].