Journal of Organometallic Chemistry 696 (2011) 3911–3923

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Review

# Osmium–carbon multiple bonds: Reduction and C–C coupling reactions

Tamara Bolaño, Miguel A. Esteruelas*, Enrique Oñate

*Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Universidad de Zaragoza, CSIC, 50009 Zaragoza, Spain*

ARTICLE INFO

*Article history:*
Received 31 March 2011
Received in revised form
26 April 2011
Accepted 27 April 2011

*Keywords:*
Osmium
Hydride
Carbyne
Carbene
Allenylidene
Metallacycle

ABSTRACT

This paper shows that the redox equilibria hydride-alkenylcarbyne/alkenylcarbene and alkenyl-alkenylcarbyne/dienylcarbene are readily governed by the electronic properties of the ligands of the complexes. Because we have learned to control the position of these equilibria, we are able to build, step by step, osmium derivatives with cyclic alkenylcarbene ligands and osmacyclopentapyrrole complexes. The dihydride $OsH_2Cl_2(P^iPr_3)_2$ reacts with alkynols, allenes, enynes, and dienes to give hydride–alkenylcarbyne derivatives, $OsHCl_2(\equiv CCR'{=}CR_2)(P^iPr_3)_2$, which can be transformed into dicationic species by replacement of chloride ligands by acetonitrile molecules. The selective deprotonation of the alkenylcarbyne ligand of $[OsH(\equiv CCH{=}CPh_2)(CH_3CN)_2(P^iPr_3)_2]^{2+}$ affords the hydride–allenylidene $[OsH({=}C{=}C{=}CPh_2)(CH_3CN)_2(P^iPr_3)_2]^+$, which undergoes the reduction of the $C_\alpha$–$C_\beta$ double bond of the cumulene in the presence of alcohols. The insertion of monosubstituted alkynes into the Os–H bond of the hydride–allenylidene complex leads to alkenyl–allenylidene derivatives, which are transformed into dienylcarbene compounds. The coordination of carbon monoxide to the osmium atom of the latter promotes the 4$\pi$-conrotation of the dienylcarbene ligand, to afford a cyclic alkenylcarbene complex via an $\eta^1$-cyclopentadienyl intermediate. Through a similar cyclization, in acetonitrile under reflux, the alkenyl–allenylidene complexes are converted into osmapyrrole derivatives by means of the formation of three C–C bonds involving the three carbon atoms of the cumulene, the alkenyl ligand, and an acetonitrile molecule.

## Contents

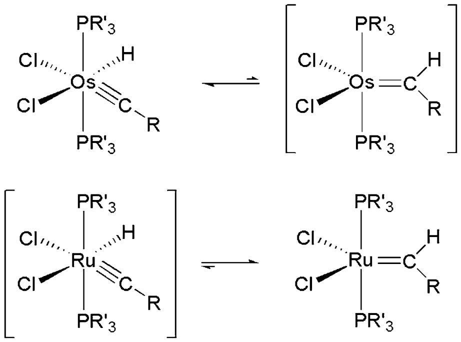
## 1. Introduction

In the search for new processes, novel types of compounds, and new bonding situations, in the last years, our research group has been interested in the design of metallic homogeneous systems that were effective in the synthesis of functionalized organic molecules from basic hydrocarbon units [1]. The first steps of such processes could involve the entry, in a consecutive and controlled way, of the organic fragments into a transition–metal complex to afford organometallic compounds through coupling reactions.

---

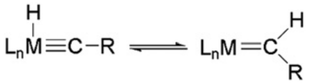
* Corresponding author.
*E-mail address:* maester@unizar.es (M.A. Esteruelas).

0022-328X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2011.04.029



**Scheme 1.** Equilibrium between hydride-carbyne and carbene species in osmium- and ruthenium-bisphosphine systems.

Osmium exhibits one of the widest ranges of oxidation states. Thus, at first glance, its use should allow to have a first forecast about the behavior of a wide variety of metallic ions with one only element. Transition–metal complexes containing a metal–carbon multiple bond are established members of the tools utilized in modern organic synthetic chemistry and organometallics, since they represent real catalysts or reaction intermediates for a number of highly valuable processes including carbon–carbon and carbon–heteroatom coupling reactions [2]. So, we anticipated that osmium–carbynes and –carbenes would be of particular interest for our aim. Among the transformations involving both types of compounds, the equilibrium between hydride–carbyne and carbene species (Eq (1)) should be one of the most relevant processes.



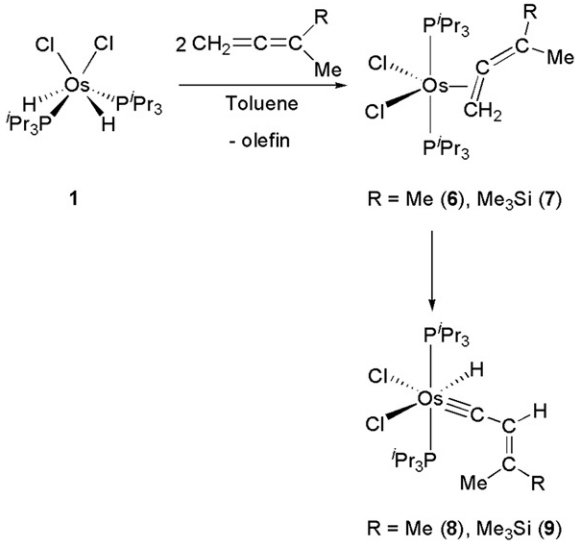
$$L_n\overset{H}{M}\equiv C-R \rightleftharpoons L_nM=C\genfrac{}{}{0pt}{}{H}{R} \qquad (1)$$

The 1,2-hydrogen shift from the carbene carbon atom to the metal had been the process generally observed for osmium [3]. This was consistent with the existence of $OsHCl_2(\equiv CR)(PR'_3)_2$ [4], i.e., the oxidized isomers of the still unknown $OsCl_2(=CHR)(PR'_3)_2$. The latter should be the osmium counterparts to the Grubbs-type carbene ruthenium derivatives $RuCl_2(=CHR)(PR'_3)_2$ [5] (Scheme 1). In this context, it should be noted that osmium is more reducing that ruthenium and prefers to be coordinatively saturated and forms redox isomers with greater metal–carbon bond multiplicity [1,6].

In the following pages, we show how the equilibrium summarized in Eq (1) for hydride–alkenylcarbyne complexes of the type $[OsH(\equiv CCH=CPh_2)L^1L^2(P^iPr_3)_2]^{n+}$ ($n$ = 0, 1, 2) can be governed. Because we have learned how to control it, we are able to build organic fragments on the metal center in the manner like a child plays with a LEGO®.

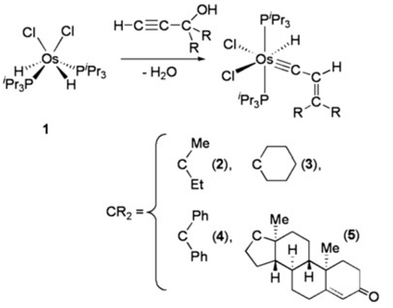
## 2. Preparation of hydride–alkenylcarbyne complexes of the type $[OsH(\equiv CCH=CPh_2)L^1L^2(P^iPr_3)_2]^{n+}$

The reactions of the osmium compounds containing two hydrogen atoms bonded to metal center with terminal alkynes are not easily rationalized, when the co-ligands of the complexes have some direct participation in the processes. However, when the co-ligands contribute only to the electronic structure of the metal center, the difference in energy between the dihydride and dihydrogen tautomers seems to be the factor determining the formed product. Thus, dihydride complexes, which afford dihydrogen species by coordination of electron poor-Lewis bases, and dihydrogen compounds react with terminal alkynes, HC≡CR, to give hydride–carbyne derivatives [7], including $OsHCl_2(\equiv CCH_2R)(P^iPr_3)_2$ [4a]. Alkenylcarbyne counterparts, $OsHCl_2\{\equiv CCR'=CR^1R^2\}(P^iPr_3)_2$, have been prepared by means of the reactions of the known dihydride starting complex $OsH_2Cl_2(P^iPr_3)_2$ (**1**) [8] with four different types of organic substrates: alkynols, allenes, enynes, and dienes.



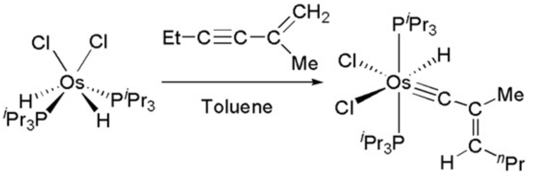
**Scheme 2.** Reaction of $OsH_2Cl_2(PiPr_3)_2$ with allenes.

Treatment of toluene solutions of **1** with 3-methyl-1-pentyne-3-ol, 1-ethynyl-1-cyclohexanol, 1,1-diphenyl-2-propyn-1-ol and ethisterone under reflux leads to the corresponding complexes **2**–**5** (Eq (2)). The reactions proceed through hydroxy-carbyne intermediates, which spontaneously dehydrate into the alkenylcarbyne products [4a,9].

 (2)

The reactions of **1** with 2 equiv of 1,1-dimethylallene and 1-methyl-1-(trimethylsilyl)allene in toluene under reflux initially afford 1 equiv of olefin and the π-allene derivatives **6** and **7**, which evolve into the corresponding hydride–alkenylcarbyne compounds **8** and **9** (Scheme 2). The isomerization involves the migration of both hydrogen atoms of the coordinated $CH_2$ group of the allene. The first of them, which has an activation energy higher than the second one, occurs between the terminal and central carbon atoms of the coordinated allene and takes place through the metal center. The second migration is a 1,2-hydrogen shift from the allene to the osmium atom [10].

Complex **1** also reacts with 2-methyl-1-hexen-3-yne in toluene under reflux. The reaction gives **10**, which is isolated in 55% yield (Eq (3)).

 (3)

**1** **10**