

Chromium(0)–rhodium(I) metal exchange: Synthesis and X-ray structure of new Fischer (NHC)carbene complexes of rhodium(I)

José Barluenga^{*}, Rubén Vicente, Luis A. López, Miguel Tomás

Instituto Universitario de Química Organometálica “Enrique Moles”, Unidad Asociada al CSIC, Universidad de Oviedo, Julián Clavería 8, 33006 Oviedo, Spain

Received 28 July 2006; received in revised form 4 September 2006; accepted 4 September 2006
Available online 19 September 2006

Dedicated to Professor Stefano Maiorana on the occasion of his 70th birthday for his excellent contribution to the field of organometallic chemistry and for his sincere friendship.

Abstract

An easy approach to Fischer (NHC)carbene complexes of rhodium(I) **3** from methoxy- and aminocarbene complexes of chromium **1** and (NHC)(cod)RhCl (**2**) is described. The process involves the transfer of the carbene unit and a CO ligand from chromium to rhodium. The X-ray analysis is provided for **3d** and the preliminary results on their thermal stability and reactivity toward alkynes and allenes are also reported.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Rhodium; NHC-complexes; Fischer carbene complexes; carbene transfer

1. Introduction

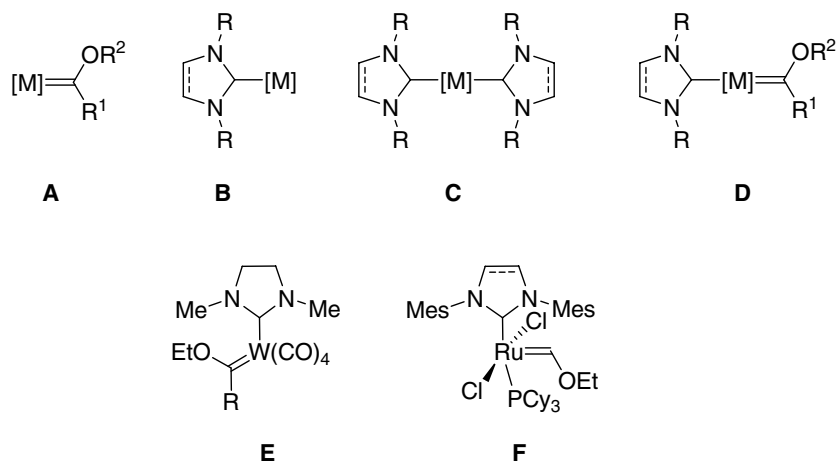
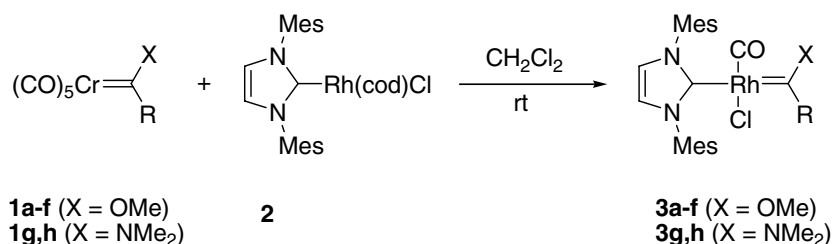
Since their discovery in 1964, Fischer carbene complexes of type **A** have been developed into versatile intermediates in stoichiometric transition metal-mediated organic synthesis (Fig. 1) [1]. In particular, complexes of groups 6–8 containing carbonyl ligands have played a prominent role in this area. Despite that N-heterocyclic carbenes, particularly 1,3-substituted imidazolidin-2-ylidene and imidazolin-2-ylidene (NHC ligands) were reported in the 1960s by Wanzlick [2] and Öfele [3], their increasing use in transition metal chemistry had to wait up to the isolation of a free N-heterocyclic carbene in 1991 by Arduengo et al. [4]. Now, it is well conceived why the appearance of N-heterocyclic carbene ligands (NHC) pushed the chemists involved in organometallic chemistry to evaluate the beneficial influence of this sort of ligands in the most relevant metal-cat-

alyzed organic reactions [5,6]. Thus, a number of NHC-based carbene and biscarbene complexes of types **B** and **C** were reported in the last years for a variety of transition metals (Fig. 1). Surprisingly, this event has found much less relevance in the case of Fischer carbene complexes as few examples of mixed complexes of type **D** have been hitherto reported. Early reports by Lappert described the preparation of tungsten biscarbene complexes **E** [7]. More recently, Louie and Grubbs described the synthesis of a number of (NHC)ruthenium Fischer-type carbene complexes **F** and their application in olefin metathesis [8,9].

Currently, we are particularly focused on Fischer carbene complexes of late transition metals, which have demonstrated to follow different reaction patterns than the group 6 analogs towards unsaturated substrates [10]. Herein, we report a facile procedure for the synthesis of the first Fischer rhodium(I) carbene complexes containing an NHC ligand (carbenes of type **D**) which is based on the chromium(0)–rhodium(I) metal exchange [11,12]. Moreover, preliminary results on their thermal stability and reactivity are provided.

^{*} Corresponding author.

E-mail address: barluenga@uniovi.es (J. Barluenga).

Fig. 1. Fischer carbene and NHC metal complexes, $[M] = ML_n$.Scheme 1. Preparation of rhodium(I) biscarbene complexes **3**.

2. Results and discussion

We selected the rhodium NHC-carbene complex **2**, recently reported by Evans [13], as the appropriate starting rhodium(I) complex (Scheme 1). Firstly, chromium (methoxy)carbene complexes **1a–f** ($X = \text{OMe}$) were reacted with 1 equiv. of rhodium(I) carbene complex **2** (CH_2Cl_2 , 25°C , 1–4 h). Removal of the solvent and column chromatography purification allowed to isolate (NHC)rhodium(I) carbene complexes **3a–f** as a sole stereoisomer. Thus, a variety of alkenyl and aryl carbene complexes could be prepared in a pure form in moderate yields (Table 1, entries 1–6). Despite that (amino)carbene complexes are much less reactive, or even they are inert, than the alkoxy derivatives towards the metal exchange reaction [11], we found that the reaction of (amino)carbene complexes **1g,h** and the rhodium(I) complex **2** (CH_2Cl_2 , 25°C) produced the corre-

sponding (NHC)rhodium(I) (amino)carbene complexes **3g,h** in comparable yields (Table 1, entries 7–8), though longer reaction times (16 h) were required. The whole transmetalation process comprises the transfer of two ligands – (alkoxy)carbene or (amino)carbene and CO – from chromium to rhodium and displacement of the cod ligand. It is noteworthy the simultaneous transfer of two ligands found in this Cr–Rh metal exchange reaction as it rather represents a rare process in the literature [10a,14].

Compounds **3a–h** were characterized spectroscopically and by elemental analysis. The spectroscopic data of **3a–h** clearly evidences the presence of, (i) the CO ligand (^{13}C NMR: $\delta = 186\text{--}188$ ppm; $^1J_{\text{C-Rh}} = 84.8\text{--}86.5$ Hz), (ii) the Rh–C(alkoxy) ligand (^{13}C NMR: $\delta = 313\text{--}304$ ppm; $^1J_{\text{C-Rh}} = 35.4\text{--}32.1$ Hz) and the Rh–C(amino) ligand (^{13}C NMR: $\delta = 245\text{--}234$ ppm; $^1J_{\text{C-Rh}} = 32.1\text{--}32.3$ Hz), and (iii) the Rh–C(NHC) ligand (^{13}C NMR: $\delta = 188\text{--}189$ ppm; $^1J_{\text{Rh-C}} = 36.6\text{--}39.9$ Hz).

The structure of the (methoxy)carbene **3d** was confirmed by a single-crystal X-ray structure analysis (Fig. 2) [15]. Complex **3d** shows a slightly distorted square planar geometry at the rhodium(I) center with a *trans* disposition of the two carbene ligands. The imidazole ring carbene and the acyclic carbene moieties are almost coplanar and perpendicular to the coordination plane (torsion angles in the range of $83\text{--}87^\circ$).

Next, we decided to check the thermal behavior of these new rhodium(I) biscarbene complexes. Thus, heating of complex **3a** in toluene at 60°C for 4 h resulted in the

Table 1
Preparation of rhodium(I) biscarbene complexes **3a–h**

Entry	R	X	3	Yield (%) ^a
1	(<i>E</i>)-CH=CH- C_6H_5	OMe	3a	40
2	(<i>E</i>)-CH=CH- <i>p</i> -MeOC $_6\text{H}_4$	OMe	3b	42
3	(<i>E</i>)-CH=CH-2-furyl	OMe	3c	35
4	(<i>E</i>)-CH=CH-ferrocenyl	OMe	3d	44
5	C_6H_5	OMe	3e	50
6	<i>p</i> -MeOC $_6\text{H}_4$	OMe	3f	40
7	(<i>E</i>)-CH=CH- C_6H_5	NMe $_2$	3g	50
8	(<i>E</i>)-CH=CH-2-furyl	NMe $_2$	3h	46

^a Yields of isolated products.

Download English Version:

<https://daneshyari.com/en/article/1328387>

Download Persian Version:

<https://daneshyari.com/article/1328387>

[Daneshyari.com](https://daneshyari.com)