

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

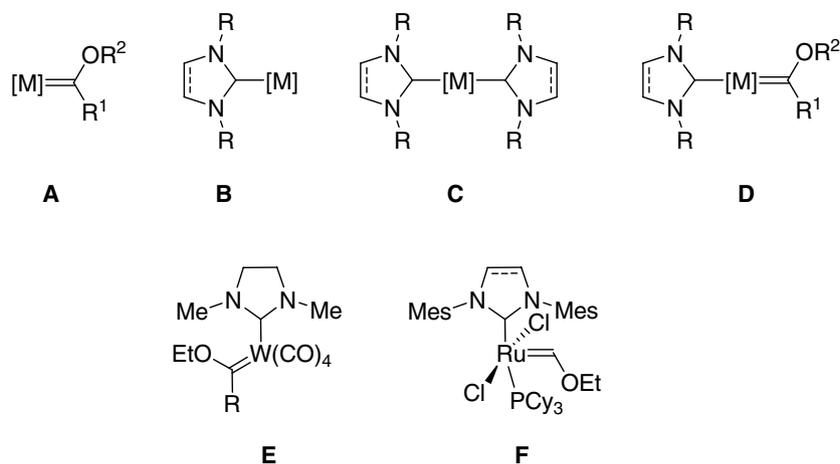
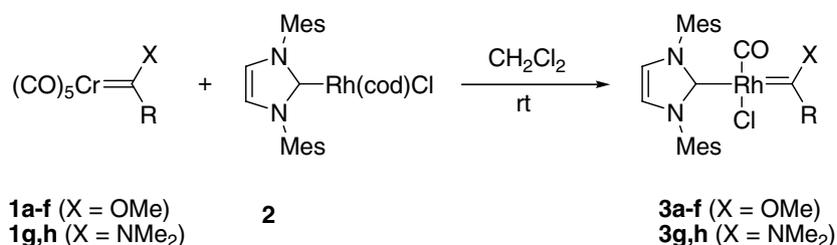
Since their discovery in 1964, Fischer carbene complexes of type **A** have been developed into versatile intermediates in stoichiometric transition metal-mediated organic synthesis (Fig. 1) [1]. In particular, complexes of groups 6–8 containing carbonyl ligands have played a prominent role in this area. 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 ₆ H ₅	OMe	3a	40
2	(<i>E</i>)-CH=CH- <i>p</i> -MeOC ₆ 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 ₆ H ₅	OMe	3e	50
6	<i>p</i> -MeOC ₆ H ₄	OMe	3f	40
7	(<i>E</i>)-CH=CH-C ₆ H ₅	NMe ₂	3g	50
8	(<i>E</i>)-CH=CH-2-furyl	NMe ₂	3h	46

^a Yields of isolated products.

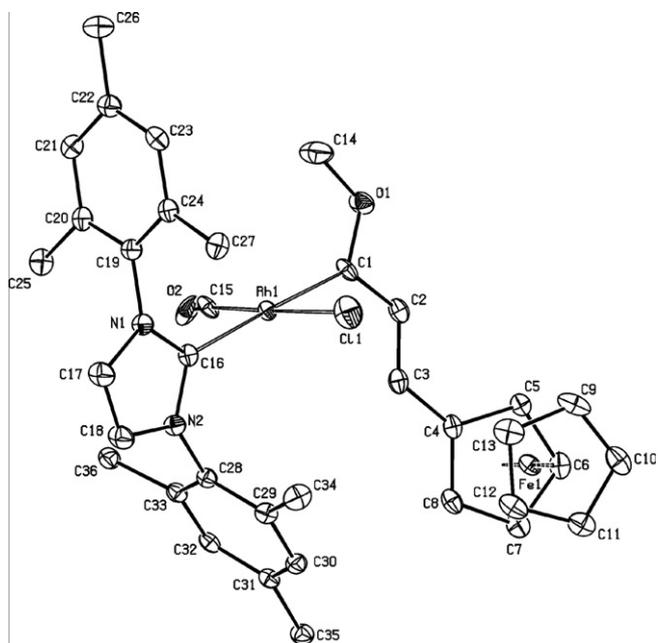
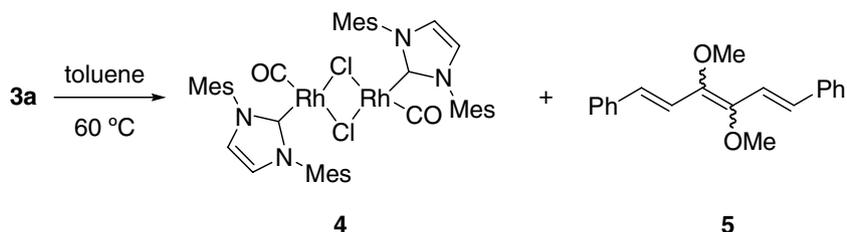
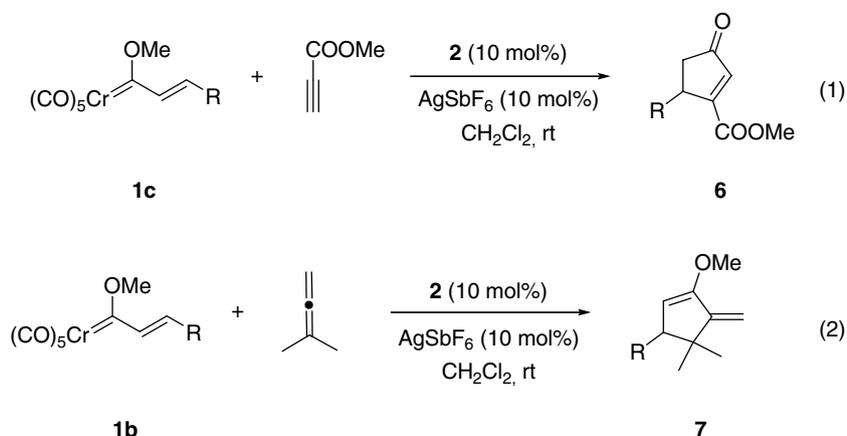


Fig. 2. X-ray structure of bis-carbene complex **3d** (ellipsoids at 30% probability level). Selected distances [Å] and angles [°]: Rh–C₁ 2.011(4), Rh–C₁₆ 2.078(4), Rh–C₁₅ 2.008(5), Rh–Cl 2.3735(15), C₁–Rh–C₁₅ 88.58(18), C₁–Rh–Cl 85.28(12), C₁₅–Rh–C₁₆ 93.75(17), C₁₆–Rh–Cl 92.35(12), C₁₅–Rh–Cl 173.70(13).

dimerization of the (methoxy)carbene ligand affording, after column chromatography, the dimer NHC-Rhodium(I) complex **4** (60% yield) and the triene **5** (1:1 mixture of *E/Z* stereoisomers, 56% yield) (Scheme 2).



Scheme 2. Thermal behaviour of carbene complex **3a**.



Scheme 3. Rhodium(I)-catalyzed [3 + 2] cyclization reactions of complex **1c** (R = 2-furyl) and **1b** (R = *p*-CH₃OC₆H₄) with methyl propiolate and 1,1-dimethylallene.

Interestingly, (NHC)Rh(I) complexes of type **4** have not been reported as far as we are aware. Compound **4** was characterized spectroscopically and by elemental analysis. Two sets of doublets centered at 184.5 ($^1J_{\text{Rh-C}} = 84.8$ Hz) and 175.0 ($^1J_{\text{Rh-C}} = 60.8$ Hz) in the ^{13}C NMR spectrum were attributed to the carbene and carbonyl carbon atoms, respectively. Moreover, a peak at $m/z = 940$ in the FAB-LR mass spectrum strongly supports the dimeric nature of complex **4** [16].

The synthetic application of this new ligand transfer process was then studied. First, we checked the behaviour of the rhodium complexes themselves **3** and found that the treatment of carbene complexes **3a,e** with unsaturated substrates, e.g. olefins, alkynes and allenes, at room temperature led to clean recovering of the starting materials. However, using a halide abstractor to *in situ* generate a cationic complex was more gratifying as it was encountered in the reaction of chromium carbene complexes and alkynes or allenes catalyzed by rhodium(I) (Scheme 3). Thus, stirring a CH₂Cl₂ solution of chromium carbene complex **1c** and methyl propiolate in the presence of the rhodium complex **2** (10 mol%) and AgSbF₆ (10 mol%) for 12 h at room temperature resulted in the regioselective formation of the cyclopentenone derivative **6** in 65% yield after chromatographic purification (Eq. (1)). On the other hand, when the carbene complex **1b** was mixed with 1,1-dimethylallene (3 equiv.) (CH₂Cl₂, rt, 48 h) in the presence of 10 mol% of **2** and 10 mol% of AgSbF₆, the cyclopentene derivative **7** was obtained in moderate yield (55%) after column chromatography (Eq. (2)).

Although, this catalytic process has been observed previously using the analogous rhodium complex containing a cod ligand instead of the NHC ligand [(cod)(CO)Rh=C(OMe)R]⁺ [10a,10b], this result demonstrates that the new catalyst reported herein is potentially useful for other catalytic reactions and even it might be superior if one notes that the active catalytic species seems to be a 14-electron rhodium complex [(NHC)(CO)Rh=C(OMe)R]⁺. Moreover, it opens the opportunity to undertake asymmetric catalysis on the basis of the great development of enantiopure NHC carbenes [17] and of the strength of the metal-NHC carbene carbon.

In summary a new type of metal carbene complex of group 9, specifically an NHC/Fischer hybrid biscarbene complex of rhodium(I), has been synthesized from chromium carbenes and characterized in solution and in the solid state. While these new complexes show low reactivity, the cationic complexes resulting from extraction of the chloride appears to be reactive intermediates towards alkynes and allenes. Further work using chiral NHC ligands which would generate suitable candidates for asymmetric catalysis is being currently studied in our group.

3. Experimental

General considerations: ¹H NMR and ¹³C NMR spectra were recorded at room temperature in CDCl₃, on a Bruker AC-300 (300 and 75.5 MHz) and Bruker AMX-400 (400 and 100 MHz) spectrometers. Chemical shifts are given in ppm relative to TMS (¹H, 0.0 ppm) or CDCl₃ (¹³C, 77.0 ppm). Carbon multiplicities were assigned by DEPT techniques. IR spectra were obtained in a Mattson 3000 FTIR spectrometer. High-resolution mass spectrometry was carried out on a Finnigan-Mat 95 spectrometer. Elemental analyses were carried out on a Perkin–Elmer 2400 and Carlo Erba 1108 microanalyzers. TLC was performed on aluminum-backed plates with silica gel 60 with F₂₅₄ indicator. All reactions involving organometallic species were carried out under nitrogen using standard Schlenck techniques. CH₂Cl₂ was distilled from CaH₂. Flash column chromatography was carried out on silica gel (230–240 mesh). Fischer carbene complexes **1** and [(IMes)(cod)CIRh] (**2**) were prepared according to literature methods. All other reagents and solvents used in this work were of the best commercial grade available and used without further purification.

3.1. General procedure for the synthesis of rhodium(I) biscarbene complexes **3a–3h**

To a solution of chromium carbene complex **1** (0.14 mmol) in CH₂Cl₂ (10 mL) was added [Rh(η⁴-1,5-cod)(IMes)Cl] **2** (80 mg, 0.14 mmol) and the mixture was stirred at rt until disappearance of the starting carbene complex (checked by TLC; 1–4 h for alkoxy carbene complexes and 16 h for aminocarbene complexes). The solvent was then removed and the resulting residue was subjected to flash chromatography (SiO₂, 5:1 hexane:ethyl acetate for

complexes **3a–f**, 3:1 hexane:ethyl acetate for **3g–h**). Analytical samples were obtained by recrystallization by slowly diffusing of diethyl ether into a saturated CH₂Cl₂ solution at –20 °C. In the case of compound **3d** a second recrystallization afforded crystals suitable for X-ray analysis.

3.1.1. (Carbonyl)(chloro)(1,3-dimesitylimidazol-2-ylidene)(1-methoxy-3-phenyl-2-propenylidene) rhodium(I) (**3a**)

¹H NMR (CDCl₃): 2.29 (s, 12H), 2.42 (s, 6H), 4.53 (s, 3H), 6.88 (d, *J* = 15.5 Hz, 1H), 7.08 (s, 4H), 7.15 (s, 2H), 7.35–7.42 (m, 5H), 8.42 (d, *J* = 15.5 Hz, 1H); ¹³C NMR (CDCl₃): 18.6 (CH₃), 21.1 (CH₃), 68.0 (CH₃), 122.8 (CH), 128.7 (CH), 129.1 (CH), 131.2 (CH), 135.3 (C), 136.1 (C), 136.5 (C), 136.8 (CH), 138.2 (C), 166.8 (C), 187.6 (C, d, *J*(Rh,C) = 85.9 Hz), 188.4 (C, d, *J*(Rh,C) = 37.4 Hz), 310.6 (C, d, *J*(Rh,C) = 35.4 Hz); IR (CH₂Cl₂): ν 3053, 2986, 1952, 1609, 1421, 1265, 895, 739 cm⁻¹. Anal. Calcd for C₃₂H₃₄ClN₂O₂Rh: C, 62.29; H, 5.55. Found: C, 62.00; H, 5.44%.

3.1.2. (Carbonyl)(chloro)(1,3-dimesitylimidazol-2-ylidene)[1-methoxy-3-(4-methoxyphenyl)-2-propenylidene] rhodium(I) (**3b**)

¹H NMR (CDCl₃): 2.29 (s, 12H), 2.42 (s, 6H), 3.87 (s, 3H), 4.48 (s, 3H), 6.80 (d, *J* = 15.3 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 7.07 (s, 4H), 7.14 (s, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 8.39 (d, *J* = 15.6 Hz, 1H). ¹³C NMR (CDCl₃): 18.6 (CH₃), 21.1 (CH₃), 55.4 (CH₃), 67.5 (CH₃), 114.2 (CH), 122.7 (CH), 128.3 (C), 128.7 (CH), 131.1 (CH), 134.8 (CH), 136.1 (C), 136.6 (C), 138.2 (C), 162.2 (C), 167.0 (CH), 187.1 (C, d, *J*(Rh,C) = 84.9 Hz), 188.7 (C, d, *J*(Rh,C) = 37.4 Hz), 308.0 (C, d, *J*(Rh,C) = 35.4 Hz); IR (CH₂Cl₂): ν 3054, 2986, 1949, 1597, 1421, 1265, 1168, 739 cm⁻¹. Anal. Calcd for C₃₃H₃₆ClN₂O₃Rh: C, 61.26; H, 5.61. Found: C, 61.15; H, 5.46%.

3.1.3. (Carbonyl)(chloro)(1,3-dimesitylimidazol-2-ylidene)[1-methoxy-3-(2-furyl)-2-propenylidene] rhodium(I) (**3c**)

¹H NMR (CDCl₃): 2.29 (s, 12H), 2.42 (s, 6H), 4.50 (s, 3H), 6.52 (dd, *J* = 1.8 and 3.4 Hz, 1H), 6.68 (d, *J* = 3.4 Hz, 1H), 6.74 (d, *J* = 15.2 Hz, 1H), 7.06 (s, 4H), 7.15 (s, 2H), 7.56 (d, *J* = 1.3 Hz, 1H), 8.10 (d, *J* = 15.3 Hz, 1H). ¹³C NMR (CDCl₃): 18.6 (CH₃), 21.2 (CH₃), 67.8 (CH₃), 113.0 (CH), 118.0 (CH), 122.7 (CH), 128.7 (CH), 134.5 (CH), 136.1 (C), 136.5 (C), 138.2 (C), 145.9 (CH), 150.3 (CH), 152.2 (C), 187.3 (C, d, *J*(Rh,C) = 85.2 Hz), 188.7 (C, d, *J*(Rh,C) = 37.5 Hz), 308.2 (C, d, *J*(Rh,C) = 5.4 Hz); IR (CH₂Cl₂): ν 3053, 2979, 1951, 1616, 1265, 1198, 738, 705 cm⁻¹. Anal. Calcd for C₃₀H₃₂ClN₂O₃Rh: C, 59.37; H, 5.31. Found: C, 59.19; H, 5.23%.

3.1.4. (Carbonyl)(chloro)(1,3-dimesitylimidazol-2-ylidene)(1-methoxy-3-ferrocenyl-2-propenylidene) rhodium(I) (**3d**)

¹H NMR (CDCl₃): 2.30 (s, 12H), 2.43 (s, 6H), 4.15 (s, 5H), 4.38 (s, 3H), 4.40 (d, *J* = 1.7 Hz, 2H), 4.55 (d, *J* = 1.7 Hz,

2H), 6.48 (d, $J = 15.1$ Hz, 2H), 7.08 (s, 4H), 7.13 (s, 2H), 8.45 (d, $J = 15.1$ Hz, 1H). ^{13}C NMR (CDCl_3): 18.7 (CH₃), 21.2 (CH₃), 69.7 (CH₃), 70.6 (CH), 72.6 (CH), 76.6 (CH), 78.7 (C), 122.7 (CH), 128.7 (CH), 133.5 (C), 136.2 (CH), 136.7 (C), 138.1 (C), 171.1 (CH), 187.5 (C, d, $J(\text{Rh,C}) = 85.9$ Hz), 189.3 (C, d, $J(\text{Rh,C}) = 37.4$ Hz), 304.3 (C, d, $J(\text{Rh,C}) = 34.4$ Hz); IR (CH_2Cl_2): ν 3054, 2986, 1946, 1599, 1421, 1265, 895, 739 cm^{-1} . Anal. Calcd for $\text{C}_{36}\text{H}_{38}\text{ClFeN}_2\text{O}_2\text{Rh}$: C, 59.65, 5.28. Found: C, 59.40, H, 5.19%.

3.1.5. (Carbonyl)(chloro)(1,3-dimesitylimidazol-2-ylidene)(methoxybenzylidene) rhodium(I) (3e)

^1H NMR (CDCl_3): 2.28 (s, 12H), 2.43 (s, 6H), 4.73 (s, 3H), 7.07 (s, 4H), 7.15 (s, 2H), 7.19–7.26 (m, 2H), 7.43–7.48 (m, 1H), 8.03 (d, $J = 8.1$ Hz, 2H). ^{13}C NMR (CDCl_3): 18.6 (CH₃), 21.2 (CH₃), 68.8 (CH₃, d, $J(\text{Rh,C}) = 2.3$ Hz), 122.8 (CH), 127.6 (CH), 128.7 (CH), 132.8 (CH), 134.0 (CH), 136.0 (C), 136.4 (C), 138.3 (C), 145.2 (C), 186.9 (C, d, $J(\text{Rh,C}) = 85.0$ Hz), 188.0 (C, d, $J(\text{Rh,C}) = 36.6$ Hz), 313.9 (C, d, $J(\text{Rh,C}) = 34.9$ Hz); IR (CH_2Cl_2): ν 3054, 2986, 1954, 1642, 1422, 1265, 895, 738 cm^{-1} . Anal. Calcd for $\text{C}_{30}\text{H}_{32}\text{ClN}_2\text{O}_2\text{Rh}$: C, 60.97; H, 5.46. Found: C, 60.70; H, 5.25%.

3.1.6. (Carbonyl)(chloro)(1,3-dimesitylimidazol-2-ylidene)[methoxy(4-methoxy)benzylidene] rhodium(I) (3f)

^1H NMR (CDCl_3): 2.38 (s, 12H), 2.45 (s, 6H), 3.85 (s, 3H), 4.66 (s, 3H), 6.71 (d, $J = 9.0$ Hz, 2H), 7.09 (s, 4H), 7.17 (s, 2H), 8.06 (d, $J = 9.0$ Hz, 2H). ^{13}C NMR (CDCl_3): 18.6 (CH₃), 21.2 (CH₃), 55.4 (CH₃), 68.0 (CH₃), 112.8 (CH), 122.7 (CH), 128.7 (CH), 135.6 (CH), 136.0 (C), 136.5 (C), 138.2 (C), 139.3 (C), 164.4 (C), 187.2 (C, d, $J(\text{Rh,C}) = 85.9$ Hz), 188.6 (C, d, $J(\text{Rh,C}) = 37.4$ Hz), 307.4 (C, d, $J(\text{Rh,C}) = 35.4$ Hz); IR (CH_2Cl_2): ν 3054, 2986, 1950, 1597, 1421, 1264, 896, 733 cm^{-1} . Anal. Calcd for $\text{C}_{31}\text{H}_{34}\text{ClN}_2\text{O}_2\text{Rh}$: C, 59.96; H, 5.52. Found: C, 59.74; H, 5.36%.

3.1.7. (Carbonyl)(chloro)(1,3-dimesitylimidazol-2-ylidene)(1-dimethylamino-3-phenyl-2-propenylidene) rhodium(I) (3g)

^1H -RMN(CDCl_3): 2.34 (s, 12H), 2.42 (s, 6H), 3.25 (s, 3H), 3.65 (s, 3H), 7.06 (d, $J = 15.0$ Hz, 1H), 7.08 (s, 4H), 7.14 (s, 2H), 7.37 (s, 5H), 8.20 (d, $J = 15.0$ Hz, 1H). ^{13}C -RMN(CDCl_3): 18.6 (CH₃), 21.1 (CH₃), 41.2 (CH₃), 51.5 (CH₃), 122.3 (CH), 128.2 (CH), 128.4 (CH), 128.6 (CH), 129.2 (CH), 129.4 (CH), 136.2 (C), 136.4 (C), 136.9 (C), 138.0 (C), 156.7 (CH), 188.1 (C, d, $J(\text{Rh,C}) = 85.9$ Hz), 189.6 (C, d, $J(\text{Rh,C}) = 39.4$ Hz), 245.4 (C, d, $J(\text{Rh,C}) = 32.3$ Hz); IR (CH_2Cl_2): ν 3053, 2986, 1931, 1611, 1421, 1265, 895, 737 cm^{-1} . Anal. Calcd for $\text{C}_{33}\text{H}_{37}\text{ClN}_3\text{ORh}$: C, 62.91; H, 5.92. Found: C, 62.69; H, 5.77%.

3.1.8. (Carbonyl)(chloro)(1,3-dimesitylimidazol-2-ylidene)[1-dimethylamino-3-(2-furyl)-2-propenylidene] rhodium(I) (3h)

^1H NMR (CDCl_3): 2.28 (s, 12H), 2.37 (s, 6H), 3.19 (s, 3H), 3.60 (s, 3H), 6.39 (d, $J = 3.3$ Hz, 1H), 6.43 (dd,

$J = 3.5$ y 1.9 Hz, 1H), 6.92 (d, $J = 14.7$ Hz, 1H), 7.02 (s, 4H), 7.09 (s, 2H), 7.40 (bs, 1H), 7.93 (d, $J = 14.7$ Hz, 1H). ^{13}C NMR (CDCl_3): 18.6 (CH₃), 21.1 (CH₃), 41.1 (CH₃), 51.5 (CH₃), 112.0 (CH), 114.6 (CH), 122.2 (CH), 126.9 (CH), 128.5 (CH), 136.2 (C), 136.9 (C), 137.8 (C), 142.4 (CH), 143.9 (CH), 152.7 (C), 188.1 (C, d, $J(\text{Rh,C}) = 86.5$ Hz), 189.6 (C, d, $J(\text{Rh,C}) = 39.4$ Hz), 243.5 (C, d, $J(\text{Rh,C}) = 32.1$ Hz); IR (CH_2Cl_2): ν 3154, 2921, 1932, 1621, 1485, 1266, 907, 733 cm^{-1} . Anal. Calcd for $\text{C}_{31}\text{H}_{35}\text{ClN}_3\text{O}_2\text{Rh}$: C, 60.05; H, 5.69. Found: C, 59.87; H, 5.44%.

3.2. Thermal behaviour of complex 3a

A solution of complex **3a** (62 mg, 0.1 mmol) in toluene (2 mL) was heated at 60 °C. The mixture was stirred at this temperature until disappearance of the starting complex (checked by TLC, 4 h). The solvent was then removed and the resulting residue was subjected to flash chromatography (SiO_2 , 5:1 hexane:ethyl acetate) yielding the dimers **4** and **5**. The spectroscopic data of compound **5** were identical to those previously reported in the literature [18].

3.2.1. (Carbonyl)(μ -chloro)(1,3-dimesitylimidazol-2-ylidene) rhodium(I) dimer (4)

^1H NMR (CDCl_3): 2.14 (s, 24H), 2.35 (s, 12H), 6.90–6.96 (bs, 12H). ^{13}C NMR (CDCl_3): 18.7 (CH₃), 21.1 (CH₃), 123.3 (CH), 128.7 (CH), 135.2 (C), 138.3 (C), 175.0 (C, d, $J(\text{Rh,C}) = 60.8$ Hz), 184.5 (C, d, $J(\text{Rh,C}) = 84.8$ Hz); IR (CH_2Cl_2): ν 3053, 2986, 1956, 1643, 1421, 1265, 895, 738 cm^{-1} . Anal. Calcd for $\text{C}_{44}\text{H}_{48}\text{Cl}_2\text{N}_4\text{O}_2\text{Rh}_2$: C, 56.13; H, 5.14. Found: C, 55.85; H, 5.07%. HR-MS; calcd.: 940.1276, found: 940.1265.

3.3. Rh(I)-catalyzed [3 + 2]-cyclization reaction of alkenyl Fischer carbene complex 1c with methyl propiolate

To a solution of carbene complex **1c** (164 mg, 0.5 mmol) and methyl propiolate (126 mg, 1.5 mmol) in CH_2Cl_2 (5 mL) was added the complex **2** (28 mg, 0.05 mmol) and AgSbF_6 (17 mg, 0.05 mmol). The mixture was stirred at room temperature until disappearance of the starting carbene complex (checked by TLC, 12 h). The solvent was then removed and the resulting residue was subjected to flash chromatography (SiO_2 , 15:1 hexane:ethyl acetate) to give pure compound **6**.

3.3.1. 4-(2-Furyl)-3-methoxycarbonyl-2-cyclopentenone (6)

^1H NMR (CDCl_3): 2.66 (dd, $J = 18.9$ and 2.3 Hz, 1H), 2.93 (dd, $J = 18.9$ and 7.1 Hz, 1H), 3.80 (s, 3H), 4.54 (td, $J = 7.1$ and 2.3 Hz, 1H), 6.13 (d, $J = 3.3$ Hz, 1H), 6.30 (dd, $J = 3.1$ and 1.8 Hz, 1H), 6.82 (d, $J = 2.0$ Hz, 1H), 7.29–7.31 (m, 1H). ^{13}C NMR (CDCl_3): 39.0 (CH), 42.6 (CH₂), 52.6 (CH₃), 106.4 (CH), 110.6 (CH), 138.1 (CH), 142.0 (CH), 152.3 (C), 162.3 (C), 164.0 (C), 207.1 (C). Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{O}_4$: C, 64.07; H, 4.89. Found: C, 63.99; H, 4.96%.

3.4. *Rh(I)*-catalyzed [3 + 2]-cyclization reaction of alkenyl Fischer carbene complex **1b** with dimethylallene

To a solution of carbene complex **1b** (184 mg, 0.5 mmol) and dimethylallene (102 mg, 1.5 mmol) in CH₂Cl₂ (5 mL) was added the complex **2** (28 mg, 0.05 mmol) and AgSbF₆ (17 mg, 0.05 mmol). The mixture was stirred at room temperature until disappearance of the starting carbene complex (checked by TLC, 48h). The solvent was then removed and the resulting residue was subjected to flash chromatography (SiO₂, 15:1 hexane:ethyl acetate) to give pure compound **7**. The spectroscopic data of compound **7** were identical to those previously reported in the literature [10b].

Acknowledgements

We are grateful to the Ministerio de Educación y Ciencia (MEC, Project CTQ2004-08077), the Principado de Asturias (Project IB05-136) and the Fundación Ramón Areces for the support of this research. We acknowledge the MEC for a predoctoral fellowship to R.V. We are also grateful to Dr César J. Pastor (SIIdI, Universidad Autónoma de Madrid) for his assistance in the collection of the X-ray data.

References

- [1] (a) For recent reviews on Fischer carbene complexes, see: W.D. Wulff, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), *Comprehensive Organometallic Chemistry II*, vol. 12, Pergamon, New York, 1995;
 - (b) D.F. Harvey, D.M. Sigano, *Chem. Rev.* 96 (1996) 271;
 - (c) F. Zaragoza Dörwall, *Metal Carbenes in Organic Synthesis*, Wiley, Weinheim, 1999;
 - (d) M.A. Sierra, *Chem. Rev.* 100 (2000) 3591;
 - (e) A. De Meijere, H. Schirmer, M. Duestch, *Angew. Chem., Int. Ed.* 39 (2000) 3964;
 - (f) J. Barluenga, J. Santamaría, M. Tomás, *Chem. Rev.* 104 (2004) 2259;
 - (g) J. Barluenga, M.A. Fernández-Rodríguez, E. Aguilar, *J. Organomet. Chem.* 690 (2005) 539;
 - (h) J.W. Herndon, *Coord. Chem. Rev.* 250 (2006) 1889.
- [2] (a) H.-W. Wanzlick, E. Schikora, *Angew. Chem.* 72 (1960) 494;
 - (b) H.-W. Wanzlick, H.-J. Kleiner, *Angew. Chem.* 73 (1961) 493;
 - (c) W. Wanzlick, *Angew. Chem.* 74 (1962) 129.
- [3] K. Öfele, *J. Organomet. Chem.* 12 (1968) P42.
- [4] A.J. Arduengo III, R.L. Harlow, M. Kline, *J. Am. Chem. Soc.* 113 (1991) 361.
- [5] (a) For comprehensive reviews on NHC carbenes, see: M. Regitz, *Angew. Chem., Int. Ed. Engl.* 35 (1996) 725;
 - (b) A.J. Arduengo III, R. Krafczyk, *Chem. Unserer Zeit* 32 (1998) 6;
 - (c) D. Bourissou, O. Guerret, F.P. Gabbaï, G. Bertrand, *Chem. Rev.* 100 (2000) 39;
 - (d) W.A. Herrmann, *Angew. Chem., Int. Ed. Engl.* 41 (2002) 1290.
- [6] (a) For reviews of NHC carbenes as reagents and catalysts see: D. Enders, H. Gielen, *J. Organomet. Chem.* 617–618 (2001) 70;
 - (b) D. Enders, T. Balensiefer, *Acc. Chem. Res.* 37 (2004) 534.
- [7] (a) M.F. Lappert, P.L. Pye, G.M. McLaughlin, *J. Chem. Soc., Dalton Trans.* (1977) 1272;
 - (b) M.F. Lappert, P.L. Pye, *J. Chem. Soc., Dalton Trans.* (1977) 1283;
 - (c) P.B. Hitchcock, M.F. Lappert, P.L. Pye, *J. Chem. Soc., Dalton Trans.* (1977) 2160.
- [8] J. Louie, R.H. Grubbs, *Organometallics* 21 (2002) 2153.
- [9] For a Fischer tungsten carbene complex with an oxazolin-2-ylidene ligand, see: J. Barluenga, F. Aznar, B. Weyerhausen, S. García-Granda, E. Martín, *Chem. Commun.* (1996) 2455.
- [10] (a) For recent contributions involving rhodium(I) and nickel(0) carbene complexes, see: J. Barluenga, R. Vicente, L.A. López, E. Rubio, M. Tomás, C. Álvarez-Rúa, *J. Am. Chem. Soc.* 126 (2004) 470;
 - (b) J. Barluenga, R. Vicente, P. Barrio, L.A. López, M. Tomás, *J. Am. Chem. Soc.* 126 (2004) 5974;
 - (c) J. Barluenga, R. Vicente, P. Barrio, L.A. López, M. Tomás, J. Borge, *J. Am. Chem. Soc.* 126 (2004) 14354;
 - (d) J. Barluenga, R. Vicente, P. Barrio, L.A. López, M. Tomás, *J. Am. Chem. Soc.* 128 (2006) 7050;
 - (e) J. Barluenga, P. Barrio, L.A. López, M. Tomás, S. García-Granda, C. Álvarez-Rúa, *Angew. Chem. Int. Ed.* 42 (2003) 3008.
- [11] For an excellent, comprehensive review on metal exchange, see: M.A. Sierra, M.J. Mancheño, M. Gómez-Gallego, *Acc. Chem. Res.* 37 (2005) 44.
- [12] For a previous example of chromium-rhodium exchange, see: I. Göttker-Schnetmann, R. Aumann, K. Bergander, *Organometallics* 20 (2001) 3574.
- [13] P.A. Evans, E.W. Baum, A.N. Fazal, M. Pink, *Chem. Commun.* (2005) 63.
- [14] (a) For the transfer of carbene and carbonyl ligands from a tungsten diaminocarbene complex to platinum, see: S.-T. Liu, T.-Y. Hsieh, G.-H. Lee, S.-M. Peng, *Organometallics* 18 (1998) 993;
 - (b) R.-Z. Ku, J.-C. Huang, J.-Y. Cho, F.-M. Kiang, K.R. Reddy, Y.-C. Chen, K.-J. Lee, J.-H. Lee, G.-H. Lee, S.-M. Peng, S.-T. Liu, *Organometallics* 18 (1999) 2145.
- [15] Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 616191 for compound **3d**.
- [16] Unfortunately, we were not able to obtain crystals of compound **4** of enough quality for a X-ray structure analysis.
- [17] (a) For recent applications of chiral NHC complexes in asymmetric catalysis, see: K.-S. Lee, M.K. Brown, A.W. Hird, A.H. Hoveyda, *J. Am. Chem. Soc.* 128 (2006) 7182;
 - (b) S.-S. Ng, T.F. Jamison, *J. Am. Chem. Soc.* 127 (2005) 7320.
- [18] J. Barluenga, P. Barrio, R. Vicente, L.A. López, M. Tomás, *J. Organomet. Chem.* 689 (2004) 3793.