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Bimetallic Cr, Ru alkenyl carbene derivatives: synthesis from organometallic prop-2-yn-1-ols and stereochemical aspects

Natividad Ruiz [a], Daniel Péron [a], Sourisak Sinbandith [b], Pierre H. Dixneuf [a,*], Clara Baldoli [c], Stefano Maiorana [c,*]

[a] *Laboratoire de Chimie de Coordination Organique, URA CNRS 415, Campus de Beaulieu, Université de Rennes, 35042 Rennes, France*
[b] *CRMPO, Campus de Beaulieu, Université de Rennes, 35042 Rennes, France*
[c] *Dipartimento di Chimica Organica e Industriale dell'Universita CNR, Centro Studio Sintesi e Stereochimica Speciali Sistemi Organici, Via C. Golgi 19, I-20133 Milano, Italy*

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Abstract

The reaction of $RuCl_2(PMe_3)(\eta^6\text{-}C_6Me_6)$ **1** with HC≡C–CHOH–(2-MeO–C_6H_4) **2** and $NaPF_6$ in methanol led to the *trans*-alkenylcarbene complex [LnRu=C(OMe)CH=CH(2-MeO–C_6H_4)]PF_6 **3** (LnRu = $Ru(Cl)(PMe_3)(\eta^6\text{-}C_6Me_6)$) with the *s-cis* conformation of the carbene ligand. The activation by **1** of the *racemic* and of the (S,S) stereoisomer of the organometallic alcohol HC≡CCHOH(η^6-(2-Me–C_6H_4)$Cr(CO)_3$ **4** afforded the same two diastereoisomers [LnRu=C(OMe)CH=CH(η^6-(2-Me–C_6H_4)$Cr(CO)_3$]PF_6 **5a/b** with low stereoselectivity in the ratio 55:45 (80%) and in the *s-cis* conformation. By contrast, the activation of HC≡CCOH(Me)(η^6-C_6H_5)$Cr(CO)_3$ **8** by **1** led to two diastereoisomers [LnRu=C(OMe)CH=CMe(η^6-C_6H_5)$Cr(CO)_3$]PF_6 **9a/b** (64:34) with the *s-trans* conformation of the organometallic carbene ligand.

Keywords: Carbenes; Chromium; Stereochemistry; Ruthenium; Prop-2-yn-1-ols

1. Introduction

The activation of prop-2-yn-1-ols by ruthenium(II) complexes has first resulted in its dehydration to afford ruthenium allenylidene complexes such as $[Ru=C=C=CPh_2(PMe_3)_2C_5H_5]PF_6$ [1] or $[Ru=C=C=CPh_2(Cl)(Ph_2PCH_2PPh_2)_2]PF_6$ [2]. With the electrophilic (arene)ruthenium(II) complexes of type **I**, the allenylidene intermediate **II** is very reactive towards weak nucleophiles such as methanol to give the alkenyl carbene complexes **III** [3] (Scheme 1). As complex **1** is prochiral it might be expected that a chiral prop-2-yn-1-ol could more easily approach one of the two faces of the 16-electron transient species **IV**. This would stereoselectively produce one of the two diastereoisomers of the alkyne adducts **Va** or **Vb**, which would lead to an excess of one enantiomer of the allenylidene intermediate of type **II** and thus of the alkenylcarbene complexes **VIa** or **VIb**. Alternatively, the use of an alkynol bearing two stereocenters (with chiral R^1 or R^2) could lead to an excess of one of the alkenyl carbene ruthenium diastereoisomers. We report here (i) the activation of an optically active 1-aryl prop-2-yn-1-ol by $RuCl_2(PMe_3)(C_6Me_6)$ complex **1** which leads to a new alkenyl–carbene complex in methanol but without transfer of chirality, and (ii) the activation of organometallic prop-2-yn-1-ol diastereoisomers, having an *ortho*-disubstituted and $Cr(CO)_3$ coordinated 1-aryl substituent, by the same derivative **1** which gives new mixed chromium and ruthenium containing alkenyl carbenes, existing as two diastereoisomers.

2. Results and discussion

In order to study the activation of a chiral 1-aryl prop-2-yn-1-ol by $RuCl_2(PMe_3)(\eta^6\text{-}C_6Me_6)$ **1**, the reaction was first studied with the *racemic* alcohol. Thus complex **1** was reacted in the presence of $NaPF_6$ and methanol with one equivalent of the (R,S)-HC≡C–

* Corresponding authors.

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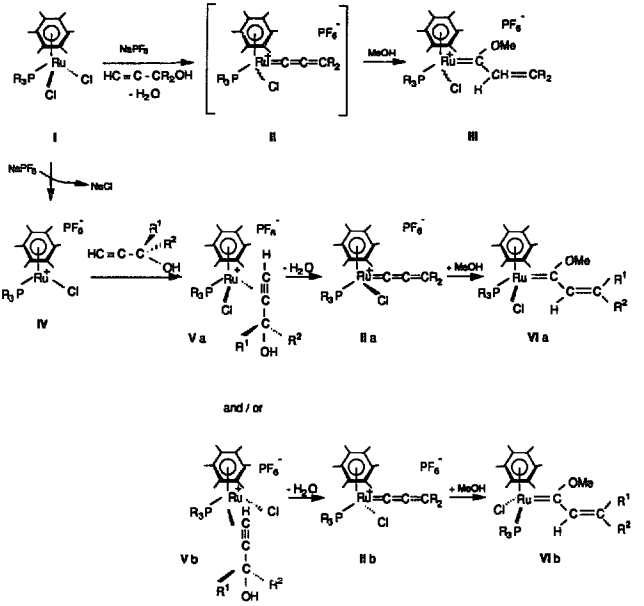
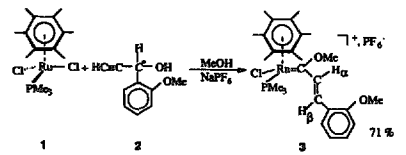


Scheme 1.

CHOH–(2-MeO–C_6H_4) derivative **2** [4]. The new alkenyl carbene complex **3** was isolated in 71% yield (Scheme 2).

The structure of **3** was established by NMR. The NMR spectra are consistent with the *trans* configuration of the CH=CH bond [δ ppm: 8.69 (d) and 7.36 (dd), $^3J_{HH}$ = 15.1 Hz, $^4J_{PH}$ = 1.7 Hz]. The ^{13}C NMR spectrum shows a doublet at low field for the (Ru=C) carbon nucleus [δ ppm: 301.19 (d, $^2J_{PC}$ = 20.9 Hz)]. These data are analogous to those found for the related complex [Ru=C(OMe)CH=CHPh(Cl)(PMe_3)(η^6-C_5Me_6)]PF_6 [3] [δ (Ru=C) = 302.56 ppm (d, $^2J_{PC}$ = 20.3 Hz)].

A nuclear Overhauser effect was observed by irradiation of the Ru=C(OMe) methoxy protons (δ = 4.38 ppm (s)) which led to an increase of 15% of the =CHα signal (δ = 7.36 ppm (dd)), whereas the irradiation at δ = 3.97 ppm (s), under the same conditions, of the arylmethoxy group led only to an increase of 5% of the *ortho* proton signal (δ = 7.76 ppm) and not of the =CH_α and =CH_β signals. These observations are consistent with the privileged *s-cis* conformation of the carbene ligand. Such a conformation was also observed for monosubstituted alkenylcarbene–ruthenium complexes [3].



Scheme 2.

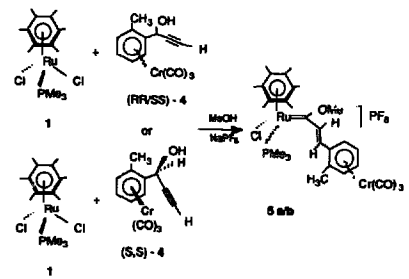
The same reaction has been performed at room temperature but with the enantiomeric pure alcohol (S)-HC≡C–CHOH–(2-MeO–C_6H_4) (S)-**2** which was already prepared by addition of ethynylmagnesium bromide to the complexed aldehyde (+)-(1S)-(2-MeO–C_6H_4CHO)$Cr(CO)_3$, followed by photochemical decomplexation [4,5]. Complex **1** and $NaPF_6$ reacted with (S)-**2** to afford the same alkenyl carbene complex **3*** which was isolated in similar yield (70%) (Scheme 2). The study of the optical rotation of the latter complex **3*** showed no optical activity at all. The absence of an enantiomeric excess in the synthesis of **3*** from (S)-**2** was also supported by the NMR spectra of **3*** with an optically active europium(III) salt. Thus, on the basis that stable stereochemistry had previously been observed [6] for chiral arene ruthenium(II) complexes, this

observation indicates that the homochiral alcohol (S)-2 leads to the *racemic* chiral complex 3 without transfer of chirality. This absence of stereoselectivity may be due to a fast equilibrium between the 16-electron species IV and its alkyne adducts Va, Vb with respect to the dehydration rate of the latter to generate the allenylidene II (Scheme 1).

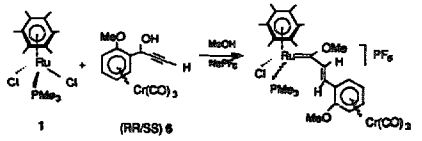
The activation of a diastereoisomeric prop-2-yn-1-ol, having both a planar chirality and a stereogenic C_1 carbon by a ruthenium(II) complex, as an attempt to generate a heterobimetallic allenylidene intermediate [1–3,7], was never undertaken from an organometallic 1-aryl propargylic alcohol derivative. Thus we examined the activation of $Cr(CO)_3$-complexed alkynols 4 and 6. The complex $RuCl_2(PMe_3)(\eta^6\text{-}C_6Me_6)$ 1 was reacted with an excess (1.5 equiv.) of the diastereoisomer (RR/SS) 4 [4], in the presence of $NaPF_6$ and methanol, at room temperature. Complex 1 was completely converted after 48 h into two violet mixed (Cr, Ru) metal containing alkenyl carbene complexes obtained as a mixture 5a/b (55:45) in 84% yield.

The reaction of complex 1 with one equivalent of the optically pure diastereoisomer (S,S)-4 and of $NaPF_6$ in methanol was attempted. The reaction was stopped before completion, after 23 h at room temperature, the resulting complex mixture contained 17% of the starting product 1, 30% of 5b and 53% of 5a. The 5a/b diastereoisomers are in the ratio 55:45, but could not be separated (Scheme 3). Thus, the coordination of the chiral alkyne 4 to the ruthenium shows a slight preference for one face of the 16-electron ruthenium intermediate (Scheme 1), although this asymmetric induction is low.

Under similar conditions the activation of the *racemic* prop-2-yn-1-ol $HC{\equiv}CCHOH(\eta^6\text{-}(2\text{-}MeO\text{-}C_6H_4)Cr(CO)_3$ 6 [4] occurred. The activation of 6 by complex 1 in methanol led to a mixture (79%) of two violet carbene complexes 7a/b in almost equimolecular amount (49.5:50.5) and analogous to 5a/b (Scheme 4).



Scheme 3.



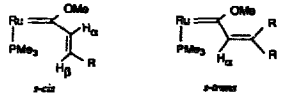
Scheme 4.

The NMR spectra of the mixture of complexes 5 showed the presence of two isomers a/b in the ratio 55:45. Two singlets were shown in ^{31}P NMR [δ ppm = 11.26 (a) and 11.95 (b)]. The ^1H NMR spectrum showed two singlets for the (MeO) protons [δ ppm = 4.40 (a) and 4.39 (b)] and two sets of AB systems for two *trans*-CH=CH– groups [CH=CH–C(OMe)=Ru: δ ppm 7.05 (a, $^3J_{HH}$ = 14.8 Hz) and 7.03 (b, $^3J_{HH}$ = 15.6 Hz)].

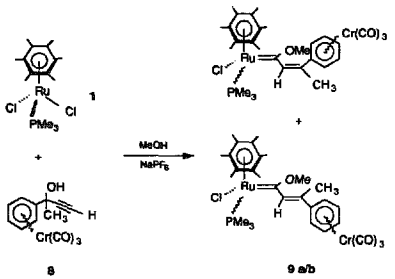
It was shown previously by Le Bozec and coworkers [3] that for related alkenyl carbene complexes $[(C_6Me_6)(PMe_3)ClRu{=}C(OMe)CH{=}CR^1R^2]PF_6$ the *s-cis* conformation was favoured for monosubstituted derivatives (CR^1R^2 = CHR), whereas with disubstituted compounds (CR^1R^2 = CPh_2) the *s-trans* conformation was observed (Scheme 5). The ^{31}P chemical shift for the PMe_3 group was observed in the range δ 5–8 ppm for the latter and δ 12–14 ppm for the former. Thus, on the basis of this observation, the ^{31}P NMR of 5a/b suggested that both isomers adopted the favoured *s-cis* conformation [δ ppm: 11.95 and 11.26].

To support this hypothesis in the case of alkenyl carbene containing arene–$Cr(CO)_3$ as one R group, the synthesis of a *gem* disubstituted ethylidenylcarbene was undertaken in order to check whether the *s-trans* conformation was generated and could be observed by ^{31}P NMR. The reaction of the precursor 1 with $HC{\equiv}C\text{-}C(OH)(Me)(\eta^6\text{-}C_6H_5Cr(CO)_3)$ 8 in the presence of $NaPF_6$ and methanol led to the formation of a mixture of two deep red alkenyl carbene complexes 9a/b in the ratio 64:36 (Scheme 6). The ^{31}P NMR showed two singlets at δ ppm = 8.41 (a) and 7.75 (b) that were consistent with the *s-trans* conformation already observed for other disubstituted derivatives [3].

These data support the idea that arene tricarbonylchromium containing ethylydenyl complexes 5a/b retain the *s-cis* conformation, as do their chromium free counterparts. However, no information was given



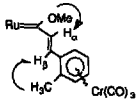
Scheme 5.



Scheme 6.

on the relative conformation of the ruthenium moiety and the (*o*-MeC_6H_4)$Cr(CO)_3$ groups of **5**. A nuclear Overhauser effect study of complexes **5** was performed in order to observe on which H_α or H_β proton signal the irradiation of the methoxy protons could be reflected. The irradiation of the OMe signal at δ = 4.40 ppm (**5a**) led to an increase of 11% of the H_α signal (δ = 7.05 ppm) and not of the H_β signal. Analogously, the irradiation of the OMe signal at δ = 4.39 ppm (**5b**) led to an increase of 11% of the H_α signal (δ = 7.03 ppm) and not of the H_β signal (Scheme 7). The irradiation of the *ortho*-methyl group, linked to the (arene)$Cr(CO)_3$ group of the same complex **5**, led to an increase of the H_β signal only: the irradiation of the signal at δ 2.46 ppm (**5a**) or δ = 2.47 ppm (**5b**) led to an increase of 15% of the signal at δ 8.49 ppm (H_β, $H_{\beta'}$) without affecting the H_α, $H_{\alpha'}$ signals (Scheme 7). These observations are consistent not only with a preferred conformation of the *ortho*-methyl group close to the H_β atom but also with a coplanarity of the arene and the alkenylcarbene moiety as a rotation around the C_β–C(aryl) bond would lead to an increase of both H_α and H_β signals. Moreover, these data are also in line with the preferred conformation generally adopted by *ortho*-substituted styrene chromiumtricarbonyl complexes [8].

The above NMR and NOE studies are consistent with the structure for **5a** and **5b** as shown in Scheme 3. From the *racemic* diastereoisomer **4**, the two diastereoisomers **5a/b** are produced: they differ only by the relative position of the PMe_3 ligand with respect to the $Cr(CO)_3$ group. However, it is not possible at this stage to identify them by spectroscopy.



Scheme 7.

3. Conclusion

The activation of the chiral, organometallic pro-2-yn-1-ols HC≡CC(R^1)OH(η^6-(2-R-C_6H_4)$Cr(CO)_3$ by $RuCl_2(PMe_3)(\eta^6$-$C_6Me_6)$ **1** takes place with low stereoselectivity in the chloride substitution at the ruthenium center by the alkyne, but constitutes a convenient route to new bimetallic *trans*-alkenylcarbene–ruthenium derivatives containing an aryl–$Cr(CO)_3$ complexed ligand with the *s-cis* and *s-trans* conformation according to the nature of the R^1 group.

4. Experimental

4.1. Synthesis of [(η^6-C_6Me_6)Cl(PMe_3)-Ru=C(OMe)CH=CH(*o*-MeO-C_6H_4)]PF_6 3

4.1.1. From the racemic HC≡CCHOH-(*o*-MeO-C_6H_4) 2

In a Schlenk tube containing 0.61 mmol (0.25 g) of $RuCl_2(PMe_3)(\eta^6$-$C_6Me_6)$ **1** and 0.61 mmol (0.10 g) of $NaPF_6$ were successively introduced 10 ml of degassed methanol and 0.62 mmol (0.10 g) of HC≡C–CHOH–(*o*-MeO–C_6H_4) [4]. The solution color changed from red to dark yellow. After 3 h stirring at room temperature, the solvent was removed under vacuum and the solid was washed with diethyl ether. The complex was dissolved in 10 ml of CH_2Cl_2 and the solution was filtrated in order to eliminate NaCl. The obtained complex was dissolved in 5 ml of CH_2Cl_2 and slowly, in order to maintain two phases, 15 ml of diethylether and 15 ml of *n*-pentane were added. 30 mg (71%) of complex **3** was obtained.

IR (KBr, ν cm^{-1}): 1587 (s, $\nu_{C=C}$), 839 (s, ν_{P-F}). ^1H NMR (CD_2Cl_2, 297 K, 300.134 MHz): δ ppm 8.68 (d, 1H, ≡C*H*–C_6H_4–OMe, $^3J_{(H,H)}$ = 15.1 Hz), 7.76 (dd, $^3J_{(H,H)}$ = 7.9 Hz, $^4J_{(H,H)}$ = 1.6 Hz, 1H, C_6H_4), 7.59 (td, $^3J_{(H,H)}$ = 7.5 Hz, $^4J_{(H,H)}$ = 1.7 Hz, 1H, C_6H_4), 7.36 (dd, $^3J_{(H,H)}$ = 15.1 Hz, $^4J_{(P,H)}$ = 1.3 Hz, 1H, HC=), 7.05 (m, 2H, C_6H_4), 4.38 (s, 3H, Ru=C–OMe), 3.97 (s, 3H, OMe), 2.06 (d, $^4J_{(P,H)}$ = 0.5 Hz, 18H, C_6Me_6), 1.36 (d, $^2J_{(P,H)}$ = 10.7 Hz, 9H, PMe_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 297 K, 121.496 MHz): δ ppm 11.73 (s, PMe_3), −143.49 (sept, $^1J_{(P,F)}$ = 710 Hz, PF_6^-). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 297 K, 75.469 MHz): δ ppm 301.19 (d, $^2J_{(P,C)}$ = 20.9 Hz, Ru=C), 165.13 (s, =*C*H–C_6H_4–OMe), 160.76 (s, Co(MeO–*C*)), 136.21, 130.67 (s, C_6H_4), 125.68 (s, Ru=C–*C*), 123.96 (s, Ci (C_6H_4)), 121.75, 112.61 (s, (C_6H_4)), 105.83 (d, $^2J_{(P,C)}$ = 2.6 Hz, C_6Me_6), 64.62 (d, $^4J_{(P,C)}$ = 1.4 Hz, Ru=C–O*Me*), 56.36 (s, OMe), 16.39 (s, C_6Me_6), 16.00 (d, $^1J_{(P,C)}$ = 34.9 Hz, PMe_3). ^{13}C

NMR (CD_2Cl_2, 297 K, 75.469 MHz): δ ppm 165.16 (d, $^1J_{(C,H)}$ = 160 Hz, =CH–C_6H_4–OMe), 136.21 (dd, $^1J_{(C,H)}$ = 161.5 Hz, $^2J_{(C,H)}$ = 8.5 Hz, Co or Cm (C_6H_4)), 130.66 (dt, $^1J_{(C,H)}$ = 159.2 Hz, $^2J_{(C,H)}$ = 6.8 Hz, Cp (C_6H_4)), 125.68 (d, $^1J_{(C,H)}$ = 155 Hz, Ru=C–CH), 121.76 (dd, $^1J_{(C,H)}$ = 164 Hz, $^2J_{(C,H)}$ = 7.6 Hz, Co or Cm (C_6H_4)), 112.60 (dd, $^1J_{(C,H)}$ = 160.7 Hz, $^2J_{(C,H)}$ = 7.7 Hz, Co or Cm (C_6H_4)), 64.63 (q, $^1J_{(C,H)}$ = 149 Hz, Ru=C–O*Me*), 56.36 (q, $^1J_{(C,H)}$ = 145.5 Hz, OMe), 16.39 (q, $^1J_{(C,H)}$ = 128.8 Hz, C_6Me_6), 16.00 (qdm, $^1J_{(C,H)}$ = 130.3 Hz, $^1J_{(P,C)}$ = 34.8 Hz, PMe_3). Anal. Found: C, 43.78; H, 5.57; Cl, 7.10. $C_{26}H_{39}ClF_6O_2P_2Ru \cdot 0.25CH_2Cl_2$ Calc.: C, 43.96; H, 5.55; Cl, 7.41%.

4.1.2. From the optically pure (S)-HC≡C–CHOH–(o-MeO-C_6H_4) (S)-2

The above procedure was applied to 0.48 mmol (0.20 g) of **1**, 0.48 mmol (0.08 g) of $NaPF_6$, 10 ml of methanol and 0.52 mmol of (S)-**2** [4] [$[\alpha]_D$ = +25.3° [C = 0.3($CHCl_3$)], *ee* 98%]. 24 mg of **3*** (70%) was obtained. Complex **3*** was identified as the previous one by NMR spectroscopy.

4.2. [(η⁶-C_6Me_6)Cl(PMe_3)Ru(=C(OMe)CH=CH–(η⁶-o-MeC_6H_4)Cr($CO)_3$]PF_6 5

4.2.1. Method A: from the racemic diastereoisomer 4

In a Schlenk tube were introduced successively 165 mg (0.401 mmol) of $RuCl_2(PMe_3)(C_6Me_6)$ **1**, 87 mg (0.52 mmol) of $NaPF_6$ and 170 mg (0.602 mmol) of HC≡CCH(OH)–(η⁶-o-MeC_6H_4)Cr($CO)_3$ **4** [4] in 15 ml of methanol. The mixture was stirred for 48 h at room temperature and in the dark, and thus led to the complete transformation of **1**. After solvent removal under vacuum the solid was washed twice with 10 ml of diethylether and dissolved in 15 ml of dichloromethane. After filtration, the addition of diethylether led to the precipitation of a violet solid. 274 mg (84%) of the violet diastereoisomer complexes **5a/b** was obtained. An attempt to separate them by recrystallisation was not successful.

4.2.2. Method B: from the optically pure 4

According to the above procedure the reaction was performed with 128 mg (0.313 mmol) of **1**, 52 mg (0.314 mmol) of $NaPF_6$ and 89 mg (0.315 mmol) of the pure optically active diastereoisomer HC≡CCH(OH)–(η⁶-o-MeC_6H_4)Cr($CO)_3$ **4** [4], and 15 ml of degassed methanol. The mixture was stirred for 23 h at room temperature and in the dark. After filtration, the addition of diethylether led to the precipitation of a violet solid (180 mg). The NMR spectrum showed the presence of 17% of the starting product **1** and 83% of complexes **5** (30% of **5b** and 53% of **5a**).

IR (KBr, ν cm^{-1}): 1968, 1897 (s, ν_{CO}), 1581 (m, $\nu_{C=C}$), 840 (s, ν_{PF}). ^1H NMR (CD_2Cl_2, 300.133 MHz, 297 K): δ ppm (H′, P′ correspond to the major product **a**, **a/b** (55:45%)) 8.49 (mt, 2H, =C*H*(C_6H_4(Me), 7.05 (d, $^3J_{HH}$ = 14.8 Hz, 1H, =CH′), 7.03 (d, $^3J_{HH}$ = 15.59 Hz, 1H, =CH_α), 6.21 (d, J_o = 6.8 Hz, 1H′$_{arom}$), 6.17 (d, J_o = 6.5 Hz, 1H$_{arom}$), 5.93 (t, J_o = 6.8 Hz, 1H′$_{arom}$), 5.82 (t, J_o = 6.5 Hz, 1H$_{arom}$), 5.36–5.21 (m, 4H, H$_{arom}$), 4.40 (s, 3H, OMe′), 4.39 (s, 3H, OMe), 2.47 (s, 3H, Me), 2.46 (s, 3H, Me′), 2.09 (s, 18H, C_6Me_6), 2.05 (s, 18H, C_6Me_6′), 1.36 (d, $^2J_{PH}$ = 10.7 Hz, 9H, PMe_3), 1.35 (d, $^2J_{PH}$ = 10.7 Hz, 9H, PMe_3′). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.496 MHz, 297 K): δ ppm 11.95 (s, PMe_3), 11.26 (s, P′Me_3), −143.90 (sept, $^1J_{PF}$ = 710 Hz).

4.3. [(η⁶-C_6Me_6)Cl(PMe_3)Ru(=C(OMe)CH=CH–(η⁶-o-$MeOC_6H_4$)Cr($CO)_3$]PF_6 7

According to the above procedure leading to **5** the reaction of **1** (180 mg, 0.439 mmol) with 209 mg (0.702 mmol) of HC≡C–CHOH(η⁶-o-$MeOC_6H_4$–)Cr($CO)_3$ **6** [4] and $NaPF_6$ (95 mg, 0.57 mmol) led after 48 h at room temperature to 287 mg (79%) of a violet powder identified as a mixture of complexes **7a/b**. IR (KBr, ν cm^{-1}): 1964, 1894 (s, ν_{CO}), 1576 (m, $\nu_{C=C}$), 840 (s, ν_{PF}). ^1H NMR (CD_2Cl_2, 300.133 MHz, 297 K): δ ppm (H′, P′ correspond to the major product **a**, **a/b** (50.5:49.5%)) 8.44 (d, $^3J_{HH}$ = 15.1 Hz), 1 H, =C*H*Ph(Cr($CO)_3$)), 8.26 (d, $^3J_{H'H'}$ = 14.8 Hz, 1H, =C*H*′Ph(Cr($CO)_3$)), 7.10 (d, $^3J_{H'H'}$ = 14.8 Hz, 1H, =CH′), 6.97 (d, $^3J_{HH}$ = 15.1 Hz, 1H, =CH), 6.27 (d, J_o = 6.6 Hz, 1H$_{arom}$), 6.09 (d, J_o = 6.2 Hz, 1H$_{arom}$), 6.04 (t, J_o = 6.7 Hz, 1H′$_{arom}$), 5.98 (t, J_o = 6.6 Hz, 1H$_{arom}$), 5.33–5.17 (m, 3H, H$_{arom}$), 5.09 (t, J_o = 6.2 Hz, 1H$_{arom}$), 4.37 (s, 3H, =OMe′), 4.34 (s, 3H, =OMe), 3.92 (s, 3H, OMe′$_{arom}$), 3.87 (s, 3H, OMe$_{arom}$), 2.08 (s, 18H, C_6Me_6′), 2.06 (s, 18H, C_6Me_6), 1.36 (d, $^2J_{PH}$ = 10.7 Hz, 9H, PMe_3′), 1.34 (d, $^2J_{PH}$ = 10.7 Hz, 9H, PMe_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.496 MHz, 297 K): δ ppm 11.45 (s, P′Me_3), 10.95 (s, PMe_3), −143.91 (sept, $^1J_{PF}$ = 711 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2 (15:85), 121.496 MHz, 193 K): δ ppm 14.66 (s, P′Me_3), 14.0 (s, PMe_3).

4.4. [(η⁶-C_6Me_6)Cl(PMe_3)Ru(=C(OMe)CH=C(Me)–(η⁶-C_6H_5)Cr($CO)_3$]PF_6 9

According to the above general procedure complex **1** (116 mg, 0.283 mmol) and $NaPF_6$ (51 mg, 0.311 mmol) were reacted with the organometallic prop-2-yn-1-ol HC≡C–C(OH)Me(η⁶-C_6H_5Cr($CO)_3$ **8** in 15 ml of methanol. After 48 h of the reaction at room temperature 179 mg (78%) of a deep red powder of complexes **9a/b** was obtained.

IR (KBr, ν cm^{-1}): 1966, 1890 (s, ν_{CO}), 1560 (m, $\nu_{C=C}$), 840 (s, ν_{PF}). ^1H NMR (CD_2Cl_2, 300.133 MHz, 297 K): δ ppm (H′, P′ correspond to the major product

a, a/b (64:36%)) 7.28 (s, 1H, =CH), 6.88 (s, 1H, =CH'), 6.18–6.08 (m, 2H, H_{arom}), 5.80–5.54 (m, 4H, H_{arom}), 5.42, 5.23 (m, 4H, H_{arom}), 4.63 (s, 3H, =OMe), 4.22 (s, 3H, =OMe'), 2.29 (s, 3H, Me), 2.12 (s, 18H, C_5Me_6), 2.11 (s, 18H, $C_5Me'_6$), 2.05 (s, 3H, Me'), 1.42 (d, $^2J_{PH}$ = 10.2 Hz, 9H, PMe_3), 1.12 (d, $^2J_{PH}$ = 9.31 Hz, 9H, PMe'_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.496 MHz, 297 K): δ ppm 8.41 (s, $P'Me_3$), 7.75 (s, PMe_3), −143.94 (sept, $^1J_{PF}$ = 711 Hz). Anal. Found: C, 42.07; H, 4.87. $C_{29}H_{39}ClCrF_6O_4P_2Ru$ Calc.: C, 42.68; H, 4.82%.

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References

[1] J.P. Selegue, *Organometallics, 1* (1982) 217.
[2] D. Touchard, N. Pirio and P.H. Dixneuf, *Organometallics, 14* (1995) 4920.
[3] D. Pilette, K. Ouzzine, H. Le Bozec, P.H. Dixneuf, C.E.F. Rickard and W.R. Roper, *Organometallics, 11* (1992) 809.
[4] C. Baldoli, P. Del Buttero, E. Licandro, S. Maiorana, A. Papagni and M. Torchio, *Tetrahedron Lett., 34* (1993) 7943.
[5] E. Miano, *Thesis of Laurea*, University of Milano, 1993–4.
[6] H. Le Bozec, D. Touchard and P.H. Dixneuf, *Adv. Organomet. Chem., 29* (1989) 163; H. Brunner and R. Gastinger, *J. Chem. Soc., Chem. Commun.*, (1977) 488; *J. Organomet. Chem., 145* (1978) 365; P. Pertici, P. Salvadori, A. Biasci, G. Vitulli, M.A. Bennett and L.A.P. Kane-Maguire, *J. Chem. Soc., Dalton Trans.*, (1983).
[7] D. Touchard, N. Pirio, L. Toupet, M. Fettouhi, L. Ouahab and P.H. Dixneuf, *Organometallics, 14* (1995) 5263.
[8] C. Baldoli, P. Del Buttero, S. Maiorana, G. Zecchi and M. Moret, *Tetrahedron Lett., 34* (1993) 2529.