ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 601 (2000) 78–86

Journal of Organometallic Chemistry

Functionalised alkenylcarbene metal complexes (M = Ru, W, Cr) by activation of propargyl alcohol derivatives

Karine Ulrich, Emmanuel Porhiel, Vincent Péron, Vincent Ferrand, Hubert Le Bozec *

UMR 6509 CNRS-Université de Rennes 1, Organométalliques et Catalyse: Chimie et Electrochimie Moléculaire, Campus de Beaulieu, F-35042 Rennes, Cedex, France

Received 15 December 1999; accepted 19 January 2000

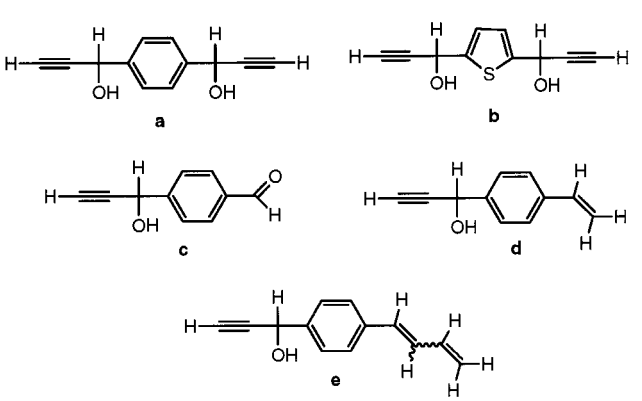
Abstract

The reaction of arene ruthenium(II) complexes $[Ru(\eta^6\text{-}C_6Me_4R_2)(PMe_3)Cl_2]$ (**1**, R = Me; **1′**, R = H) with propargyl alcohol derivatives HC≡C(H)(OH)(*p*-C_6H_4–X) (**a**, X = HC≡C(H)(OH); **c**, X = CHO; **d**, X = CH=CH_2; **e**, X = CH=CH–CH=CH_2) and methanol gives the (methoxy)-alkenylcarbene ruthenium complexes $[Ru(\eta^6\text{-}C_6Me_4R_2)(PMe_3)(Cl)$ (=C(OMe)(CH=CH-*p*-C_6H_4–X)][PF_6] (**2a**) and (**2′c**–**e**). Similarly, the half-sandwich carbene complexes $[Ru(\eta^5\text{-}C_5H_5)(CO)(PPh_3)$(=C(OMe)(CH=CH-*p*-$C_6H_4$–X)][$BF_4$] (**4a** and **4d**) are obtained from $[Ru(\eta^5\text{-}C_5H_5)(CO)(PPh_3)(Cl)]$ (**3**) and propargyl alcohol derivatives **a** and **d**, respectively. Treatment of $M(CO)_5(THF)$ (M = W, Cr) with **a** and HC≡C(H)(OH)–C_4H_2S–(OH)(H)C≡CH (**b**) yields the monometallic complexes $(CO)_5M$=C(OMe)(=C(OMe)(CH=CH–*Ar*–(OH)(H)C≡CH)] (**5a**) (M = W; –*Ar*– = –C_6H_4–), **5b** (M = W; –*Ar*– = –C_4H_2S–), and **7a** (M = Cr; –*Ar*– = –C_6H_4–) as the major products, and the bimetallic complexes $(CO)_5$W=C(OMe)CH=CH–*Ar*–CH=CH(OMe)C=W$(CO)_5$ (**6a**) and (**6b**) as the minor products. Finally, the reaction of **5a** and **5b** with amines (^{i}PrNH_2, Me_2NH, Et_2NH), and diamines such as ethylene diamine and piperazine produces the expected amino alkenyl–tungsten complexes **9a**–**13a** and **9b** in high yields. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Tungsten; Chromium; Alkenylcarbene; Alkynols

1. Introduction

Propargyl alcohol derivatives are a useful class of compounds that can be readily activated by transition metals and allow the preparation of a variety of multiple metal–carbon bond species such as vinylidene, allenylidene and alkenylcarbene complexes. Thus, a wide range of stable allenylidene complexes of Group 8 metals has been prepared from various substituted 2-propyn-1-ols and electron-rich and/or bulky metal complexes [1]. On the other hand, the use of more electron-poor complexes generates very reactive electrophilic allenylidene intermediates, which can be trapped by addition of nucleophiles, such as alcohols. This reactivity has offered an easy synthetic route to (alkoxy)-alkenylcarbene-containing organometallic fragments such as $[Ru(\eta^6\text{-}C_6R_6)(PR_3)(Cl)]^+$ [2,3], $[Ru(\eta^5\text{-}C_5H_5)(CO)(PPr^i_3)]^+$ [4], $[Ru(\eta^5\text{-}C_9H_7)(dppm)]^+$ [5] and $[M(CO)_5]$ (M = Cr, W) [6,7]. The synthesis of α,β-unsaturated acyl complexes containing the elec-



Scheme 1.

* Corresponding author.

PII: S0022-328X(00)00038-3

trophilic moiety $[Fe(\eta^5\text{-}C_5Me_5)(CO)_2]^+$ has also been recently reported [8]. The success of this stategy to prepare alkenylcarbene complexes has prompted us to examine the generalisation of this procedure by using more sophisticated 2-propyn-1-ols such as **a**–**e** (Scheme 1). This study aims at developing access to new α,β-unsaturated carbene derivatives as building blocks for the elaboration of bimetallic complexes. Here we report (i) the preparation of new propargylic alcohol derivatives, and (ii) the synthesis and characterisation of the corresponding (methoxy)-alkenylcarbene complexes obtained by activation of these alkynols in methanol with the half-sandwich precursors $[Ru(\eta^6\text{-}C_6M_4R_2)(PMe_3)Cl_2]$ (R = Me, H) and $[Ru(\eta^5\text{-}C_5H_5)(CO)(PPh_3)(Cl)]$, and with the chromium and tungsten carbonyl adducts $[M(CO)_5(THF)]$. In addition, we describe the aminolysis reactions of the (methoxy)-alkenylcarbene–tungsten complexes [9].

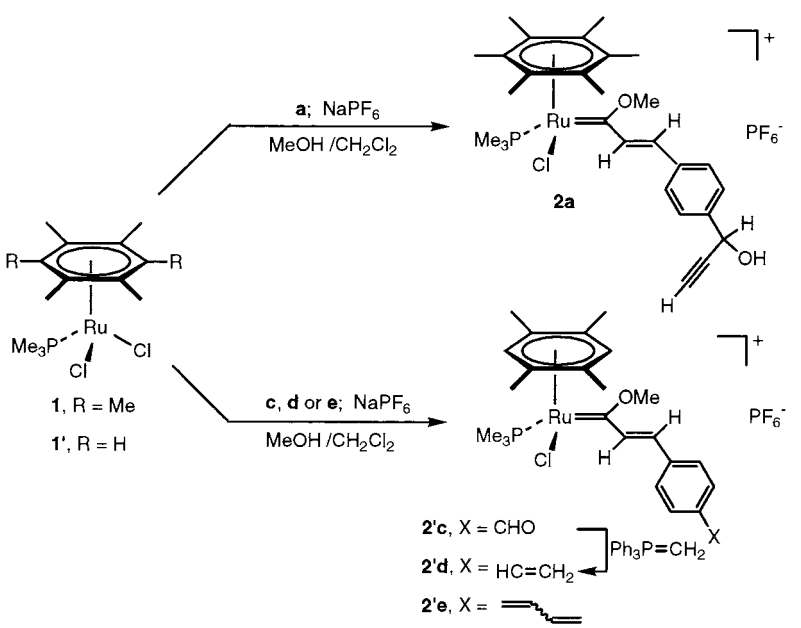
2. Results and discussion

2.1. Synthesis of the propargyl alcohol derivatives

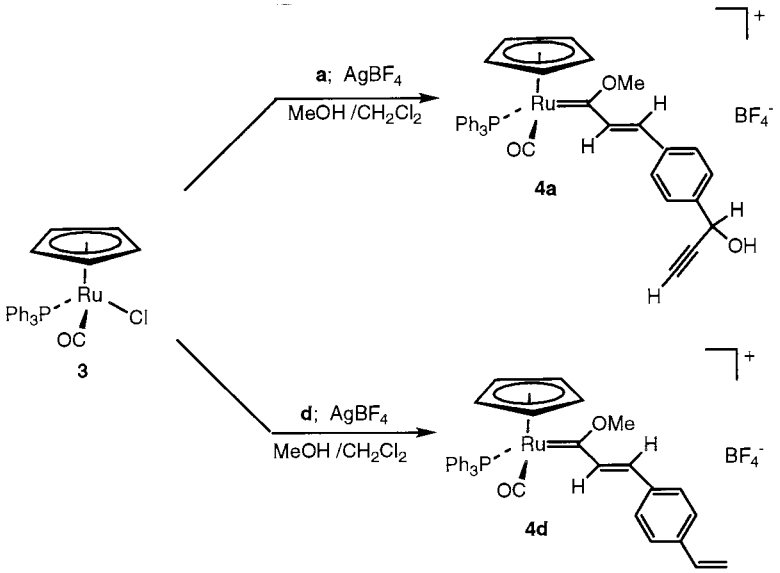
The dialkynol derivatives **a** and **b** were readily prepared in approximately 80% yield upon addition of LiC≡CH (two equivalents) to the corresponding dialdehydes [10]. A two-step procedure was used for the synthesis of **c** in 66% overall yield from terephthaldehyde monodiethyl acetal. The preparation of propargyl alcohol derivatives **d** and **e** was achieved by a Wittig reaction between **c** and the in situ-prepared ylide reagents $Ph_3P{=}CH_2$ and $Ph_3P{=}CH{-}CH{=}CH_2$, respectively (Scheme 1). Compound **e** was obtained as a mixture of *cis*/*trans* isomers (2/3) which could not be separated.

2.2. Synthesis of (methoxy)-alkenylcarbene–ruthenium complexes

Treatment of a methanol–dichloromethane solution of **1** with the dialkynol **a** in the presence of $NaPF_6$ led slowly to a dark-red solution, from which the (methoxy)-alkenylcarbene complex **2a** was isolated as a black powder in 48% yield (Scheme 2). The clean formation of **2a** requires the addition of an excess of **a** (three equivalents) to a dilute solution of **1**, otherwise a stoichiometric reaction gives a mixture of intractable organometallic compounds including **2a** along with the corresponding bimetallic bis-carbene derivative. In a similar way, complexes **2′c**, **2′d** and **2′e** were isolated in good yield (60–75%) from alcohols **c**–**e** and the tetramethylbenzene ruthenium precursor **1′** (Scheme 2). The carbene complex **2′d** was also synthesised by reacting the free aldehyde group in **2′c** with $Ph_3P{=}CH_2$, but could not be fully separated from triphenylphosphine oxide. The complex **2′e**, containing the dienyl substituent $C_6H_4{-}CH{=}CH{-}CH{=}CH_2$ on the alkenylcarbene moiety, was isolated as *cis*/*trans* isomers (≈ 2:3). The spectroscopic properties of **2a** and **2′c**–**e** are similar to those of the previously synthetised arene (methoxy)-alkenylcarbene ruthenium complexes [3] (see Section 3). In particular, the ^{1}H-NMR spectra show, besides the methoxy and aryl resonances, two typical doublets assigned to the C*H* olefinic protons. The high values of the vicinal coupling constants ($^3J_{HH}$ = 15–16 Hz) confirm the *E* configuration of the CH=CH bond. The presence of the carbene ligand is evidenced by the



Scheme 2.



Scheme 3.

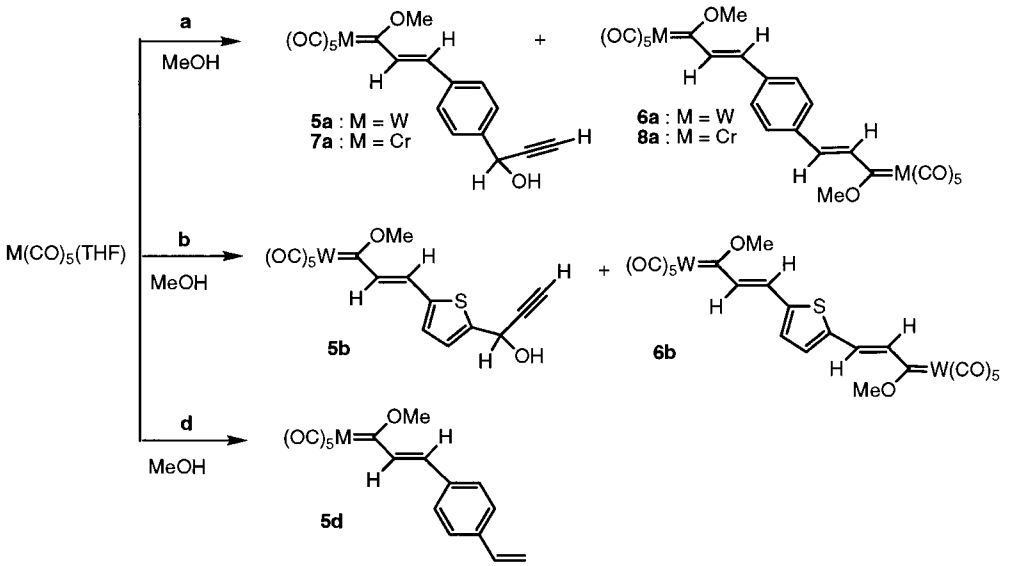
low-field doublet in the ^{13}C-NMR spectra at $\delta \approx 305$ ppm ($^{2}J_{CP} = 19–20$ Hz).

Only one example of a cyclopentadienyl ruthenium complex containing an (alkoxy)-α,β-unsaturated carbene ligand has been previously reported in the literature [4]. This complex was obtained by nucleophilic addition of methanol (or ethanol) to the isolated diphenylallenylidene cations $[Ru(\eta^5\text{-}C_5H_5)(CO)(P^iPr_3)(C{=}C{=}CPh_2]^+$, a behaviour which contrasts with the inertness of the same ligand bonded to the more electron-rich fragment $[Ru(\eta^5\text{-}C_5H_5)(PR_3)_2]^+$ ($PR_3 = PPh_3$, PMe_3) [11,12]. In our case, we used the isoelectronic, readily available $[Ru(\eta^5\text{-}C_5H_5)(CO)(PPh_3)(Cl)]$ (**3**) [13] to prepare the corresponding (methoxy)-alkenylcarbene complexes. Thus, the reaction of **3** with 2-propyn-1-ol derivatives **a** (large excess) and **d** in methanol–dichloromethane, in the presence of $AgBF_4$, gave the expected complexes **4a** and **4d** as orange microcrystalline solids in 74 and 51% yield, respectively (Scheme 3). Both complexes were characterised by spectroscopic means. Typically, the low-field resonances of the carbenic Ru=C appear as broad signals at $\delta \approx 300$ ppm, and the strong vicinal coupling constants ($^{3}J_{HH} = 15.3$ Hz) observed in the ^{1}H-NMR spectra are typical of an *E* configuration for the alkenyl substituents.

2.3. Synthesis of (methoxy)- and (amino)-alkenylcarbene–tungsten and chromium complexes

Treatment of a methanol solution of **a** with the photogenerated $M(CO)_5$·THF adducts (M = W, Cr) afforded a mixture of products, whatever the amount of dialkynol used (1.5–3 equivalents). They were readily separated by chromatographic workup, and the first fraction contained the violet binuclear biscarbene complexes **6a**–**8a** (9–10%), whereas the second fraction gave the red monometallic alkenylcarbene complexes **5a**–**7a** (33–41%) (Scheme 4). Similarly, the propargyl alcohol **b** containing a thienyl bridge afforded the corresponding tungsten carbene and biscarbene derivatives **5b** and **6b** in yields of 33 and 9%, respectively. The methoxy-alkenylcarbene tungsten **5d** was also formed in good yield (60%) under the same reaction conditions from the 2-propyn-1-ol (**d**) (Scheme 4). The spectroscopic data of **5a**,**b**,**d** and **7a** are in accordance with the presence of the (methoxy)-alkenylcarbene moieties, and can be compared with those of the related tungsten and chromium derivatives [6]. Thus, ^{1}H-NMR spectra exhibit typical resonances for the alkenyl fragments with the *E* configuration; the ^{13}C-NMR spectra show two resonances each for the *cis* and *trans* CO ligands, and low-field carbene resonances in the range expected for alkoxy-carbene–tungsten and –chromium complexes [δ(W=C) ≈ 305 ppm and δ(Cr=C) ≈ 335 ppm]. The NMR spectra of the bimetallic complexes are more simple due to their high symmetry; for example, the ^{1}H-NMR spectrum of **6a** exhibits only two doublets for the vinylic protons ($^{3}J_{HH} = 15.5$ Hz), one resonance for the protons of the phenyl bridge and another one for the methoxy protons.

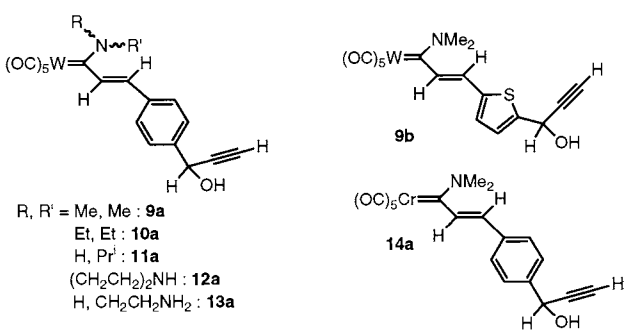
(Methoxy)-carbene–tungsten complexes **5** were easily transformed into the corresponding amino-carbene complexes by aminolysis with secondary and primary amines. Thus, low-temperature treatment of **5a**,**b** with dimethylamine or diethyl amine in diethyl ether afforded quantitatively the (dialkylamino)-alkenylcarbene derivatives **9a**,**b** and **10a** in almost quantitative yield as bright-orange powders (Scheme 5). Upon reacting **5a**



Scheme 4.

with *iso*-propylamine the aminocarbene **11a** was formed as a mixture of *E* and *Z* isomers, which could not be separated by chromatography ($E/Z \approx 3/1$). Finally, the aminolysis route was extended to the high-yield synthesis of the (diamino)-carbene complexes **12a** and **13a** ($E/Z \approx 9/1$) by using piperazine and ethylene diamine, respectively. The ^{1}H- and ^{13}C-NMR data are in good agreement with those previously reported for other (amino)-alkenylcarbene–tungsten complexes [6,14,15]. The protons and carbons of the alkenyl moieties are typically shifted upfield relative to those of the methoxy-carbene precursor **5a**, and the carbene resonances are usually found at $\delta \approx 245$–250 ppm.

In summary, the above results offer a convenient route to a variety of functionalised (alkoxy)- and (amino)-alkenylcarbenes of Group 6 and 8 metal complexes. These monometallic species could be used as building blocks for the preparation of new mixed bimetalllic complexes, for example, by activation of the free propargyl alcohol substituents with another organometallic moiety. We are currently studying the access of such dissymmetric π-conjugated bridged carbene complexes [9].



Scheme 5.

3. Experimental

All manipulations were carried out under an argon atmosphere with Schlenk techniques. Solvents were dried and distilled before use by standard techniques. Complexes (η^6-$C_6Me_4R_2$)$RuCl_2(PMe_3)$ (R = H, Me) [16] and (η^5-C_5H_5)$RuCl(CO)(PPh_3)$ [13] were prepared according to the literature procedure. NMR spectra were recorded on Bruker DPX-200 and AM-300 spectrometers. Infrared spectra were obtained on a Nicolet FTIR spectrometer. High-resolution mass spectra were obtained on Varian MAT 311 and Micromass ZABSpec TOF spectrometers at the CRMPO (University of Rennes, France). Microanalyses were performed by the 'Centre de Microanalyse du CNRS' at Vernaison, France.

3.1. 1,4-[H–C≡C–CH(OH)]C_6H_4 (a)

Acetylene (120 mmol) was dissolved in 140 ml THF at − 78°C. After dropwise addition of ^{n}BuLi (1.6M, 42 ml, 40 mmol), the solution was stirred at − 78°C for 15 min. A solution of terephthaldehyde (4.02 g, 30 mmol) in 30 ml THF was slowly added and the reaction mixture was stirred for 20 min at − 78°C. Saturated aqueous sodium carbonate (20 ml) was then slowly added at room temperature (r.t.). After extraction of the organic phase, the aqueous layer was washed twice with diethyl ether (2×30 ml). The combined organic phases were dried over $MgSO_4$ and the solvent was evaporated in vacuo. Compound **a** was obtained as a white powder in 80% yield (4.468 g). M.p. 110°C. IR (KBr): *v* 3400

(br, OH), 2115 (w, C≡C). ^{1}H-NMR (300.135 MHz, $CDCl_3$): δ 7.55 (s, 4H, C_6H_4–), 5.49 (dd, 2H, $J = 5.9$ and 2.2 Hz, C*H*(OH)), 5.06 (d, 2H, $J = 6.0$ Hz, CH(O*H*)), 3.07 (d, 2H, $J = 2.2$ Hz, ≡C–*H*). Anal. Calc. for $C_{12}H_{10}O_2$ (186.2): C, 77.42; H, 5.38. Found: C, 77.14; H, 5.65%.

3.2. 2,5-[H–C≡C–CH(OH)]C_4H_2S (b)

By using the same procedure, compound **b** was obtained as a brown powder in 86% yield (4.950 g) from thiophene 2,5-carbaldehyde (30 mmol, 4.2 g). IR (KBr): *v* 3340 (br, OH), 2119 (w, C≡C). ^{1}H-NMR (300.135 MHz, $CDCl_3$): δ 6.99 (s, 2H, C_4H_2S–); 5.66 (d, 2H, $J = 2.1$ Hz, C*H*(OH)), 5.31 (br, 2H, CH(O*H*)), 3.14 (d, 2H, $J = 2.1$ Hz, ≡C–*H*). Anal. Calc. for $C_{10}H_8O_2S$ (192.2): C, 62.48; H, 4.19; S, 16.47. Found: C, 62.56; H, 4.25; S, 16.47%.

3.3. H–C≡C–CH(OH)–C_6H_4–CHO (c)

By using the same procedure, H–C≡C–CH(OH)–C_6H_4–$CH(OEt)_2$ was obtained as a yellow oil in 75% yield (2.632 g) from terephthaldehyde monodiethyl acetal (15 mmol, 3.1 g). IR (KBr): *v* 3400 (br, OH), 2115 (w, C≡C). ^{1}H-NMR (300.135 MHz, $CDCl_3$): δ 7.55 (s, 4H, C_6H_4-), 5.45 (s, 1H, C*H*–), 5.35 (d, 1H, $J = 2.3$ Hz, C*H*(OH)), 3.48 (q, 4H, $J = 7.5$ Hz, OCH_2–), 2.57 (d, 1H, $J = 2.3$ Hz, ≡C–*H*), 1.14 (t, 6H, $J = 7.5$ Hz, CH_3).

The propargylic alcohol was then dissolved in 40 ml of dichoromethane, and 40 g of SiO_2 and 8 ml of H_2SO_4 (3%) were added. The reaction mixture was stirred at r.t. overnight. After extraction of the organic phase and evaporation of the solvent in vacuo, the crude oil was chromatographed on silica gel. Elution with dichloromethane gave **c** as a yellow oil in 85% yield (2.100 g). IR (KBr): *v* 3450 (br, OH), 2115 (w, C≡C), 1700 (s,CHO). ^{1}H-NMR (300.135 MHz, $CDCl_3$): δ 9.90 (s, 1H, C*H*O), 7.73 (m, 4H, C_6H_4–), 5.45 (d, 1H, $J = 2.5$ Hz, C*H*(OH)), 2.69 (d, 1H, $J = 2.5$ Hz, ≡C–*H*). HRMS (EI) Calc. for $C_{10}H_8O_2$ $[M]^+$: 160.0524. Found: 160.0522.

3.4. H–C≡C–CH(OH)–C_6H_4–CH=CH_2 (d)

In a Schlenk flask containing 6 mmol of $Ph_3P{=}CH_2$ (obtained from 2.4 g of $Ph_3PCH_3^+I^-$ and 0.67 g of ^{t}BuOK) in 40 ml of THF, was added 900 mg of H–C≡C–CH(OH)–C_6H_4–CHO (**c**) (5.6 mmol). The reaction mixture was stirred at r.t. for 2 h and water (20 ml) was then added. The organic phase was extracted, dried over $MgSO_4$ and the solvent was evaporated in vacuo to give a pale-yellow oil, which was purified by column chromatography on alumina (CH_2Cl_2) to yield **d** in 74% yield (0.890 g). IR (KBr): *v* 3430 (br, OH), 2115 (w, C≡C), 1602 (s, C=C). ^{1}H-NMR (300.135 MHz, $CDCl_3$): δ 7.50 (s, 4H, C_6H_4–), 6.71 (dd, 1H, $J = 17.0$ and 11.0 Hz, C*H*=), 5.73 (dd,1H, $J = 17.0$ and 1.0 Hz, CH_2=), 5.42 (d, 1H, $J = 2.3$ Hz, C*H*(OH)), 5.25 (dd,1H, $J = 11.0$ and 1.0 Hz, CH_2=), 3.1 (d, 1H, $J = 2.3$ Hz, ≡C–*H*). Anal. Calc. for $C_{11}H_{10}O$ (158.2): C, 83.52; H, 6.37. Found: C, 82.07; H, 6.36%.

3.5. H–C≡C–CH(OH)–C_6H_4–CH=CH–CH=CH_2 (e)

The synthesis follows the method outlined for the synthesis of **d**. Compound **e** was obtained as a pale-yellow oil in 72% yield (1.061 g) from H–C≡C–CH(OH)–C_6H_4–CHO (**c**) (1.28 g, 8 mmol) and $Ph_3P{=}CH{-}CH{=}CH_2$, and was used in the next step without further column chromatography purification. IR (KBr): *v* 3450 (br, OH), 2114 (w, C≡C). ^{1}H-NMR (300.135 MHz, $CDCl_3$), trans/cis: δ 7.30 (m, 4H, C_6H_4–), 6.80 (m, 1H, C*H*=), 6.48 (d, 1H, $J = 15.9$ Hz, C*H*=, *trans* isomer), 6.38 (d, 1H, $J = 13.5$ Hz, C*H*=, *cis* isomer), 5.38 (d, 1H, $J = 2.2$ Hz, C*H*(OH)), 5.30 (m, 1H, CH_2=), 5.15 (m, 1H, CH_2=), 2.60 (d, 1H, $J = 2.2$ Hz, ≡C–*H*).

3.6. [(C_6Me_6)(Cl)(PMe_3)Ru=C(OMe)CH=CH–C_6H_4–C(H)(OH)(C≡CH)]PF_6 (2a)

In a Schlenk flask, **1** (1 mmol, 0.41g) was dissolved in 80 ml of a 1:3 methanol–dichloromethane mixture. To the red solution was added sodium hexaflurophosphate (1.2 mmol, 0.2 g) and **a** in excess (3.3 mmol, 0.61 g). After 18 h of stirring at r.t., the solvent was removed under vacuum. The black precipitate was washed with diethyl ether (2 × 20 ml) and then dissolved in 20 ml of dichloromethane. The solution was filtered through a filter paper tipped cannula. Complex **2a** was obtained in 48% yield (0.345 g) by recrystallisation of the precipitate by slow diffusion of ether into a CH_2Cl_2 solution. ^{1}H-NMR (300.135 MHz, acetone-d_6): δ 8.50 (d, 1H, $J = 15.5$ Hz, C*H*=), 7.95 (d, 2H, $J = 8.3$ Hz, C_6H_4–), 7.70 (d, 1H, $J = 15.5$ Hz, C*H*=); 7.60 (d, 2H, $J = 8.3$ Hz, C_6H_4–), 5.60 (s, 1H, C*H*(OH)), 4.70 (s, 3H, OCH_3), 3.15 (d, 1H, $J = 2.3$ Hz, ≡C–*H*), 2.15 (s, 18H, C_6Me_6), 1.50 (d, 1H, $J = 10.9$ Hz, PMe_3). ^{13}C{^{1}H}-NMR (acetone-d_6): δ 303.4 (d, $J = 20.6$ Hz, Ru=*C*), 167.7 (*C*H=), 147.9 (*C*H=), 135.4, 131.2, 128.4, 127.6 (C_6H_4–), 106.8 (C_6Me_6), 84.9 (*C*≡C–H), 75.8 (C≡*C*–H), 65.8 (OCH_3), 63.5 (*C*H(OH)), 16.4 (C_6Me_6), 15.8 (d, $J = 35$ Hz, PMe_3). ^{31}P-NMR (acetone-d_6): δ 17.7 (PMe$_3$), −142.0 (sept, $J = 709$ Hz, PF_6^-). Anal. Calc. for $C_{28}H_{39}ClF_6O_2P_2Ru$ (720): C, 46.66; H, 5.41. Found: C, 46.96; H, 5.35%.

3.7. $[(C_6Me_4H_2)(Cl)(PMe_3)Ru{=}C(OMe)\text{-}CH{=}CH\text{–}C_6H_4\text{–}CHO]PF_6$ (**2′c**)

The synthesis follows the method outlined for the synthesis of **2a**. Complex **2′c** was obtained as brown microcrystals in 60% yield (0.399 g) from **c** (0.50 g, 3 mmol), **1′** (0.38 g, 1 mmol) and $NaPF_6$ (0,50g, 3 mmol). IR (KBr): *ν* 1700 (s, C=O). ^{1}H-NMR (300.135 MHz, CD_2Cl_2): *δ* 10.05 (s, 1H, C*H*O), 8.52 (d, 1H, *J* = 15.1 Hz, C*H*=), 7.92 (s, 4H, C_6H_4–), 7.43 (d, 1H, *J* = 15.1 Hz, C*H*=), 5.85 (s, 2H, $C_6H_2Me_4$), 4.50 (s, 3H, OCH_3), 2.10 (s, 6H, $C_6H_2Me_4$), 1.96 (s, 6H, $C_6H_2Me_4$), 1.50 (d, 1H, *J* = 11.0 Hz, PMe_3). ^{13}C{^{1}H}-NMR (CD_2Cl_2): *δ* 302.8 (d, *J* = 19.1 Hz, Ru=*C*), 139.9 (*C*H=), 139.3 (*C*H=), 131.4, 131.0, 130.8 (C_6H_4–), 106.9, 106.8, 99.8, 99.7 ($C_6Me_4H_2$), 66.3 (O*C*H_3), 17.4 (d, *J* = 29 Hz, PMe_3), 17.1 ($C_6Me_4H_2$). ^{31}P-NMR (acetone-d_6): *δ* 13.7 (*P*Me_3). HRMS (FAB$^+$) Calc. for $C_{24}H_{33}O_2PClRu$ $[M-PF_6]^+$: 521.0954. Found: 521.0959.

3.8. $[(C_6Me_4H_2)(Cl)(PMe_3)Ru{=}C(OMe)\text{-}CH{=}CH\text{–}C_6H_4\text{–}CH{=}CH_2]PF_6$ (**2′d**)

The synthesis follows the method outlined for the synthesis of **2a**. Complex **2′d** was obtained as black microcrystals in 75% yield (0.510 g) from **c** (0.32 g, 2 mmol), **1′** (0.38 g, 1 mmol) and $NaPF_6$ (0,17g, 1.1 mmol). ^{1}H-NMR (300.135 MHz, acetone-d_6): *δ* 8.15 (d, 1H, *J* = 14.9 Hz, C*H*=), 7.95 (d, 2H, *J* = 8.4 Hz, C_6H_4–), 7.80 (d, 1H, *J* = 14.9 Hz, C*H*=), 7.65 (d, 2H, *J* = 8.4 Hz, C_6H_4–), 6.85 (dd, 1H, *J* = 17.5 and 10.0 Hz, C*H*=), 6.35 (s, 2H, $C_6H_2Me_4$), 6.05 (d, 1H, *J* = 17.5 Hz, CH_2=), 5.50 (d, 1H, *J* = 11.0 Hz, CH_2=), 4.70 (s, 3H, OCH_3), 2.20 (s, 6H, $C_6H_2Me_4$), 2.0 (s, 6H, $C_6H_2Me_4$), 1.55 (d, 1H, *J* = 11.3 Hz, PMe_3). ^{13}C{^{1}H}-NMR (CD_2Cl_2): *δ* 301.1 (d, *J* = 19.1 Hz, Ru=*C*), 170.0 (*C*H=), 143.0 (*C*H=), 136.0, 134.0, 131.0 (C_6H_4–), 117.0 (*C*H_2=), 107.1 ($C_6Me_4H_2$), 65.0 (O*C*H_3), 17.4 ($C_6Me_4H_2$), 17.0 (d, *J* = 35 Hz, PMe_3). ^{31}P-NMR (acetone-d_6): *δ* 15.3 (*P*Me_3). Anal. Calc. for $C_{25}H_{35}ClF_6O_2P_2Ru$ (680): C, 45.22; H, 5.31; P, 9.33. Found: C, 44.92; H, 5.32; P, 9.44%.

3.9. $[(C_6Me_4H_2)(Cl)(PMe_3)Ru{=}C(OMe)\text{-}CH{=}CH\text{–}C_6H_4\text{–}CH{=}CH\text{–}CH{=}CH_2]PF_6$ (**2′e**)

The synthesis follows the method outlined for the synthesis of **2a**. Complex **2′e** was obtained as black microcrystals in 73% yield (0.515 g) from **c** (0.37 g, 2 mmol), **1′** (0.38 g, 1 mmol) and $NaPF_6$ (0,17g, 1.1 mmol). ^{1}H-NMR (300.135 MHz, CD_2Cl_2): *δ trans* 8.58 (d, 1H, *J* = 14.8 Hz, C*H*=), 7.77 (d, 2H, *J* = 8.4 Hz, C_6H_4–), 7.54 (d, 2H, *J* = 8.4 Hz, C_6H_4–), 7.40 (d, 1H, *J* = 14.8 Hz, C*H*=), 7.0 (dd, 1H, *J* = 15.7 and 10.1 Hz, C*H*=), 6.60 (d, 1H, *J* = 15.7 Hz, C*H*=), 6.52 (dd, 1H, *J* = 14.1 and 10.5 Hz, C*H*=), 5.79 (s, 2H, $C_6H_2Me_4$), 5.47 (m, 1H, CH_2=), 5.27 (m, 1H, CH_2=), 4.43 (s, 3H, OCH_3), 2.05 (s, 6H, $C_6H_2Me_4$), 1.89 (s, 6H, $C_6H_2Me_4$), 1.48 (d, 1H, *J* = 10.9 Hz, PMe_3); *cis* 8.58 (d, 1H, *J* = 14.8 Hz, C*H*=), 7.78 (d, 2H, *J* = 8.3 Hz, C_6H_4–), 7.47 (d, 2H, *J* = 8.4 Hz, C_6H_4–), 7.40 (d, 1H, *J* = 14.8 Hz, C*H*=), 6.90 (m, 1H, C*H*=), 6.45 (m, C*H*=), 6.41 (d, 1H, *J* = 9.9 Hz, C*H*=); 5.70 (s, 2H, $C_6H_2Me_4$), 5.50 (m, 1H, CH_2=), 5.33 (m, 1H, CH_2=), 4.45 (s, 3H, OCH_3), 2.05 (s, 6H, $C_6H_2Me_4$), 1.89 (s, 6H, $C_6H_2Me_4$), 1.48 (d, 1H, *J* = 10.9 Hz, PMe_3). ^{31}P-NMR (acetone-d_6): *δ* 13.5 (*P*Me_3). Anal. Calc. for $C_{27}H_{37}ClF_6O_2P_2Ru$ (706.05): C, 46.69; H, 5.33. Found: C, 46.89; H, 5.30%.

3.10. $[(C_5H_5)(CO)(PPh_3)Ru{=}C(OMe)\text{-}CH{=}CH\text{–}C_6H_4\text{–}C(H)(OH)(C{\equiv}CH)]BF_4$ (**4a**)

In a Schlenk flask, **3** (1 mmol, 0.49 g) was dissolved in 120 ml of a 1:2 methanol–dichloromethane mixture. To the orange solution was added silver tetrafluroborate (1.1 mmol, 0.21 g). After 1 h of stirring at r.t., an excess of **a** (3 mmol, 0.56 g) was added and the reaction mixture was stirred overnight. The solution was then decanted and filtered through a filter paper tipped cannula. The solvent was removed under vacuum. Recrystallisation of the precipitate by slow diffusion of ether into a CH_2Cl_2 solution afforded **4a** as orange microcrystals in 74% yield (0.550 g). IR (KBr): *ν* 2115 (w, C≡C), 1972 (s, CO). ^{1}H-NMR (300.135 MHz, CD_2Cl_2): *δ* 7.60–7.30 (m, 20H, PPh_3, C_6H_4– and C*H*=), 6.91 (d, 1H, *J* = 15.4Hz, C*H*=), 5.49 (d, 1H, *J* = 2.1 Hz, C*H*(OH)), 5.34 (s, 5H, C_5H_5), 4.16 (s, 3H, OCH_3), 2.72 (d, 1H, *J* = 2.3 Hz, ≡C–*H*). ^{31}P-NMR (acetone-d_6): *δ* 50.5 (*P*Ph_3). Anal. Calc. for $C_{37}H_{32}BF_4O_3PRu{\cdot}0.5Et_2O$: C, 60.01; H, 4.78; P, 3.97. Found: C, 60.02; H, 4.47; P, 3.59%.

3.11. $[(C_5H_5)(CO)(PPh_3)Ru{=}C(OMe)CH{=}CH\text{–}C_6H_4\text{–}CH{=}CH_2)]BF_4$ (**4d**)

The synthesis follows the method outlined for the synthesis of **4a**. Complex **4d** was obtained as orange microcrystals in 50% yield (0.357 g) from **d** (0.24 g, 1.5 mmol) and **3** (0.49 g, 1 mmol). IR (KBr): *ν* 1972 (s, CO), 1588(s, C=C). ^{1}H-NMR (300.135 MHz, acetone-d_6): *δ* 7.50–7.20 (m, 20H, PPh_3, C_6H_4 and C*H*=), 6.90 (d, 1H, *J* = 15.4 Hz, C*H*=), 6.70 (dd, 1H, *J* = 17.6 and 10.9 Hz, C*H*=), 6.0 (d, 1H, *J* = 17.6 Hz, C*H*=), 5.40 (d, 1H, *J* = 10.9 Hz, C*H*=), 5.30 (s, 5H, C_5H_5), 4.15 (s, 3H, OCH_3). ^{13}C{^{1}H}-NMR (acetone-d_6): *δ* 299.2 (br,

Ru=*C*), 202.2 (d, $J = 19.0$ Hz, CO), 148.9 (*C*H=), 142.3 (*C*H=), 136.0–130.0 (P*Ph*$_3$, *C*H=, and *C*$_6$H$_4$–), 117.3 (*C*H$_2$=), 90.2 (*C*$_5$H$_5$), 66.1 (O*C*H$_3$). ^{31}P-NMR (acetone-d_6): δ 48.7 (*P*Ph$_3$). HRMS (FAB$^+$) Calc. for $C_{36}H_{32}O_2PRu$ [M − BF$_4$]$^+$: 629.1194. Found: 629.1192.

3.12. General procedure for the synthesis of (methoxy)-alkenyl carbene–tungsten and chromium complexes

A solution of W(CO)$_6$ or Cr(CO)$_6$ (1 mmol) in 60 ml of THF was irradiated for 6 h at r.t. by using a Rayonet and a Pyrex photochemical reactor. The yellow solution of M(CO)$_5$(THF) was then transferred into a Schlenk flask containing a solution of the dialkynol derivative **a** or **b** (1.5 mmol) in 30 ml of methanol. The reaction mixture was then stirred for 18 h at r.t. After evaporation of the solvent under vacuum, the red residue was chromatographed on silica gel. Elution with 1:3 dichloromethane–pentane gave first the violet bimetallic complexes and then the red monometallic complexes as solids or oils.

3.13. (CO)$_5$W=C(OMe)CH=CH–C$_6$H$_4$–C(H)(OH)(C≡CH) (**5a**)

Yield: 41% (0.214 g). IR (KBr): ν 2130 (w, C≡C), 2059 (m, CO), 1940 (s, CO). ^{1}H-NMR (300.135 MHz, acetone-d_6): δ 8.10 (d, 1H, $J = 15.5$ Hz, C*H*=), 7.84 (d, 2H, $J = 8.3$ Hz, C$_6$*H*$_4$–), 7.65 (d, 2H, $J = 8.3$ Hz, C$_6$*H*$_4$–), 7.43 (d, 1H, $J = 15.5$ Hz, C*H*=), 5.53 (dd, 1H, $J = 5.8$ and 2.1 Hz, C*H*(OH)), 5.21 (d, 1H, $J = 5.9$ Hz, CH(O*H*)), 4.76 (s, 3H, OC*H*$_3$), 3.12 (d, 1H, $J = 2.1$ Hz, ≡C–*H*). ^{13}C{^{1}H}-NMR (acetone-d_6): δ 307.4 (W=*C*), 203.8 (CO), 195.5 (CO), 143.8 (*C*H=), 142.8, 134.8 (*C*$_6$H$_4$–), 133.2 (*C*H=), 129.5, 127.1 (*C*$_6$H$_4$–), 83.0 (*C*≡C–H), 75.2 (C≡*C*–H), 69.1 (O*C*H$_3$), 63.9 (*C*H(OH)). HRMS (FAB$^+$) Calc. for $C_{18}H_{12}O_7^{184}W$ [M]$^+$: 524.0093. Found: 524.0095.

3.14. (CO)$_5$W=C(OMe)CH=CH–C$_6$H$_4$–CH=CH(MeO)C=W(CO)$_5$ (**6a**)

Yield: 10% (0.090 g). IR (KBr): ν 2065 (m, CO), 1941 (s, CO). ^{1}H-NMR (300.135 MHz, CDCl$_3$): δ 7.85 (d, 2H, $J = 15.5$ Hz, C*H*=), 7.50 (s, 4H, C$_6$*H*$_4$–), 7.10 (d, 1H, $J = 15.5$ Hz, C*H*=), 4.55 (s, 6H, OC*H*$_3$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 307.0 (W=*C*), 203.8 (CO), 197.4 (CO), 144.2 (*C*H=), 137.1 (*C*$_6$H$_4$–), 131.8 (*C*H=), 129.0 (*C*$_6$H$_4$–), 69.1 (O*C*H$_3$).

3.15. (CO)$_5$Cr=C(OMe)CH=CH–C$_6$H$_4$–C(H)(OH)(C≡CH) (**7a**)

Yield: 33% (0.130 g). IR (KBr): ν 2123 (w, C≡C), 2059 (m, CO), 1940 (s, CO). ^{1}H-NMR (300.135 MHz, acetone-d_6): δ 8.13 (d, 1H, $J = 15.4$ Hz, C*H*=), 7.81 (d, 2H, $J = 8.1$ Hz, C$_6$*H*$_4$–), 7.66 (d, 2H, $J = 8.1$ Hz, C$_6$*H*$_4$–), 7.25 (d, 1H, $J = 15.4$ Hz, C*H*=), 5.54 (s, 1H, C*H*(OH)), 5.21 (s, 1H, CH(O*H*)), 4.89 (s, 3H, OC*H*$_3$), 3.12 (s, 1H, ≡C–*H*). ^{13}C{^{1}H}-NMR (75.47 MHz, acetone-d_6): δ 334.4 (Cr=*C*), 225.7 (CO), 217.8 (CO), 145.9 (*C*$_6$H$_4$–), 139.9 (*C*H=), 134.9 (*C*H=), 130.5, 128.2 (*C*$_6$H$_4$–), 83.2 (*C*≡C–H), 75.5 (C≡*C*–H), 67.5 (O*C*H$_3$), 63.7 (*C*H(OH)). HRMS (FAB$^+$) Calc. for $C_{18}H_{12}O_7^{52}Cr$ [M]$^+$: 391.9988. Found: 391.9999.

3.16. (CO)$_5$Cr=C(OMe)CH=CH–C$_6$H$_4$–CH=CH(MeO)C=Cr(CO)$_5$ (**8a**)

Yield: 10% (0.060 g). IR (KBr): ν 2055 (m, CO), 1944 (s, CO). ^{1}H-NMR (200.135 MHz, CDCl$_3$): δ 7.95 (d, 2H, $J = 15.3$ Hz, C*H*=), 7.60 (s, 4H, $J = 8.3$ Hz, C$_6$*H*$_4$–), 6.90 (d, 1H, $J = 15.3$ Hz, C*H*=), 4.85 (s, 6H, OC*H*$_3$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 333.4 (Cr=*C*), 222.0 (CO), 216.6 (CO), 140.0 (*C*H=), 136.9 (*C*$_6$H$_4$–), 129.9 (*C*$_6$H$_4$–), 127.4 (*C*H=), 66.6 (O*C*H$_3$).

3.17. (CO)$_5$W=C(OMe)CH=CH–C$_4$H$_2$S–C(H)(OH)(C≡CH) (**5b**)

Yield: 33% (0.175 g). IR (KBr): ν 2124 (w, C≡C), 2065 (m, CO), 1929 (s, CO). ^{1}H-NMR (300.135 MHz, acetone-d_6): δ 7.70 (d, 1H, $J = 15.1$ Hz, C*H*=), 7.50 (dd, 1H, $J = 15.5$ and 0.6 Hz, C*H*=), 7.45 (d, 1H, $J = 3.8$ Hz, C$_4$*H*$_2$S–), 7.14 (dd, 1H, $J = 3.8$ and 0.6 Hz, C$_4$*H*$_2$S–), 5.70 (d, 1H, $J = 2.1$ Hz, C*H*(OH)), 5.50 (s, 1H, CH(O*H*)), 4.65 (s, 3H, OC*H*$_3$), 3.15 (d, 1H, $J = 2.3$ Hz, ≡C–*H*). ^{13}C{^{1}H}-NMR (75.47 MHz, acetone-d_6): δ 304.9 (W=*C*), 205.1 (CO), 198.6 (CO), 153.7 (*C*$_4$H$_2$S–), 142.4 (*C*H=), 140.5 (*C*$_4$H$_2$S–), 136.3 (*C*$_4$H$_2$S–), 131.0 (*C*H=), 127.9 (*C*$_4$H$_2$S–), 84.1 (*C*≡C–H), 75.6 (C≡*C*–H), 70.0 (O*C*H$_3$), 60.5 (*C*H(OH)). Anal. Calc. for $C_{16}H_{10}O_7SW$ (530.2): C, 36.20; H, 1.90; S, 6.03. Found: C, 35.60; H, 2.20; S, 6.10%.

3.18. (CO)$_5$W=C(OMe)CH=CH–C$_4$H$_2$S–CH=CH(MeO)C=W(CO)$_5$ (**7b**)

Yield: 9% (0.080 g). IR (KBr): ν 2063 (m, CO), 1946 (s, CO). ^{1}H-NMR (200.13 MHz, CDCl$_3$): δ 7.68 (d, 2H, $J = 15.1$ Hz, C*H*=), 7.32 (s, 2H, C$_4$*H*$_2$S–), 7.22 (d, 1H, $J = 15.1$ Hz, C*H*=), 4.58 (s, 6H, OC*H*$_3$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 304.2 (W=*C*), 203.9 (CO), 197.4 (CO), 144.6 (*C*$_4$H$_2$S–), 143.6 (*C*H=), 134.7 (*C*H=), 125.4 (*C*$_4$H$_2$S–), 68.9 (O*C*H$_3$).

3.19. (CO)$_5$W=C(OMe)CH=CH–C$_6$H$_4$–CH=CH$_2$) (**5d**)

The synthesis follows the method outlined for the synthesis of **5a**. Complex **5d** was obtained as orange powder in 60% yield (0.300 g) from **c** (0.24 g, 1.5

mmol). IR (KBr): ν 2066 (m, CO), 1942 (s, CO). ^{1}H-NMR (300.135 MHz, $CDCl_3$): δ 8.85 (d, 1H, J = 15.5 Hz, C*H*=), 7.55 (d, 2H, J = 8.4 Hz, C_6H_4–), 7.45 (d, 2H, J = 8.4 Hz, C_6H_4–), 7.20 (d, 1H, J = 15.5 Hz, C*H*=), 6.70 (d, 1H, J = 17.6 and 9.9 Hz, C*H*=), 5.85 (d, 1H, J = 17.6 Hz, CH_2=), 5.85 (d, 1H, J = 9.9 Hz, CH_2=), 4.65 (s, 3H, OCH_3). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 306.10 (W=*C*), 203.8 (CO), 197.6 (CO), 143.2 (*C*H=), 140.3 (C_6H_4–), 136.4 (*C*H=), 134.0 (C_6H_4–), 133.8 (*C*H=), 129.6, 127.0 (C_6H_4–), 115.9 (CH_2=), 69.0 (OCH_3). Anal. Calc. for $C_{17}H_{12}O_6W$ (496.1): C, 41.14; H, 2.42. Found: C, 41.20; H, 2.59%.

3.20. General procedure for the synthesis of (amino)-alkenyl carbene–tungsten and chromium complexes

To a solution of methoxyalkenyl carbene complexes (1 mmol) in 20 ml of diethyl ether at −80°C was added five equivalents of amine. The colour rapidly changed from red to orange. After stirring for 15 min at −80°C, the solvant was removed in vacuo at 0°C and the crude product was chromatographed on silica gel using 1:2 pentane–dichloromethane as eluent. Evaporation of the solvent gave the amino carbene complexes as orange to red solids or oils.

3.21. $(CO)_5W$=C(NMe_2)CH=CH–C_6H_4–C(H)(OH)(C≡CH) (**9a**)

Yield: 97% (0.520 g). IR (KBr): ν 2130 (w, C≡C), 2059 (m, CO), 1919 (s, CO). ^{1}H-NMR (300.135 MHz, acetone-d_6): δ 7.50 (m, 4H, C_6H_4–), 7.20 (d, 1H, J = 16.8 Hz, C*H*=), 6.10 (d, 1H, J = 16.8 Hz, C*H*=), 5.40 (dd, 1H, J = 5.5 and 2.2 Hz, C*H*(OH)), 5.10 (s, 1H, CH(O*H*)), 3.85 (s, 3H, NCH_3), 3.57 (s, 3H, NCH_3), 3.0 (d, 1H, J = 2.2 Hz, ≡C–*H*). ^{13}C{^{1}H}-NMR (75.47 MHz, acetone-d_6): δ 248.6 (W=*C*), 204.6 (CO), 199.5 (CO), 142.6 (C_6H_4–), 140.4 (*C*H=), 136.7, 127.9, 127.5 (C_6H_4–), 124.4 (*C*H=), 85.6 (*C*≡C–H), 75.1 (C≡*C*–H), 63.9 (*C*H(OH)), 54.3, 45.0 (NCH_3). HRMS (FAB$^+$) Calc. for $C_{19}H_{15}NO_6^{184}W$ [M]$^+$: 537.0412. Found: 537.0423.

3.22. $(CO)_5W$=C(NMe_2)CH=CH–C_4H_2S–C(H)(OH)(C≡CH) (**9b**)

Yield: 82% (0.445 g). IR (KBr): ν 2116 (w, C≡C), 2061 (m, CO), 1899 (s, CO). ^{1}H-NMR (300.135 MHz,CD_2Cl_2): δ 7.04 (dd, 1H, J = 3.7 and 0.8 Hz, C_4H_2S–), 6.89 (d, 1H, J = 3.7 Hz, C_4H_2S–), 6.88 (d, 1H, J = 16.3 Hz, C*H*=), 6.14 (dd, 1H, J = 16.3 and 0.6 Hz, C*H*=), 5.61 (s, 1H, C*H*(OH)), 5.30 (s, 1H, CH(O*H*)), 3.78 (s, 3H, NCH_3), 3.37 (s, 3H, NCH_3), 2.73 (d, 1H, J = 2.3 Hz, ≡C–*H*). ^{13}C{^{1}H}-NMR (75.47 MHz, acetone-d_6): δ 246.6 (W=*C*), 204.4 (CO), 199.4 (CO), 146.8, 142.0 (C_4H_2S–), 139.1 (*C*H=), 127.8, 126.4 (C_4H_2S–), 119.7 (*C*H=), 84.6 (*C*≡C–H), 75.0 (C≡*C*–H), 60.2 (*C*H(OH)), 54.4, 45.1 (NCH_3). Anal. Calc. for $C_{17}H_{13}NO_6SW$ (543.2): C, 37.57; H, 2.41; N, 2.58; S, 5.89. Found: C, 37.40; H, 2.64; N, 2.57; S, 6.01%.

3.23. $(CO)_5W$=C(NEt_2)CH=CH–C_6H_4–C(H)(OH)(C≡CH) (**10a**)

Yield: 95% (0.536 g). IR (KBr): ν 2115 (w, C≡C), 2059 (m, CO), 1918 (s, CO). ^{1}H-NMR (300.135 MHz, acetone-d_6): δ 7.55 (m, 4H, C_6H_4–), 7.40 (d, 1H, J = 16.8 Hz, C*H*=), 6.14 (d, 1H, J = 16.8 Hz, C*H*=), 5.49 (s, 1H, C*H*(OH)), 5.05 (s, 1H, CH(O*H*)), 4.28 (q, 2H, J = 7.2 Hz, NCH_2), 3.96 (q, 2H, J = 7.2 Hz, NCH_2), 3.07 (d, 1H, J = 2.2 Hz, ≡C–*H*), 1.50 (t, 3H, J = 7.2 Hz, CH_3), 1.33 (t, 3H, J = 7.2 Hz, CH_3). ^{13}C{^{1}H}-NMR (75.47 MHz, acetone-d_6): δ 248.9 (W=*C*), 204.6 (CO), 199.4 (CO), 142.3 (C_6H_4–), 140.3 (*C*H=), 136.8, 127.9, 127.4 (C_6H_4–), 123.2 (*C*H=), 85.7 (*C*≡C–H), 75.1 (C≡*C*–H), 63.9 (*C*H(OH)), 58.3, 48.7 (NCH_2–), 14.5, 14.3 (CH_3). HRMS (FAB$^+$) Calc. for $C_{20}H_{19}NO_5^{184}W$ [M − CO]$^+$: 537.0776. Found: 537.0775.

3.24. $(CO)_5W$=C(NH^iPr)CH=CH–C_6H_4–C(H)(OH)(C≡CH) (**11a**)

Yield: 88% (0.490 g). IR (KBr): ν 2119 (w, C≡C), 2059 (m, CO), 1912 (s, CO). *E* ^{1}H-NMR (300.135 MHz, acetone-d_6): δ 10.20 (s broad, 1H, N*H*–), 7.64 (m, 4H, C_6H_4–), 7.52 (d, 1H, J = 16.0 Hz, C*H*=), 7.09 (d, 1H, J = 16.0 Hz, C*H*=), 5.51 (m, 1H, C*H*(OH)), 5.11 (d, 1H, J = 6.0 Hz, CH(O*H*)), 4.51 (m, 1H, NC*H*–), 3.09 (d, 1H, J = 2.1 Hz, ≡C–*H*), 1.40 (d, 6H, J = 6.5 Hz, CH_3. ^{13}C{^{1}H}-NMR (75.47 MHz, $CDCl_3$): δ 248.0 (W=*C*), 203.0 (CO), 199.1 (CO), 143.3 (*C*H=), 133.2 (*C*H=), 83.4 (*C*≡C–H), 74.9 (C≡*C*–H), 64.0 (*C*H(OH)), 51.7 (N*C*H–), 22.7 (CH_3). *Z* ^{1}H-NMR (acetone-d_6): δ 10.20 (s broad, 1H, N*H*–), 7.70 (m, 5H, C*H*= and C_6H_4–), 6.81 (d, 1H, J = 15.7 Hz, C*H*=), 5.52 (m, 1H, C*H*(OH)), 5.06 (d, 1H, J = 5.9 Hz, CH(O*H*)), 4.51 (m, 1H, NC*H*–), 3.07 (d, 1H, J = 2.3 Hz, ≡C–*H*), 1.49 (d, 6H, J = 6.5 Hz, CH_3. ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 242.0 (W=*C*), 203.3 (CO), 198.1 (CO), 140.4 (*C*H=), 126.8 (*C*H=), 83.2 (*C*≡C–H), 75.1 (C≡*C*–H), 63.9 (*C*H(OH)), 57.5 (N*C*H–), 22.5 (CH_3). Anal. Calc. for $C_{20}H_{17}NO_6W$. 0.5 Et_2O (588.3): C,44.92; H, 3.77; N, 2.38. Found: C, 45.66; H, 3.83; N, 2.38%.

3.25. $(CO)_5W$=C($N(CH_2CH_2)_2NH$)CH=CH–C_6H_4–C(H)(OH)(C≡CH) (**12a**)

Yield: 93% (0.537 g). IR (KBr): ν 2115 (w, C≡C), 2061 (m, CO), 1902 (s, CO). ^{1}H-NMR (300.135 MHz, acetone-d_6): δ 7.54 (m, 4H, C_6H_4–), 7.30 (d, 1H, J = 16.7 Hz, C*H*=), 6.09 (d, 1H, J = 16.7 Hz, C*H*=), 5.48

(d, 1H, $J = 2.1$ Hz, C*H*(OH)), 4.37 (m, 2H, NCH_2), 4.11 (m, 2H, NCH_2), 3.19 (m, 2H, NCH_2), 3.08 (d, 1H, $J = 2.3$ Hz, ≡C–*H*), 3.01 (m, 2H, NCH_2). $^{13}C\{^1H\}$-NMR (75.47 MHz, acetone-d_6): δ 245.1 (W=*C*), 204.6 (CO), 199.2 (CO), 142.2 (C_6H_4–), 139.3 (*C*H=), 136.6, 127.7, 127.5 (C_6H_4–), 122.9 (*C*H=), 85.5 (*C*≡C–H), 74.9 (C≡*C*–H), 65.1 (N*C*H_2–), 63.6 (*C*H(OH)), 56.1, 48.3, 48.0 (N*C*H_2–). HRMS (FAB$^+$) Calc. for $C_{20}H_{18}N_2O_5^{184}W$ $[M - CO]^+$: 550.0728. Found: 550.0723.

3.26. $(CO)_5W$=C(NH($CH_2CH_2NH_2$))CH=CH–C_6H_4–C(H)(OH)(C≡CH) (**13a**)

Yield: 65% (0.358 g). IR (KBr): ν 2116 (w, C≡C), 2062 (m, CO), 1898 (s, CO). *E* ^{1}H-NMR (300.135 MHz, CD_2Cl_2): δ 9.60 (s broad, 1H, N*H*–), 7.46 (d, 2H, $J = 8.5$ Hz, C_6H_4–), 7.38 (d, 2H, $J = 8.5$ Hz, C_6H_4–), 7.36 (d, 1H, $J = 15.8$ Hz, C*H*=), 6.63 (d, 1H, $J = 15.8$ Hz, C*H*=), 5.45 (d, 1H, $J = 2.3$ Hz, C*H*(OH)), 3.90 (t, 2H, $J = 5.6$ Hz, NCH_2–), 3.15 (t, 2H, $J = 5.6$ Hz, NCH_2–), 2.69 (d, 1H, $J = 2.1$ Hz, ≡C–*H*), 2.1 (s broad, 2H, NH_2–). $^{13}C\{^1H\}$-NMR (75.47 MHz, CD_2Cl_2): δ 245.7 (W=*C*), 203.9 (CO), 199.1 (CO), 142.4 (*C*H=), 131.5 (*C*H=), 84.3 (*C*≡C–H), 74.9 (C≡*C*–H), 63.5 (*C*H(OH)), 56.8 (N*C*H_2–), 41.2(N*C*H_2–). Anal. Calc. for $C_{19}H_{16}N_2O_6W$. (552.2): C,41.30; H, 2.92; N, 5.07. Found: C, 41.32; H, 3.01; N, 4.69%.

References

[1] For a recent review see: M.I. Bruce, Chem. Rev. 98 (1998) 2797
[2] D. Pilette, K. Ouzzine, H. Le Bozec, P.H. Dixneuf, C.E.F. Rickard, W.R. Roper, Organometallics 11 (1992) 809.
[3] D. Pilette, H. Le Bozec, A. Romero, P.H. Dixneuf, J. Chem. Soc. Chem. Commun. (1992) 1220.
[4] M.A. Esteruelas, A.V. Gómez, F.J. Lahoz, A.M. López, E. Oñate, L.A. Oro, Organometallics 15 (1996) 3423.
[5] V. Cadierno, M. Pilar Gamasa, J. Gimeno, M. González-Cueva, E. Lastra, J. Borge, S. García-Granda, E. Pérez-Carreño, Organometallics 15 (1996) 2137.
[6] C. Cosset, I. Del Rio, H. Le Bozec, Organometallics 14 (1996) 1938.
[7] C. Cosset, I. Del Rio, V. Péron, B. Windmüller, H. Le Bozec, Synlett. (1996) 435.
[8] G. Poignant, F. Martin, V. Guerchais, Synlett. (1997) 913.
[9] Preliminary communication: V. Péron, E. Porhiel, V. Ferrand, H. Le Bozec, J. Organomet. Chem. 539 (1997) 201.
[10] M.M. Midland, J. Organomet. Chem. 70 (1975) 2250.
[11] J.P. Selegue, Organometallics 1 (1982) 217.
[12] J.P. Selegue, B.A. Young, S.L. Logan, Organometallics 10 (1991) 1972.
[13] S.G. Davies, S.J. Simpson, J. Chem. Soc. Dalton Trans. (1984) 993.
[14] K.H. Dötz, R. Noack, K. Harms, G. Mueller, Tetrahedron 46 (1990) 1235.
[15] B.A. Anderson, W.D. Wulff, T.S. Powers, S. Tribbitt, A.L. Rheingold, J. Am. Chem. Soc. 114 (1992) 10784.
[16] M.A. Bennett, A.K. Smith, J. Chem. Soc. Dalton. Trans. (1974) 233.