Activation of Alkynols by Half-Sandwich Ruthenium Complexes: Isolation of Hydroxyalkynyl(hydrido) and Hydroxyvinylidene Derivatives

Emilio Bustelo, Manuel Jiménez-Tenorio, M. Carmen Puerta,* and Pedro Valerga

Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Universidad de Cádiz, Aptdo. 40, 11510 Puerto Real, Cádiz, Spain

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*Summary: The complex [Cp*RuCl(PEt$_3$)$_2$] (Cp* = C$_5$Me$_5$) reacts with 2-propyn-1-ol derivatives, HC≡CC(OH)RR′ (R = R′= H; R = R′ = CH$_3$; R = CH$_3$, R′ = Ph), in MeOH in the presence of NaBPh$_4$ yielding the metastable 3-hydroxyalkynyl hydrido complexes [Cp*Ru(H)(C≡CC(OH)RR′)(PEt$_3$)$_2$][BPh$_4$], intermediates in the formation of the corresponding 3-hydroxyvinylidene complexes, to which these compounds rearrange both in solution and in the solid state.*

The discovery of a general method for the preparation of ruthenium−allenylidene complexes based on the direct activation of propargyl alcohol derivatives by electron-rich ruthenium(II) chloride complexes[1] has allowed the study in detail of these highly unsaturated compounds and of related species.[2] This process usually leads directly to the formation of ruthenium allenylidene complexes[3] which can be stable or undergo further processes such as the addition of nucleophiles.[4] In some cases, a mixture with the corresponding isomeric vinylvinylidene complex is obtained.[5] The initial formation of an hydroxyvinylidene complex,[6] which has been detected[5b] or even isolated in some instances,[7] has been postulated. Elimination of water yields the C=C=CRR′ unit in the coordination sphere of a ruthenium center. The preliminary C≡C bond coordination to the metal complex has been proposed as the first step, followed by subsequent tautomerization to give the corresponding hydroxyvinylidene complex.[1,8] Recently, Esteruelas et al. have isolated the η^2-alkyne derivative [CpOs(κ^1-OC(O)CH$_3$)(η^2-HC≡CC(OH)Ph$_2$)(P^{i}Pr$_3$)$_2$].[9] On the other hand, Werner et al. have reported formation of rhodium allenylidenes via (η^2-alkyne)- and alkynyl(hydrido)-rhodium as intermediates.[10] Likewise, the interaction of [OsCl(NO)(P^{i}Pr$_2$R)$_2$] (R = Ph, ^{i}Pr) with HC≡C−CR$_2$(OH) (R = CH$_3$, Ph) affords the alkynyl(hydrido)-osmium(II) complex.[11] However, there is no evidence for ruthenium analogue species, even considering that allenylideneruthenium(II) complexes constitute the largest group of this sort of compound.

As a continuation of our recent studies on 1-alkyne activation by [Cp*RuCl(dippe)],[12] we report now that the product of the reaction of [Cp*RuCl(PEt$_3$)$_2$][13] (**1**) with 2-propyn-1-ol derivatives and NaBPh$_4$ in MeOH is very sensitive to the order in which the reagents are added. Thus, if an excess of NaBPh$_4$ and the corresponding alkynol are dissolved in MeOH at 0 °C, and then the complex **1** is added, the hydroxyalkynyl hydrido complex [Cp*Ru(H)(C≡CC(OH)RR′)(PEt$_3$)$_2$][BPh$_4$] (R = R′ = H (**2**); R = R′= CH$_3$ (**3**); R = CH$_3$, R′= Ph (**4**))[14] precipitates immediately as a white/yellow solid. Any change in this

* E-mail address: carmen.puerta@uca.es.

(1) Selegue, J. P. *Organometallics* **1982**, *1*, 217−218.
(2) Crochet, P.; Demerseman, B.; Vallejo, M. I.; Gamasa, M. P.; Gimeno, J.; Borge J.; García-Granda, S. *Organometallics* **1997**, *16*, 5406−5415. Esteruelas, M. A.; Oro, L. A.; Schrickel, J. *Organometallics* **1997**, *16*, 796−799. Werner, H. *J. Chem. Soc., Chem. Commun.* **1997**, 903.
(3) Touchard, D.; Pirio, N.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 4920−4928. Leung, W.; Chan, E.; Wong, W. *Organometallics* **1998**, *17*, 1245−1247.
(4) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Modrego, J.; Oñate, E. *Organometallics* **1997**, *16*, 5826−5835. Cadierno, V.; Gamasa, M. P.; Gimeno, J.; López-González, M. C.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 4453−4463.
(5) (a) Selegue, J. P.; Young, B. A.; Logan, S. L. *Organometallics* **1991**, *10*, 1972. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1996**, *15*, 2137−2147.
(6) Selegue, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 5921−5923. Werner, H.; Martin, M.; Gevert, O. *J. Chem. Soc., Dalton Trans.* **1996**, 2275−2283.
(7) Le Lagadec, R.; Roman, E.; Toupet, L.; Müller, U.; Dixneuf, P. H. *Organometallics* **1994**, *13*, 5030−5039. Werner, H.; Braun, T.; Steinert, H. *J. Organomet. Chem.* **1995**, *488*, 169−176. de los Ríos, I.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Organomet. Chem.* **1997**, *549*, 221−232.
(8) Pilette, D.; Ouzzine, K.; Le Bozec, H.; Dixneuf, P. H. *Organometallics* **1992**, *11*, 809−817.
(9) Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E. *Organometallics* **1998**, *17*, 3141−3142.
(10) Werner, H.; Rappert, T.; Wiedemann, R.; Wolf, J.; Mahr, N. *Organometallics* **1994**, *13*, 2721−2727.
(11) Werner, H.; Flügel, R.; Windmüller, B.; Michenfelder, A.; Wolf, J. *Organometallics* **1995**, *14*, 612−618.
(12) de los Ríos, I.; Jiménez Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Chem. Soc., Chem. Commun.* **1995**, 1757. de los Ríos, I.; Jiménez Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **1997**, *119*, 6529−6538.
(13) Coto, A.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **1998**, *20*, 4392−4399.
(14) Experimental procedure for the preparation of complexes **2**−**4**: Complex **1** (127 mg, 0.25 mmol) was added to a solution of the corresponding alkynol (0.30 mmol) and NaBPh$_4$ (81 mg, 0.50 mmol) in 10 mL of MeOH at 0 °C (ice bath). The mixture was allowed to warm until precipitation of a white/yellow solid, which is filtered, washed with cold EtOH, and hexane, and stored at −20 °C. Yield: **2** 194 mg (91%), **3** 210 mg (95%), **4** 212 mg (90%). Selected spectral data for **2**: IR (Nujol): ν(OH) not observed, ν(C≡C) 2117, ν(Ru−H) 2024 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, 273 K): δ −9.25 (t, J_{HP} = 30.5 Hz, Ru−*H*), 1.67 (t, J_{HP} = 1.2 Hz, C$_5$(C*H*$_3$)$_5$), 4.29 (t, J_{HP} = 2.7 Hz, Ru−C≡C−C*H*$_2$-OH). ^{31}P{^{1}H} NMR (161.89 MHz, CDCl$_3$, 273 K): δ 36.8 (s). **3**: IR (Nujol): ν(OH) 3353, ν(C≡C) 2120, ν(Ru−H) 2028 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, 273 K): δ −9.28 (t, J_{HP} = 30.6 Hz, Ru−*H*), 1.46 (s, Ru−C≡C−C(C*H*$_3$)$_2$OH), 1.66 (t, J_{HP} = 1.2 Hz, C$_5$(C*H*$_3$)$_5$). ^{31}P{^{1}H} NMR (161.89 MHz, CDCl$_3$, 273 K): δ 36.8 (s). **4**: IR (Nujol): ν(OH) 3312, ν(C≡C) 2104, ν(Ru−H) 2020 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, 273 K): δ −9.35 (t, J_{HP} = 29.9 Hz, Ru−*H*), 1.65 (t, J_{HP} = 1.2 Hz, C$_5$(C*H*$_3$)$_5$), 1.82 (s, Ru−C≡C−C(C*H*$_3$)PhOH), 7.29, 7.37 and 7.55 (m, Ru−C≡C−CMe(C$_6$*H*$_5$)OH). ^{31}P{^{1}H} NMR (161.89 MHz, CDCl$_3$, 273 K): δ 37.4 and 37.6 (d, $J_{PP'}$ = 20.7 Hz).

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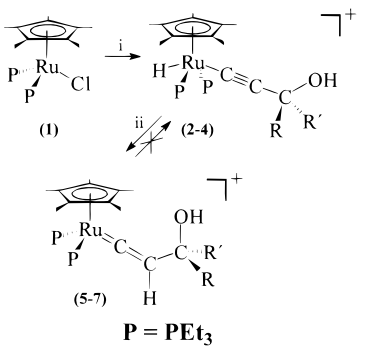
Scheme 1[a]



[a] Reagents and conditions: (i) HC≡C−C(OH)RR′, $NaBPh_4$, MeOH, 0 °C; (ii) room temperature (spontaneous and irreversible both in solution and in the solid state).

order may lead to the nondetection of these intermediates, yielding a mixture of isomerization, dehydration, and nucleophilic attack products depending on the alkynol employed, reaction time, etc. These compounds undergo irreversible isomerization to hydroxyvinylidene, both in solution and in the solid state at room temperature; hence these products must be handled and stored at temperatures close to 0 °C, to prevent their isomerization and/or dehydration.

Complexes **2**−**4** are formally derived from the insertion of the metal atom into the C−H bond of the alkynol, and therefore must be considered Ru^{IV} species. They display the ν(OH) IR absorption between 3310 and 3355 cm^{-1}, one strong ν(C≡C) band at 2100−2120 cm^{-1}, and one weak ν(Ru−H) at 2020−2030 cm^{-1}. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at 0 °C. The hydride resonance appears as one high-field triplet in all cases, whereas the $^{31}P\{^1H\}$ NMR spectra consist of one sharp singlet, except for the complex **4**, for which two doublet resonances are observed due to the presence of a chiral group on the alkynyl ligand that induces the nonequivalence of the phosphorus nuclei.[5b] These data are consistent with a transoid structure for the complexes **2**−**4** (Scheme 1). When temperature is raised, the NMR signals corresponding to $[Cp^*Ru(H)(C{\equiv}CC(OH)RR')(PEt_3)_2][BPh_4]$ decrease, whereas the signals of the hydroxyvinylidene $[Cp^*Ru(=C=CHC(OH)RR')(PEt_3)_2][BPh_4]$ (R = R′ = H (**5**); R = R′= CH_3 (**6**); R = CH_3, R′= Ph (**7**)) increase their intensity. Thus, after stirring **2** in CH_2Cl_2 solution several hours, the hydroxyvinylidene complex **5** was obtained as a stable orange solid. Attempts made to isolate the hydroxyvinylidene complexes **6** and **7** by controlling the reaction time in solution afforded a mixture of such species together with the hydroxyalkynyl hydride and/or dehydration products. Solid-state isomerization to hydroxyvinylidene at 30−35 °C allowed the isolation and spectroscopic characterization of these intermediates.[15] This process can be monitored following the ν(C≡C) decrease or ν(C=C) increase by IR spectroscopy. $^{31}P\{^1H\}$ NMR spectra consist of one sharp singlet in all cases except for the complex **7**, which, like its precursor, shows an AB coupling pattern due to the existence of a chiral carbon on the molecule.

We can conclude that activation of propargyl alcohols by half-sandwich ruthenium(II) complex **1** occurs through 3-hydroxyalkynyl(hydrido) and 3-hydroxyvinylidene complexes as intermediates, which have been isolated as stable solids at 0 °C, independently of the propargyl alcohol used. However, it is known that the formation and stabilization of the allenylidene moiety by the metal complex depends on the nature of the substituted propargyl alcohol and on the ancillary ligands,[5b] as inferred from our investigations in progress about ulterior transformations of compounds **5**−**7**. The η^2-coordination of the propargyl alcohol before the formation of the hydroxyalkynyl hydride species has not been detected in these cases, probably due to the steric influence of the Cp* ligand.

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(15) Experimental procedure for the preparation of complexes **5**−**7**: Complexes **2**−**4** were heated as solids at 35 °C under an inert atmosphere for 3 h, the color gradually turning from white/yellow to orange, yielding a quantitative isomerization process. Complex **5** can also be obtained cleanly starting from a solution of **1** (127 mg, 0.25 mmol) in 15 mL of MeOH to which $HC{\equiv}CCH_2OH$ (14 mg, 0.30 mmol) was added. After it was stirred for 4 h at room temperature, addition of $NaBPh_4$ (81 mg, 0.50 mmol) afforded the precipitation of an orange solid, which was filtered and washed with EtOH and hexane. Selected spectral data for **5**: IR (Nujol): ν(OH) 3459, ν(C=C) 1679 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 273 K): δ 1.25 (t, J_{HbHc} = 5.4 Hz, Ru=C=CH−$CH^b_2O\mathit{H}^c$), 1.74 (t, J_{HP} = 1.8 Hz, $C_5(CH_3)_5$), 4.05 (dd, J_{HaHb} = 8.4 Hz, J_{HbHc} = 5.4 Hz, Ru=C=CH^a−$\mathit{CH}^b_2OH^c$), 4.21 (tt, J_{HaHb}= 8.4 Hz, J_{HP} = 1.6 Hz, Ru=C=CH^a−CH^b_2OH). $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 273 K): δ 30.6 (s). **6**: IR (Nujol): ν(OH) 3543, ν(C=C) 1643 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 273 K): δ 1.75 (t, J_{HP} = 1.9 Hz, $C_5(C\mathit{H}_3)_5$), 1.37 (s, Ru=C=CH−$C(\mathit{CH}_3)_2$OH), 4.05 (s, Ru=C=$C\mathit{H}$-$C(CH_3)_2$-OH). $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 273 K): δ 28.9 (s). 7 IR (Nujol): ν(OH) 3598, ν(C=C) 1633 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 273 K): δ 1.71 (t, J_{HP} = 1.1 Hz, $C_5(C\mathit{H}_3)_5$), 1.63 (s, Ru=C=CH−$C(\mathit{CH}_3)$-PhOH), 4.38 (s, Ru=C=CH−CMe(Ph)OH), 7.28, 7.34, 7.36 (m, Ru=C=CH−CMe($C_6\mathit{H}_5$)OH). $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 273 K): δ 28.9 and 29.1 (d, $J_{PP'}$ = 35.5 Hz). All new compounds gave satisfactory C and H elemental analysis.