Insight into the Mechanism of the Reduction of α,*β*-Unsaturated Chromium(0) Carbenes by $NaBH_4$

María J. Mancheño, Miguel A. Sierra,* Mar Gómez-Gallego, and Pedro Ramírez

Departamento de Química Orgánica I, Facultad de Química, Universidad Complutense, 28040-Madrid, Spain

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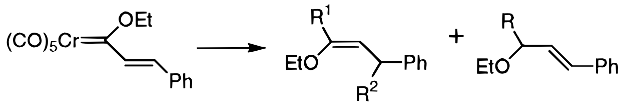
Summary: The reduction of α,β-unsaturated chromium(0) carbenes ***1*** *and* ***4*** *by $NaBH_4$ gives vinyl ethers* ***2*** *and/or allyl ethers* ***3****. Deuterium-labeling studies demonstrate that the reaction occurs by the initial addition of hydride to the carbene carbon, followed by 1,3-rearrangement of the metal center and protonation (for complexes* ***1****), or by a new hydride addition on the allenyl intermediate* ***8****, and subsequent protonation (for complexes* ***4****).*

The behavior of α,*β*-unsaturated alkoxychromium(0) carbenes in processes taking place outside of the coordination sphere of the metal is referable to that of α,*β*-unsaturated organic esters.[1] This is stated by the isolobal analogy,[2] and in consequence, these complexes may be regarded as a kind of super-esters, due to the activation of the α,*β*-unsaturated bond by the presence of the metal. Other reactions of α,*β*-unsaturated alkoxychromium(0) carbenes such as Dötz benzannulation[3] are unknown in organic esters since they require the active participation of the metal in the process. We have found that the metal actively participates in reduction of α,*β*-unsaturated alkoxychromium(0) carbenes by $NaBH_4$. These reactions succeed with 1,3-allylic (or propargylic, depending on the structure of the complex) migration of the metal center, after addition of the hydride anion to the carbene carbon.[4,5] These are striking results since the sole example of the metal hydride reduction of a group 6 Fischer carbene, namely, the reaction of $(CO)_5W(OMe)Ph$ with $KHB(O\textit{i}\text{-}Pr)_3$ to yield $(CO)_5WHPh$,[6] follows the standard addition to the carbene carbon-alkoxide elimination path.[7]

Scheme 1



1 **2** **3**

Table 1. Reduction of Pentacarbonyl[(ethoxy)(styryl)carbene]chromium(0), 1

reagent/ solvent[a]	**2** (yield)[b]	**3** (yield)[b]	**2**:**3** ratio[c]
$NaBH_4$/EtOH	**2a**, $R^1 = R^2 = H$ (56)	**3a**, R = H (12%)	80:20
$NaBH_4/CD_3OD$	**2b,** $R^1 = H$, $R^2 = D$ (59%)	**3b,** R = D (16%)	83:17
$NaBD_4$/EtOH	**2c,** $R^1 = D$, $R^2 = H$ (59%)	**3b,** R = D (12%)	85:15

[a] Reactions were performed at −20 °C. [b] In pure compound. [c] Determined by integration of well-resolved signals in the ^1H NMR spectra of crude reaction mixtures before purification.

The reaction of a cooled (−20 °C) solution of pentacarbonyl[(ethoxy)(styryl)carbene]chromium(0), **1**, in ethanol with the equimolar amount of $NaBH_4$ formed *Z*-vinyl ether **2a** and *E*-olefin **3a** (Scheme 1, Table 1).[8] The reaction of complex **1** was repeated using CD_3OD as the solvent, and monodeuterated compounds *Z*-**2b** and *E*-**3b** were obtained.[9] The reaction of complex **1** with $NaBD_4$/EtOH yielded again monodeuterated compounds *Z*-**2c** and *E*-**3b** (Scheme 1/Table 1). These results clearly ilustrate that the active participation of the metal in an apparently simple process may completely change

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(1) (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, R.; Schubert, U.; Weiss, K. In *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1983. (b) Dötz, K. H. *Angew. Chem., Int. Ed. Eng.* **1984**, *23*, 587−608. (c) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, pp 1065−1113. (d) Wulff, W. D. In *Comprehensive Organometallic Chemistry II;* Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, pp 470−547.

(2) (a) Hoffmann, R. *Science* **1981**, *211*, 995−1002. (b) Hoffmann, R. *Angew. Chem., Int. Ed. Eng.* **1982**, *21*, 711−800.

(3) (a) Dötz, K. H. *Angew. Chem., Int. Ed. Eng.* **1975**, *14*, 644−645. Some recent examples: (b) Wang, H.; Wulff, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 10573-10574. (c) Pulley, S. R.; Carey, J. P. *J. Org. Chem.* **1998**, *63*, 5275−5279. (d) Eastham, S. A., Herbert, J.; Painter, J. E.; Patel, P.; Quayle, P. *Synlett* **1998**, 61−63. (e) Hohmann, F.; Siemoneit, S.; Nieger, M.; Kotila, S.; Dötz, K. H. *Chem. Eur. J.* **1997**, *3*, 853−859. (f) Hsung, R. P.; Quinn, J. F.; Weisenberg, B. A.; Wulff, W. D.; Yap, G. P. A.; Rheingold, A. L. *Chem. Commun.* **1997**, 615−616. (g) Merlic, C. A.; McInnes, D. M.; You, Y. *Tetrahedron Lett.* **1997**, *38*, 6787−6790. (h) Peterson, G. A.; Wulff, W. D. *Tetrahedron Lett.* **1997**, *38*, 5587−5590.

(4) For 1,3-allylic migration of a $(CO)_5M$ moiety from a carbon to a nitrogen center, see: (a) M = Cr, Hegedus, L. S.; Lundmark, B. *J. Am. Chem. Soc.* **1989**, *111*, 9194−9198. (b) M = W, Maxey, C. T.; Sleiman, H. F.; Maxey, S. T., McElwee-White, L. *J. Am. Chem. Soc.* **1992**, *114*, 5153−5160. From carbon to carbon: (c) Fischer, H.; Schlageter, A., Bidell, W.; Früh, A. *Organometallics* **1991**, *10*, 389−391. Two examples of 1,3-propargylic migration of a $(CO)_5W$ moiety through a full-carbon moiety has been reported while this paper was being prepared: (d) Barluenga, J.: Trabanco, A. A.; Flórez, J.; García-Granda, S.; Llorca, M.-A. *J. Am. Chem. Soc.* **1998**, *120*, 12129−12130. (e) Barluenga, J.: Tomás, M.; Rubio, E.; López-Pelegrín, J. A.; García-Granda, S.; Pérez Priede, M. *J. Am. Chem. Soc.* **1999**, *121*, 3065−3071.

(5) The 1,2-migration of pentacarbonylchromate moiety has been reported to occur after the addition of alkynyllithiums to alkoxychromium(0) carbenes. See: (a) Iwasawa, N.; Maeyama, K.; Saitou, M. *J. Am. Chem. Soc.* **1997**, *119*, 1486-1487. (b) Iwasawa, N.; Maeyama, K. *J. Org. Chem.* **1997**, *62*, 1918−1919. (c) Iwasawa, N.; Ochiai, T.; Maeyama, K. *Organometallics* **1997**, *16*, 5137−5139. (d) Iwasawa, N.; Ochiai, T.; Maeyama, K. *J. Org. Chem.* **1998**, *63*, 3164−3165. See also ref 4d.

(6) To the best of our knowledge this is the sole precedent for the reaction of a group 6 metal carbene with a main group metal hydride: (a) Casey, C. P.; Polichnowski, S. W.; Tuinstra, H. E.; Albin, L. D.; Calabrese, J. C. *Inorg. Chem.* **1978**, *17*, 3045−3049. (b) Casey, C. P.; Polichnowski, S. W.; Shucterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282−7292. For the reduction of ethoxymethylcarbene complexes of chromium and tungsten by dihydropyridine: (c) Cohen, F.; Goumont, R.; Rudler, H.; Daran, J. C.; Toscano, R. A. *J. Organomet. Chem.* **1992**, *431*, C6−C10.

(7) Some examples for reactions of metal carbenes and hydrides: (a) Green, M. L. H.; Mitchard, L. C.; Swanwick, M. G. *J. Chem. Soc. (A)* **1971**, 794−797. (b) Davinson, A.; Reger, D. L. *J. Am. Chem. Soc.* **1972**, *94*, 9237−9238. (c) Fischer, E. O.; Frank, A. *Chem. Ber.* **1978**, *111*, 3740−3744. (d) Gibson, D. H.; Owens, K.; Mandal, S. K.; Sattich, W. E.; Franco, J. O. *Organometallics* **1991**, *10*, 1203−1206. (e) Gibson, D. H.; Owens, K. *Organometallics* **1991**, *10*, 1216−1218.

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Scheme 2

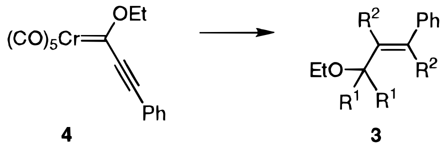

Table 2. Reduction of Pentacarbony-[(ethoxy)(phenylethynyl)carbene]chromium(0), 4

reagent/solvent[a]	**3** (yield)[b]
$NaBH_4$/EtOH	**3a,** $R^1 = R^2 = H$ (74%)
$NaBH_4/CD_3OD$	**3c,** $R^1 = H$, $R^2 = D$ (71%)
$NaBD_4$/EtOH	**3d,** $R^1 = D$, $R^2 = H$ (74%)

[a] The reactions were performed at −20 °C. [b] In pure compound.

the expected reactivity of metal carbenes toward hydrides. On the other hand, the reduction of ethyl cinnamate with $NaBH_4$/EtOH yielded unreacted starting material and only traces of ethyl 3-phenylpropanoate, even after prolonged reaction times.

Pentacarbony[(ethoxy)(phenylethynyl)carbene]chromium(0), **4**, also reacted with $NaBH_4$/EtOH at −20 °C. This time, olefin *E*-**3a** was obtained as the sole reaction product. When CD_3OD was the solvent, the reaction yielded dideuterated compound *E*-**3c**, exclusively. Finally, the reaction of complex **4** with $NaBD_4$/EtOH formed the dideuterated derivative *E*-**3d** (Scheme 2, Table 2). These results clearly demonstrate that the participation of the metal in the reduction of α,β-unsaturated chromium carbenes is general. Furthermore, while complex **1** gave compounds derived from the addition of one hydride ion, complex **4** incorporated two hydrides during the reduction process. To complete these experiments, the reduction of ethyl phenylpropiolate with $NaBH_4$/EtOH was checked, yielding 50% of a mixture of (2:1) *E*/*Z*-ethyl cinnamates and 50% of unreacted starting material after 48 h of reaction.

The results obtained in the reduction of complexes **1** and **4** may be explained by the initial 1,2-addition of the hydride to the carbene carbon to yield the intermediates **5** and **6**, respectively. The incorporation of deuterium occurs at this point when $NaBD_4$ is the reagent. The key feature of these processes is the allylic rearrangement of the chromium fragment on species **5** and **6** to form the new intermediates **7** and **8**. Protonation of **7** at the metal center followed by elimination leads to the observed vinyl ethers **2a**−**c** (when CD_3OD was the solvent, the monodeuterated vinyl ether **2b** is formed). On the other hand, the presence of ethers **3** as minor products suggests the existence of an equilibrium between intermediates **5** and **7**. Protonation of **5** would form ethers **3a**−**b** (the latter in the presence of $NaBD_4$ or when CD_3OD was the solvent). In the case of carbene **4**, the obtainment of ethers **3a**−**c** and **3d** from the allenyl intermediate **8**[10] requires the addition of a new hydride ion to yield the dianionic intermediate **9**. It is remarkable that the hydride addition takes place at the end of the allenyl system,[11] accounting for the incorporation of the second deuterium atom in product **3d**. Protonation of intermediate **9** would lead to ethers **3a**,**c** and **3d** and explained the formation of the dideuterated ether **3c** when CD_3OD was the solvent. An alternative to dianion **9** may be the protonation of allenyl intermediate **8** in the reaction media, to yield the free allene **10**. The subsequent reduction of this compound would also yield enol ethers **3**. To discard this possibility the unstable allene **10** was prepared following the literature procedure[12] from 1-ethoxy-3-phenyl-2-propyne and treated at −20 °C with $NaBH_4$ in ethanol. Compound **10** was recovered unaltered after 4 h of reaction. Additionally, when complex **4** was reduced using THF instead of EtOH as solvent, compound **3a** was the sole reaction product obtained after aqueous quenching. In view of these results, we should rule out the participation of free allene species, at least in the conditions used, and conclude that the second hydride transfer to allenyl chromium intermediate **8** should take place before protonation.

The exquisite *E*/*Z*-selectivity obtained in the formation of compounds **2** (from complex **1**) and **3a**,**c** and **3d** (from complex **4**) may arise from the chelation of the basic alkoxy oxygen to the metal center, once the 1,3-rearrangement has occurred (for intermediate **7**), or after the second hydride transfer (for intermediate **9**). This chelation may impose the relative disposition of the metal and alkoxyde groups around the C−C double bonds and hence the observed stereochemistry.[14] The

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[8] General procedure for the reduction of complexes **1** and **4**. A suspension of $NaBH_4$ in EtOH at −20 °C was placed in a flame-dried airless flask containing a magnetic stirring bar and degassed by evacuation/back-fill with argon (3 ×). A solution of the carbene in EtOH was added by syringe at −20 °C, and the mixture was stirred at this temperature until the disappearance of the starting material (checked by TLC). After the addition of water at −20 °C, the solvent was removed under reduced pressure and the mixture was dissolved in AcOEt, filtered through Celite, diluted with one volume of hexane, and air oxidized under sunlight. Then, the solvent was removed in vacuo, and the residue was purified by flash column chromatography (SiO_2, 9:1 hexane/acetate). For the deuterium experiments the same procedure was followed, using $NaBD_4$ or CD_3OD as solvent (in this case D_2O was added instead of water). The experiments under CO atmosphere were carried out by bubbling a CO stream through the solution of complex **1** for about 30 min before the addition of $NaBH_4$. A CO-filled balloon was placed at the top of the flask to maintain the CO atmosphere during the reduction process.

[9] The degree of deuteration was determined by NMR and mass spectrometry (EI, 70 eV).

[10] For the isolation and characterization of allenyl chromium complexes, see: (a) Fischer, H.; Rindl, D.; Troll, C.; Leroux, F. *J. Organomet. Chem.* **1995**, 221−227. (b) Aumann, R.; Jasper, B.; Lage, M.; Krebs, B. *Chem. Ber.* **1994**, *127*, 2475−2482. Allenyl complexes related to **8** are the postulated intermediates in the Michael addition of nucleophiles to group 6 alkynylcarbene complexes. See, for example: (c) de Meijere, A. *Pure Appl. Chem.* **1996**, *68*, 61−72. (d) Aumann, R.; Hinterding, P. *Chem. Ber.* **1993**, *126*, 421−427. (e) Pipoh, R.; van Eldik, R.; Henkel, G. *Organometallics* **1993**, *12*, 2236−2242. (f) Aumann, R.; Jasper, B.; Läge, M.; Krebs, B. *Organometallics* **1994**, *13*, 3502−3509.

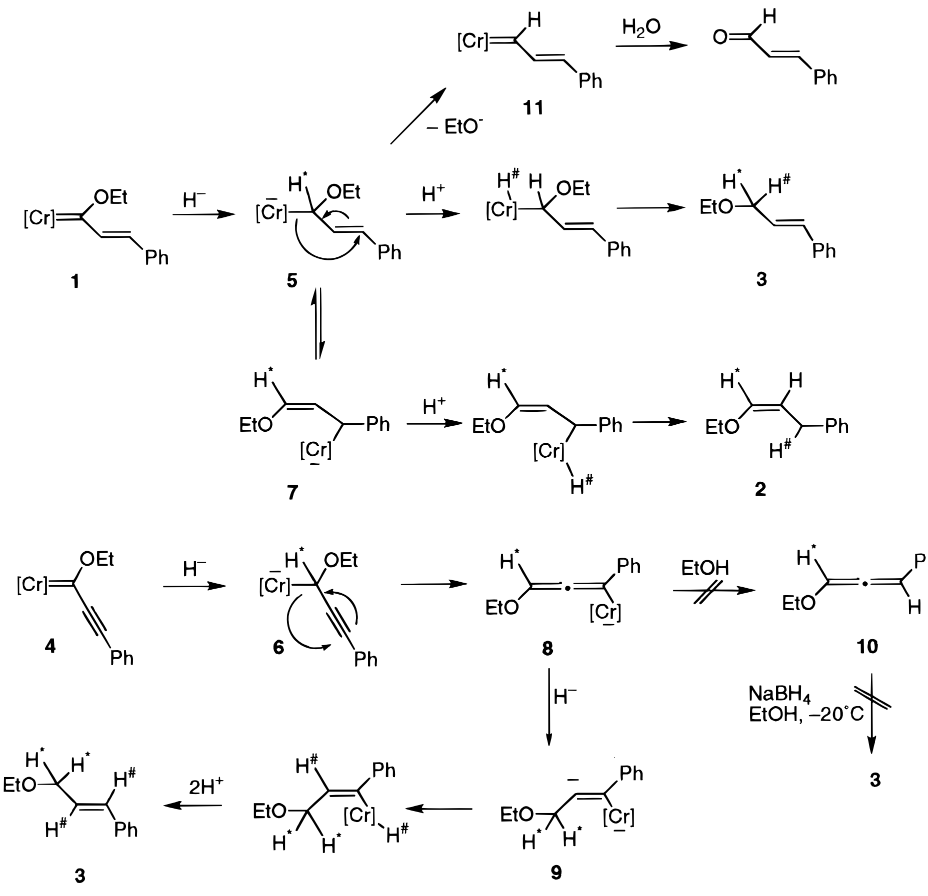
[11] The addition of nucleophiles to allenes usually takes place at the central allenic carbon, see: Jacobs, T. L In *The Chemistry of the Allenes*; Landor, S. R., Ed.; Academic Press: London, U.K., 1982; Vol 2. For aluminium hydride reductions of allenes see: Montury, M.; Gore, J. *Tetrahedron Lett.* **1980**, *21*, 51−54. Baudouy, R.; Gore, J. *Tetrahedron* **1975**, *31*, 383−389.

[12] Mantione, R.; Alves, A. *C. R. Acad. Sc., Ser. C* **1969**, *268*, 997−1000.

[13] The lack of reactivity of the allene system toward $NaBH_4$ reduction is in agreement with previous references: Collman, J. P.; Cawse, J. N.; Kang, J. W. *Inorg. Chem.* **1969**, *12*, 2574−2579. Pasto, D. J.; Timmers, D. A.; Huang, N. Z. *Inorg. Chem.* **1984**, *23*, 4117−4119.

[14] A reviewer proposed that an alternative to the participation of the alkoxyde group in defining the observed *Z*-stereochemisty of compounds **2** would be the participation of the sodium cation in the reduction process. In fact, assuming that the more stable conformer of **1** is that depicted in Scheme 3, Na^+ coordination to the ethoxy group on the same face of the allylic grouping where H^- is being delivered may force the chromium moiety to migrate to the opposite face of the 3-carbon unit. This possibility has to be discarded because the use of NH_4BH_4 as reducing agent gave again exclusively compound *Z*-**2**. No *E*-**2** isomer was observed, as it would should the sodium cation be responsible for the observed reactivity.

Scheme 3



* Position deuterated by $NaBD_4$
\# Position deuterated by CD_3OD

proposed 1,3-metal migration should involve the intermediacy of a π-allyl complex in the rearrangement of **5** to **7**, through a decarbonylation–carbonylation process which logically could be hampered in an atmosphere of CO. When the reduction of complex **1** was carried out in a CO-saturated EtOH solution, we observed that the **2**/**3** ratio decreased from 4:1 to 2.7:1. Furthermore, the stereochemistry of both **2** and **3** remained unaltered under this conditions. In addition, it was observed that the reactions were dirtier when CO was present, and variable amounts of cinnamaldehyde were obtained.[15] These results pointed to a partial inhibition of the **5** to **7** rearrangement in the presence of CO, but not of the chelation of the metal by the alkoxy group on this latter intermediate. Hence, compound **2** was formed in lower amounts when CO was present, but again only with *Z* stereochemistry. The formation of cinnamaldehyde should be a consequence of the partial inhibition of the allylic rearrangement. This compound may be formed by extrusion of the ethoxy moiety on intermediate **5** to yield metal carbene **11**, following the previously reported reaction pathway for the $KHB(O\textit{i}\text{-}Pr)_3$ reduction of $(CO)_5W(OMe)Ph$.[6] Hydrolysis of complex **11** would finally lead to cinnamaldehyde.[16]

In conclusion, an unprecedent 1,3-migration of the metal in the reduction of α,β-unsaturated chromium(0) carbene complexes has been observed. Application of these reactions to develop a method to selectively obtain deuterated vinyl and allyl ether derivatives is currently under way in our laboratories.

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[15] The **2**:**3** ratio obtained under CO pressure was the average of three separate experiments. The presence of cinnamaldehyde was checked against an authentic sample in the ^1H NMR spectra of the crude reaction mixtures. The role of CO in the 1,3-migration process was suggested by a reviewer. The experiments discussed in the text were derived therefrom.

[16] This is a known reaction for group 6 metal carbene complexes. See: Bernasconi, C. F.; Flores, F. X.; Sun, W. *J. Am. Chem. Soc.* **1995**, *117*, 4875–4880.