*Organometallics* **2003,** *22,* 5092−5099

# New Reactivity Modes of Chromium(0) Fischer Carbene Complexes: Unprecedented Insertion of a Carbene Ligand into an Active B−H Bond

Pedro Ramírez-López,[†] Miguel A. Sierra,*[,†] Mar Gómez-Gallego,[†]
María José Mancheño,[†] and Heinz Gornitzka[‡]

*Departamento de Química Orgánica, Facultad de Química, Universidad Complutense, 28040 Madrid, Spain, and Laboratoire d'Hétérochimie Fondamentale et Appliquée du CNRS (UMR 5069), Bâtiment 2R1, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 04, France*

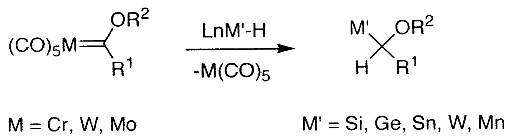
*Received July 1, 2003*

The reaction of α,β-unsaturated chromium(0) complexes with hydrides leads to different products, depending on the electronic properties of the reducing agent and the carbene carbon. Electrophilic alkynylcarbene complexes react with $NaCNBH_3$ to produce compounds derived from the insertion of the carbene ligand into the B−H bond in a process that has no precedent in the literature. This reaction does not take place if the electrophilicity of the carbene carbon is diminished by the presence of a strong electron-donating group. However, the behavior of alkenylcarbene complexes toward $NaCNBH_3$ can be interpreted by initial addition of the hydride to the C−Cr bond followed by evolution of the intermediate thus formed through different reaction pathways. These include chromium 1,3-migration and alkoxide extrusion followed by dimerization or oxidation. This route also justifies the reactivity of alkenyl and alkynyl alkoxy Fischer carbene complexes toward other boron or aluminum hydrides. Finally, when a bulky reagent such as K-Selectride is employed, the 1,2-hydride addition is disfavored and only products derived from the reduction of the C−C multiple bonds are obtained.

## Introduction

The ability of Fischer carbene complexes[1] to undergo [2 + 1] insertion reactions into M−H bonds (M = Si,[2] Ge,[3] Sn,[4] W,[5] Mn[5]) is well-known (Scheme 1). This is a general reaction of these complexes, and the carbene transfer occurs under mild conditions, offering a facile entry to valuable organic intermediates, particularly organosilanes and organostannanes. In this context, the insertions of alkenyl group 6 Fischer carbene complexes[6] into Si−H and Sn−H bonds to give allylsilanes[2] and allylstannanes[4b] have received more attention. Thus, while alkenyl Fischer carbenes undergo 1,2-addition of tin hydrides or organosilanes, alkynyl Fischer carbenes form compounds derived from 1,2- or 1,4-addition processes. Furthermore, a strong dependence of the regioselectivity of the reaction with the steric bulk of both the carbene complex and the tin hydride has been described. Less attention has been paid to the insertion of these reagents into C−H bonds, since these processes are in general undesirable side reactions during the cyclopropanation of olefins.[7]

**Scheme 1**



During our ongoing project devoted to study transition-metal-catalyzed carbene transfers from Fischer carbene complexes,[8] we have described the low-temperature cyclopropanation of olefins, a reaction that generally requires harsh reaction conditions to occur. In parallel, our work directed toward an understanding of the factors controlling the addition of nucleophiles to α,β-unsaturated complexes[9] (including the addition of

---

* To whom correspondence should be addressed. E-mail: sierraor@quim.ucm.es.

[†] Universidad Complutense.

[‡] Université Paul Sabatier. To whom inquires regarding the structural determination of compound **5a** should be addressed.

(1) Selected reviews on the chemistry of metal carbene (Fischer) complexes: (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1983. (b) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (c) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, U.K., 1991; Vol. 5, p 1065. (d) Hegedus, L. S. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 12, p 549. (e) Harvey, D. F. Sigano, D. M. *Chem. Rev.* **1996**, *96*, 271. (f) Barluenga, J.; Fañanás, F. J. *Tetrahedron* **2000**, *56*, 4597. (g) Sierra, M. A. *Chem. Rev.* **2000**, *100*, 3591.

(2) (a) Mak, C. C.; Chan, K. S. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2143. (b) Mak, C. C.; Tse, M. K.; Chan, K. S. *J. Org. Chem.* **1994**, *59*, 3585. (c) Iwasawa, N.; Saitou, M.; Kusama, H. *J. Organomet. Chem.* **2001**, *617−618*, 741.

(3) (a) Connor, J. A.; Day, J. P.; Turner, R. M. *J. Chem. Soc., Dalton Trans.* **1976**, 283. (b) Connor, J. A.; Rose P. D.; Turner, R. M. *J. Organomet. Chem.* **1973**, *55*, 111.

(4) (a) Nakamura, E.; Tanaka, K.; Aoki, S. *J. Am. Chem. Soc.* **1992**, *114*, 9715. (b) Merlic, C. A.; Albaneze, J. *Tetrahedron Lett.* **1995**, *36*, 1007, 1011.

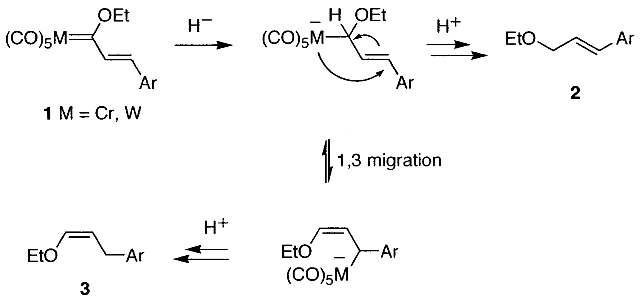
(5) Fischer, H.; Jungklaus, H. *J. Organomet. Chem.* **1999**, *572*, 105.

(6) Reviews on the chemistry of α,β-unsaturated group 6 carbene complexes: (a) Barluenga, J.; Flórez, J.; Fañanás, F. J. *J. Organomet. Chem.* **2001**, *624*, 5. (b) de Meijere, A.; Schirmer, H.; Duetsch, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3964. (c) Aumann, R.; Nienaber, H. *Adv. Organomet. Chem.* **1997**, *41*, 163.

10.1021/om034010v CCC: $25.00

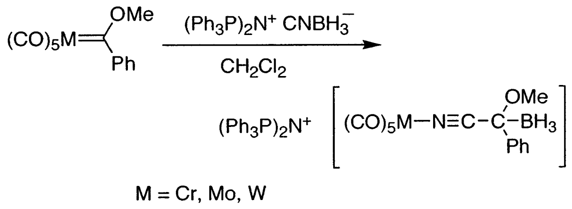
radicals[10] and SET processes[11]) has resulted in the disclosure of the participation of the metal center in the addition of hydrides to $\alpha,\beta$-unsaturated group 6 carbene complexes.[12] Thus, we have reported that the addition of $NaBH_4$ to alkenylcarbenes **1** is not a simple hydride addition to the M−C bond to yield allyl ethers **2**. The process occurs by the initial 1,2-addition of hydride followed by a 1,3-metal rearrangement, yielding an anionic $\sigma$-complex that finally leads to vinyl ethers **3** as the major reaction products.[12a,b] A similar mechanism has been proposed to account for the reduction of alkynyl Fischer carbene complexes under the same conditions (Scheme 2). Other products derived from the insertion of the carbene ligand into the B−H bond of the reagent were not detected in any case. Additionally, our studies have demonstrated that the regioselectivity of these reduction processes strongly depends on the electronic nature of the substituents attached to the carbene carbon.[13]

### Scheme 2



In a quest to connect the carbene transfer reactions with the metal-migration processes, we thought that a change in the electronic properties of the hydride used in the reactions above might lead to a different reactivity of the carbene complex. On the basis of this hypothesis, we will report here the first example of an insertion of the carbene ligand of group 6 metal−carbene complexes into an active B−H bond. The insertion of group 6 pentacarbonyl methoxyphenylcarbene complexes into the B−C bond of $[(Ph_3P)_2N][NCBH_3]$ to form nitrile complexes has been reported by Fischer (Scheme 3).[14] However, although the insertion of the carbene ligand into the boron $C_\beta$−H bond in boroxycarbenes has been described,[15] to the best of our knowledge, the insertion of a carbene ligand into the B−H bond is unknown. Additionally, a full investigation into the behavior of $\alpha,\beta$-unsaturated carbene complexes toward hydrides of different reactivity will be discussed in this paper.

### Scheme 3



## Results and Discussion

The reaction of the alkynylalkoxycarbene complex **4a** with $NaCNBH_3$ at −20 °C yielded a new product that was isolated in 73% yield after quenching with water and air oxidation. The spectroscopic data of the new compound indicated the loss of the chromium fragment and the incorporation of a new CH group in the carbon skeleton, which could be clearly identified in the $^1H$ NMR and $^{13}C$ NMR spectra. The structure of this product could not be unambiguously established by means of a combination of one- and two-dimensional NMR techniques, MS, and elemental analysis. Therefore, a single monocrystal of this compound was submitted to X-ray diffraction analysis and its structure was unambiguously established as the boron salt **5a** (Figure

---

(7) (a) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1970**, *103*, 1273. (b) Dötz, K. H. Fischer, E. O. *Chem. Ber.* **1972**, *105*, 1356, 3966. (c) Wulff, W. D.; Yang, D. C.; Murray, C. K. *Pure Appl. Chem.* **1988**, *60*, 137 and references cited therein. (d) Barluenga, J.; López, S.; Trabanco, A. A.; Fernández-Acebes, A.; Flórez, J. *J. Am. Chem. Soc.* **2000**, *122*, 8145. (e) Barluenga, J.; Fernández-Acebes, A.; Trabanco, A. A.; Flórez, J. *J. Am. Chem. Soc.* **1997**, *119*, 7591. (f) Sierra, M. A.; del Amo, J. C.; Mancheño, M. J.; Gómez-Gallego, M. *Tetrahedron Lett.* **2001**, *42*, 5435. (g) Herndon, J. W. Tumer, S. U. *J. Org. Chem.* **1991**, *56*, 286. (h) Wienand, A.; Reissig, H.-U. *Organometallics* **1990**, *9*, 3133. (i) Buchert, M.; Hoffmann, M.; Reissig, H.-U. *Chem. Ber.* **1995**, *128*, 605. (j) Merlic, C. A.; Bendorf, H. D. *Tetrahedron Lett.* **1994**, *35*, 9529. (k) Harvey, D. F.; Lund, K. P. *J. Am. Chem. Soc.* **1991**, *113*, 8916. (l) Wienand, A.; Reissig, H.-U. *Tetrahedron Lett.* **1988**, *29*, 2315. (m) Buchert, M. Reissig, H.-U. *Tetrahedron Lett.* **1988**, *29*, 2319.

(8) (a) Sierra, M. A.; del Amo, J. C.; Mancheño, M. J.; Gómez-Gallego, M.; Torres, M. R. *Chem. Commun.* **2002**, 1842. (b) Sierra, M. A.; del Amo, J. C.; Mancheño; M. J.; Gómez-Gallego, M. *J. Am. Chem. Soc.* **2001**, *123*, 851. (c) Sierra, M. A.; Mancheño, M. J.; Sáez, E.; del Amo, J. C. *J. Am. Chem. Soc.* **1998**, *120*, 6812.

(9) (a) Sierra, M. A.; Mancheño, M. J.; del Amo, J. C.; Fernández, I.; Gómez-Gallego, M.; Torres, M. R. *Organometallics* **2003**, *22*, 384. (b) Alcaide, B.; Casarrubios, L.; Domínguez, G.; Retamosa, A.; Sierra, M. A. *Tetrahedron* **1996**, *52*, 13215. (c) Alcaide, B.; Casarrubios, L.; Domínguez, G.; Sierra, M. A.; Jiménez-Barbero, J. *Organometallics* **1994**, *13*, 2934. (d) Alcaide, B.; Casarrubios, L.; Domínguez, G.; Sierra, M. A. *Organometallics* **1996**, *15*, 4612. (e) Alcaide, B.; Domínguez, G.; Rodríguez-López, J.; Sierra, M. A. *Organometallics* **1992**, *11*, 1979. For a review on the reactions of group 6 Fischer carbene complexes with ylides and ylide-like derivatives, see: (f) Alcaide, B.; Casarrubios, L.; Domínguez, G.; Sierra, M. A. *Curr. Org. Chem.* **1998**, *2*, 551.

(10) Mancheño, M. J.; Ramírez-López, P.; Gómez-Gallego, M.; Sierra, M. A. *Organometallics* **2002**, *21*, 989.

(11) Sierra, M. A.; Ramírez-López, P.; Gómez-Gallego, M.; Lejon, T.; Mancheño, M. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 3442.

(12) Crystal data for **5a**: $C_{20}H_{20}BN_4NaO_2$, $M_r = 382.20$, orthorhombic, *Pbca*, $a = 8.7633(6)$ Å, $b = 7.8939(6)$ Å, $c = 38.657(3)$ Å, $V = 2674.2(3)$ Å$^3$, $Z = 8$, $T = 193(2)$ K. A total of 14 428 reflections (2711 independent, $R_{int} = 0.0444$) were collected at low temperatures using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with Mo K$\alpha$ radiation ($\lambda = 0.710\ 73$ Å). The structures were solved by direct methods (SHELXS-97),[35] and all non-hydrogen atoms were refined anisotropically using the least-squares method on $F^2$.[36] The largest electron density residue was 0.290 e Å$^{-3}$, R1 (for $I > 2\sigma(I)$) = 0.0456 and wR2 = 0.1044 (all data), with $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = (\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)^{0.5}$. CCDC 209053 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033; e-mail deposit@ccdc.cam.ac.uk).

(13) (a) Gómez-Gallego, M.; Mancheño, M. J.; Ramírez, P.; Piñar, C.; Sierra, M. A. *Tetrahedron* **2000**, *56*, 4893. (b) Mancheño, M. J.; Sierra, M. A.; Gómez-Gallego, M.; Ramírez, P. *Organometallics* **1999**, *18*, 3252. For related rearrangements with other simple nucleophiles see: (c) Barluenga, J.; Rubio, E.; López-Pelegrín, J. A.; Tomás, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 1091. For additions of dihydropyridines see: (d) Rudler, H.; Parlier, A.; Martín-Vaca, B.; Garrier, E.; Vaissermann, J. *Chem. Commun.* **1999**, 1439. (e) Rudler, H.; Parlier, A.; Certal, V.; Vaissermann, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 3417.

(14) Ramírez-López, P.; Gómez-Gallego, M.; Mancheño, M. J.; Sierra, M. A.; Bilurbina, M.; Ricart, S. *J. Org. Chem.* **2003**, *68*, 3539.

(15) Fischer, H.; Märkl, R.; Zeuner, S. *J. Organomet. Chem.* **1985**, *286*, 17.

(16) The intramolecular insertion of the carbene ligand into the boron $C_\beta$−H bond in boroxycarbene has been reported: (a) Barluenga, J.; Rodríguez, F.; Vadecard, J.; Bendix, M.; Fañanás, F. J.; López-Ortiz, F. *J. Am. Chem. Soc.* **1996**, *118*, 6090. (b) Barluenga, J.; Rodríguez, F.; Vadecard, J.; Bendix, M.; Fañanás, F. J.; López-Ortiz, F.; Rodríguez, M. A. *J. Am. Chem. Soc.* **1999**, *121*, 8776. See also: (c) Barluenga, J.; Fañanás, F. J. *Tetrahedron* **2000**, *56*, 4597.

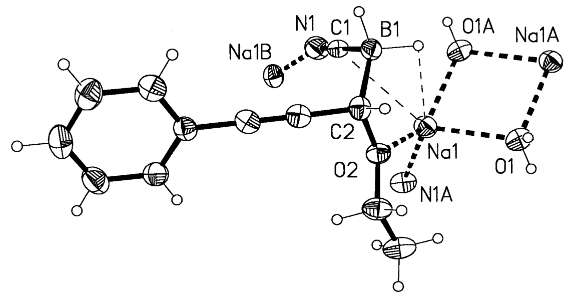
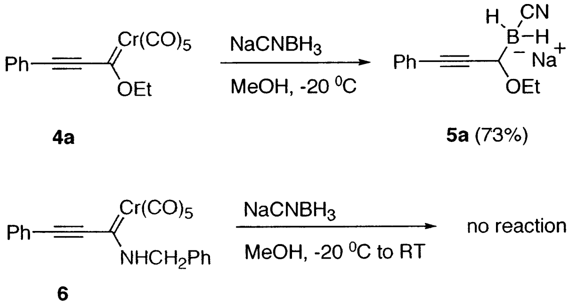


**Figure 1.** Representation of the asymmetric unit and atoms with a short contact of neighboring units in the crystal structure of **5a** (50% probability). Selected bond lengths (Å): Na1–O1 = 2.364(2), Na1–O1A = 2.385(2), Na1–O2 = 2.296(1), Na1–N1A = 2.384(2), Na1–C1 = 2.983(2), Na1–B1 = 3.020(2).

1).[16] The formation of the salt **5a** can be understood by means of an insertion of the carbene ligand into the B–H bond. In contrast, the aminocarbene **6** was completely unreactive toward $NaCNBH_3$, even when the reaction was carried out at room temperature (Scheme 4).

### Scheme 4

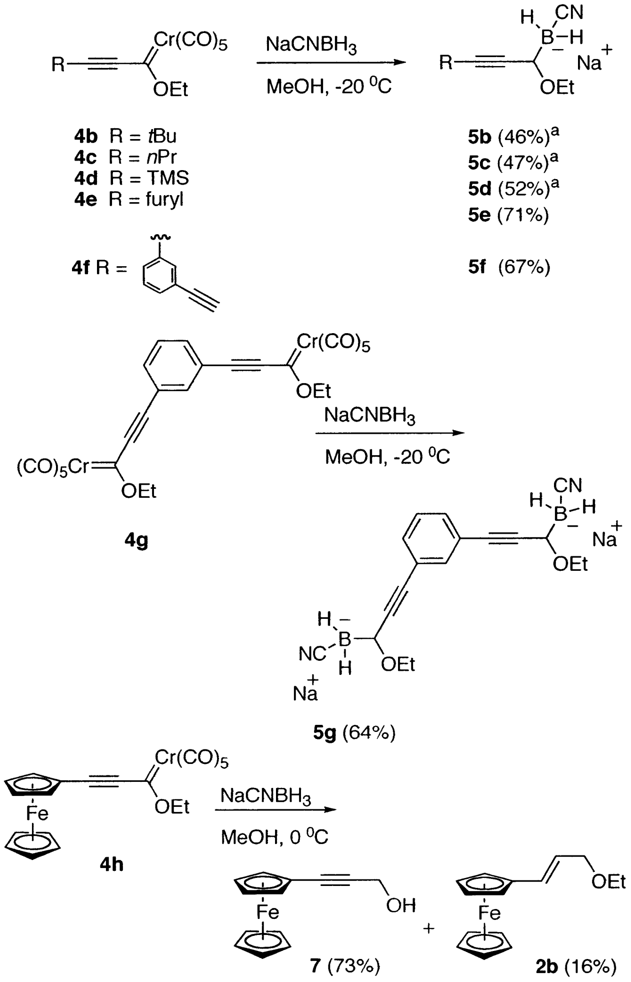


In the crystal structure of **5a** the sodium cation shows four short (Na–O1 = 2.364 Å, Na–O1A = 2.385 Å, Na–O2 = 2.296 Å, Na–N1A = 2.384 Å) and two longer (Na–B = 3.020 Å, Na–C1 = 2.983 Å) coordinations. The two water molecules form bridging groups, giving a dimeric motif. The nitrogen atom of the CN group connects this dimer to another one, forming a two-dimensional network.

It is thought that the different results obtained by Fischer (C–B insertion)[14] and in this work (B–H insertion) are related to the polarity of the solvent employed in the reactions. To discard this possibility, **4a** was reacted with $NaCNBH_3$ in $CH_2Cl_2$ and toluene at −20 °C. The starting complex **4a** was recovered unaltered after 48 h of reaction. To ensure that the inertia of **4a** toward $NaCNBH_3$ in aprotic solvents was not due to the low temperature used above, the analogous reactions were effected at room temperature with analogous results.

Alkynyl complexes **4b**–**f** also provided the corresponding boron salts **5b**–**f**. The alkyl-substituted compounds **5b**–**d** gave lower yields of isolated products due to the decomposition of the salts during the purification on silica gel, whereas aromatic compounds **4e**,**f** produced the more stable salts **5e**,**f** in good yields. Additionally, the bis(alkynyl)carbene **4g** reacted with $NaCNBH_3$ under conditions the same as those above to yield the double salt **5g** in 64% yield. The alkynylferrocene-substituted complex **4h** was considerably less reactive toward $NaCNBH_3$. In fact, in this case it was necessary to raise the temperature to 0 °C to observe a reaction. Under these conditions, alcohol **7** was obtained in 72% yield together with a small amount of allyl ether **2b** (Scheme 5).

### Scheme 5

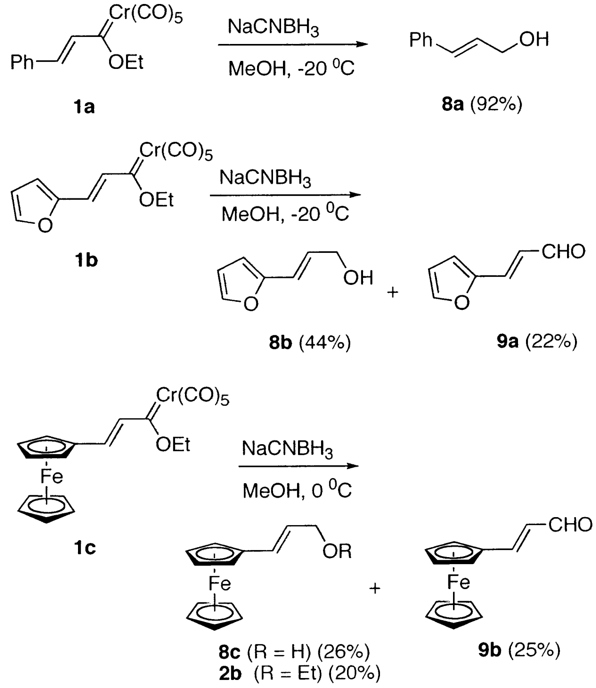


[a] Yields in pure crude product checked by NMR.

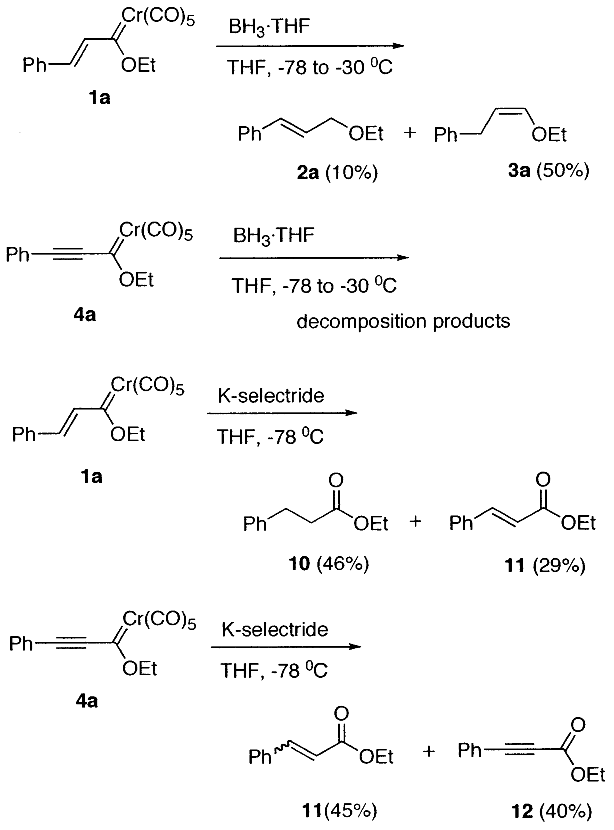
The reactivity of alkenylcarbene complexes **1a**–**c** toward $NaCNBH_3$ was also tested. The reaction of alkenylcarbene **1a** with $NaCNBH_3$ yielded alcohol **8a** in almost quantitative yield. This result was totally different from that reported previously by us for the reaction of the same compound with $NaBH_4$,[12a,b] in which vinyl ether **3a** (Scheme 2, Ar = Ph) was formed as the main product. On the other hand, the reduction of the furyl-substituted complex **1b** with $NaCNBH_3$ yielded alcohol **8b** (44%) and aldehyde **9a** (22%), whereas the alkenylferrocene carbene complex **1c** formed a mixture of alcohol **8c**, aldehyde **9b**, and ether **2b** in similar ratios (Scheme 6). Again, an increase of the temperature to 0 °C is required to observe the reaction in the case of the ferrocene-substituted complex **1c**. The corresponding boron salts analogous to **5** were not detected in any case.

Other boron hydrides were tested next. Thus, treatment of the alkenylcarbene complex **1a** with 1.5 equiv of a THF solution of borane at −30 °C yielded, after quenching with water and oxidation, a 4:1 mixture of

### Scheme 6



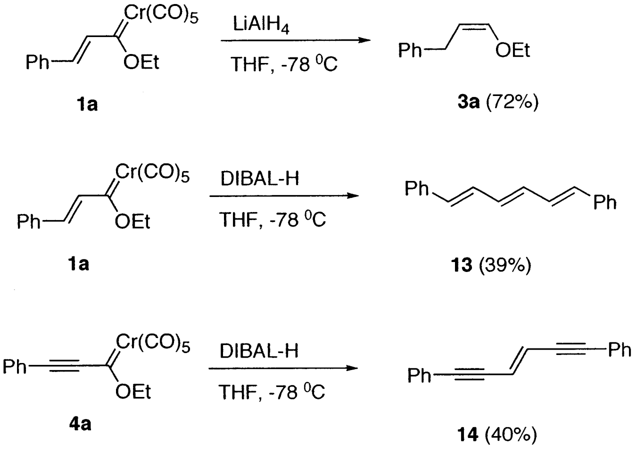
### Scheme 7



ethers **2a** and **3a** (Scheme 7). This result parallels those obtained previously by us in the reductions of α,*β*-unsaturated group 6 carbene complexes **1** with $NaBH_4$.[12a,b] Complex **4a** produced decomposition products under analogous conditions. The reduction of α,*β*-unsaturated Fischer carbene complexes with $BH_3{\cdot}SMe_2$ followed by oxidative quenching has been reported.[17] Under these conditions no migration of the $Cr(CO)_5$ fragment was observed and only alcohols and diols were obtained as reaction products. The bulky K-Selectride (potassium tri-*sec*-butylborohydride) exclusively reduced the C−C multiple bond in complexes **1a** and **4a**, yielding, after oxidation, esters **10** and **11**, respectively. The lower reactivity of the complexes **1a** and **4a** toward K-Selectride compared with that of the other boron hydrides tested is shown by the amount of unreacted starting material recovered in each case in the formation of the corresponding oxidation products **11** and **12**, respectively (Scheme 7).

The reactivity of **1a** and **4a** toward aluminum hydrides follows a different pattern. Treatment of alkenylcarbene **1a** with the very reactive $LiAlH_4$ at −78 °C in a THF solution yielded vinyl ether **3a** in excellent yield as the sole reaction product. Alkynylcarbene **4a** gave only a complex mixture of unidentifiable products under these reaction conditions. In contrast, the reaction of these complexes with the bulkier DIBAL-H at −78 °C in THF allowed the isolation of the corresponding dimerization products **13** and **14** as single isomers in 39% and 40% yields, respectively. The stereochemistry of the newly formed C=C bond was *E* in both cases, as determined by NMR and by comparison with the NMR data reported for authentic samples.[18,19] Interestingly, an increase of the temperature in the reduction process (−40 °C) resulted in the isolation of the dimerization products **13** and **14** as *Z*/*E* mixtures in analogous yields (Scheme 8). As stated above, complex **4a** was unreactive toward $NaCNBH_3$ in aprotic solvents. Therefore, it can be concluded that the different reaction patterns observed in the reaction of complex **4a** with DIBAL-H is not a consequence of the solvent change but of the hydride employed.

### Scheme 8



The behavior of the alkenyl and alkynyl Fischer carbene complexes studied in this work toward different boron and aluminum hydrides can be interpreted by following the mechanistic pathways proposed in Scheme 9. Thus, the formation of the boron salts **5** with $NaCNBH_3$ may be rationalized by assuming that the insertion of the carbene ligand into M−H bonds is a concerted [2 + 1] process.[3,5,20] This concerted pathway could justify the formation of salts **5a**−**g** from the

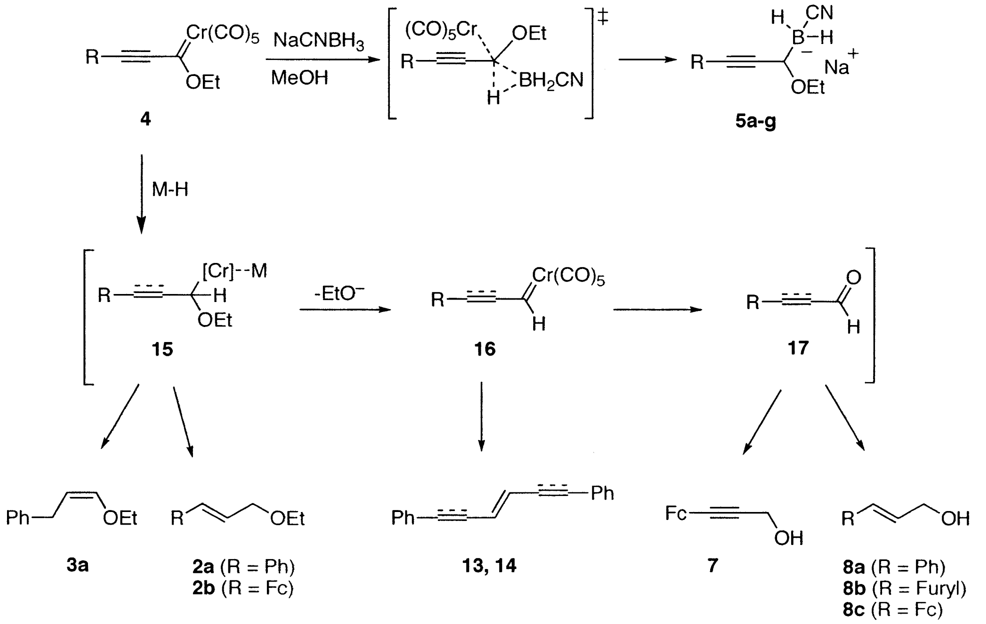
---

[17] Barluenga, J.; Granados, A.; Rodríguez, F.; Vadecard, J.; Fañanás, F. *Tetrahedron Lett.* **1997**, *38*, 6465.

[18] Kasahara, A.; Izumi, T.; Kudou, N. *Synthesis* **1988**, 704.

[19] Vollhardt, K. P. C.; Winn, L. S. *Tetrahedron Lett.* **1985**, *26*, 709.

**Scheme 9**



alkynyl complexes **4a**−**g**. However, this route is not able to explain the different outcome of the reaction with $NaCNBH_3$ in the case of alkenylcarbenes **1a**−**c** and the ferrocenyl alkynyl complex **4h**. In these cases no boron salts were detected but mixtures of products such as alcohols **7** and **8**, ethers such as **2b**, and aldehydes such as **9**. These products are not derived from the evolution of the boron salts **5** in the medium, since the salts only yield complex reaction mixtures when heated or treated under acidic or basic conditions. Another reasonable mechanistic alternative is to consider that the reaction starts from the hydride addition to the carbene carbon to form the common intermediate **15**. The salts **5** would be obtained by reductive elimination in **15**, whereas extrusion of ethoxide from this intermediate would lead to carbene intermediate **16**, which by oxidation forms aldehyde **17**, precursor of the alcohols **7** and **8** by further reduction. Alternatively, intermediate **15** could follow the pattern of reactivity described in Scheme 2 to form allyl ethers **2**. This route could also explain how ethers **2a** and **3a** are obtained in the reactions with $BH_3$·THF and $LiAlH_4$. On the other hand, the formation of stilbenes with DIBAL-H could be justified by dimerization of the nonstabilized intermediate complex **16**.[21] Finally, the bulky K-Selectride reacts in a different way, by addition to the carbene complexes in a conjugate fashion to yield, after oxidation, compounds **10** and **11**.

According to the proposed mechanistic scheme, the formation of stable boron salts derived from the insertion of the carbene ligand into the B−H bond is closely related to the electrophilicity of the carbene carbon and the hydride employed. These factors should be finely tuned to obtain the insertion products. Therefore, no insertions are observed with boron hydrides, except for $NaCNBH_3$, a reagent in which the reduction ability is greatly diminished with respect to that of $NaBH_4$ by the presence of the CN group.[22] This fact allows the carbene B−H insertion. Meanwhile, a decrease in the electrophilicity of the carbene carbon leads to a drastic reduction of the reactivity of the complex. Thus, the alkynylaminocarbene **6** was unreactive toward $NaCNBH_3$ and ferrocene-substituted $\alpha,\beta$-unsaturated carbenes **1c** and **4h** require higher reaction temperatures to react.[23] The mechanism proposed in Scheme 9 also rationalizes the behavior of the other hydrides tested, and in each case, the reaction products depend on the evolution of the different intermediates formed.

In conclusion, the reaction of $\alpha,\beta$-unsaturated chromium(0) complexes and hydrides leads to different products, depending on the electronic properties of the reducing agent and the carbene carbon. Electrophilic alkynylcarbene complexes react with $NaCNBH_3$ to produce compounds derived from the insertion of the carbene ligand into the B−H bond in a process that has no precedent in the literature. This reaction does not take place if the electrophilicity of the carbene carbon is disminished by the presence of an amino group (as in aminocarbenes) or by conjugation with a ferrocene substituent.[23] However, the behavior of alkenylcarbene complexes toward $NaCNBH_3$ can be interpreted by initial addition of the hydride to the C−Cr bond followed by evolution of the intermediate thus formed, through different reaction pathways. These include chromium 1,3-migration and alkoxide extrusion followed by dimerization or oxidation. This route also justifies the reactiv-

---

(20) Connor, J. A.; Day, J. P.; Turner, R. M. *J. Chem. Soc., Dalton Trans.* **1976**, 108.

(21) The spontaneous dimerization of nonstabilized group 6 Fischer carbene complexes has been reported; see: (a) Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127. (b) Fischer, H.; Zeuner, S.; Ackermann, K. *J. Chem. Soc., Chem. Commun.* **1984**, 684.

(22) (a) Pelter, A.; Smith, K. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Pergamon: Oxford, U.K., 1979; Vol. 3, p 781. For a complete overview of hydride reductors see: (b) Brown, H. C.; Krishnamurthy, S. *Tetrahedron* **1979**, *35*, 567.

(23) The strong electron-donating effect of a ferrocene in group 6 Fischer carbene complexes has been reported; see: (a) Jayaprakash, K. N.; Ray, P. C.; Matsuoka, I.; Bhadbhade, M. M.; Puranik, V. G.; Das, P. K.; Nishihara, H.; Sarkar, A. *Organometallics* **1999**, *18*, 3851. For a study of the correlation of $^{53}$Cr NMR chemical shifts with the donor−acceptor properties of the carbene ligands, see: (b) Hafner, A.; Hegedus, L. S.; de Neck, G.; Hawkins, B.; Dotz, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 8413.

(24) Aumann, R.; Heinen, H. *Chem. Ber.* **1987**, *120*, 537.

ity of alkenyl and alkynyl alkoxy Fischer carbene complexes toward other boron or aluminum hydrides. Finally, when a bulky reagent such as K-Selectride is employed, the 1,2-hydride addition is disfavored and only products derived from the reduction of the C−C multiple bonds are obtained.

## Experimental Section

**General Procedures.** $^1$H NMR and $^{13}$C NMR spectra were obtained on a Varian XL-300S (299.94 MHz for $^1$H and 75.43 MHz for $^{13}$C), a Bruker 200-AC (200.13 MHz for $^1$H and 50.03 MHz for $^{13}$C), or a Bruker Avance-300 spectrometer (300.13 MHz for $^1$H and 75.48 MHz for $^{13}$C) and recorded at 20 °C. Chemical shifts are given in ppm relative to TMS ($^1$H, 0.0 ppm), $CD_3OD$ ($^1$H, 3.31 ppm), $CDCl_3$ ($^{13}$C, 77.0 ppm), or $CD_3OD$ ($^{13}$C, 49.0 ppm). IR spectra were taken on a Perkin-Elmer 781 spectrometer. Melting points were determined in a Gallenkamp melting point apparatus in open capillaries and are uncorrected. Compounds **5** decomposed before melting when heated at temperatures above 130 °C. Flame-dried glassware and standard Schlenk techniques were used for all the reactions. Merck silica gel (230−400 mesh) was used as the stationary phase for purification of crude reaction mixtures by flash chromatography. Identification of products was made by TLC (Kiesegel 60F-254), with UV light ($\lambda$ 254 nm). A 10% phosphomolybdic acid solution in EtOH and iodine were also used to develop the plates. All commercially available compounds were used without further purification. The following products were prepared according to literature methods: **1a**,[24] **1b**,[24] **1c**,[25] **4a**,[26] **4b**,[27] **4c**,[27] **4d**,[26,27] **4f**,[28] **4g**,[28] **4h**,[29] and **6**.[30]

**Synthesis of Pentacarbonyl[ethoxy(2-furylethynyl)-carbene]chromium(0) (4e).** *n*-BuLi in hexanes (6.1 mL, 9.7 mmol, 1.6 M) was added to a solution of 2-ethynylfuran[31] (0.75 g, 8.1 mmol) in 40 mL of anhydrous $Et_2O$ cooled to −78 °C. After it was stirred for 50 min at −78 °C, the solution was warmed for 15 min and transferred via cannula into a suspension of $Cr(CO)_6$ (1.78 g, 8.1 mmol) in 40 mL of $Et_2O$ at 0 °C. The reaction mixture was warmed to room temperature and stirred for 1 h before 40 mL of anhydrous THF was added, and the stirring was continued overnight. Then, the solution was cooled to −78 °C, $Et_3OBF_4$ (3.08 g, 16.2 mmol) was added, and the stirred mixture was warmed and kept for 1 h at room temperature. Finally, the crude reaction was concentrated and filtered through Celite ($Et_2O$), the solvent was removed in vacuo, and the residue was purified by flash column chromatography on silica gel (hexane) to afford 1.99 g (72%) of **4e** as a green solid. $^1$H NMR (300 MHz, $CD_3Cl$): $\delta$ 1.48 (t, $J = 7.1$ Hz, 3H, $CH_3$), 4.61 (q, $J = 7.1$ Hz, 2H, $CH_2$), 6.54 (dd, $J_1 = 3.5$ Hz, $J_2 = 1.8$ Hz, 1H, furyl), 7.05 (d, $J = 3.5$ Hz, 1H, furyl), 7.59 (m, 1H, furyl). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 308.5 (Cr=C), 225.6 (CO-trans), 216.2 (CO-cis), 148.1, 135.0 (furyl), 126.1 (C≡), 124.9, 113.4 (furyl), 96.7 (Ar−C≡), 76.3 ($CH_2$), 14.9 ($CH_3$). IR (KBr): 2129 (C≡C), 2058 (CO-trans), 1998, 1932 (CO-cis) cm$^{-1}$. Anal. Calcd for $C_{14}H_8CrO_7$; C, 49.43; H, 2.37. Found: C, 49.56; H, 2.53.

**General Procedure for the Reaction with $NaCNBH_3$.** A solution of $NaCNBH_3$ in $CH_3OH$ was placed, at −20 °C, in a flame-dried airless flask containing a magnetic stirring bar, degassed by evacuation/back-fill with argon (3×). Then, a solution of the carbene complex in $CH_3OH$ was added by syringe at −20 °C and the mixture was stirred at this temperature until the complete disappearance of the starting material (checked by TLC). The reaction mixture was quenched with 0.1 mL 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 crude mixture was filtered through Celite (AcOEt), the solvent was removed in vacuo, and the residue was purified by flash column chromatography.

**Reaction of 4a with $NaCNBH_3$ in $CH_3OH$.** The general procedure was followed by using 250 mg (0.71 mmol) of **4a** and 47 mg (0.71 mmol) of $NaCNBH_3$ (95%). After 1 h of reaction, quenching with water, and further oxidation of the reaction mixture, the boron salt **5a** was obtained as a yellow viscous oil (141 mg, 83% pure by $^1$H NMR). This product was washed with $CHCl_3$ to afford 124 mg (73%) of **5a** as a white solid. $^1$H NMR (200 MHz, $CD_3OD$): $\delta$ 1.20 (t, $J = 7.1$ Hz, 3H, $CH_3$), 3.43 (dq, $J_1 = 9.8$ Hz, $J_2 = 7.1$ Hz, 1H, *H*CH), 3.80−3.92 (m, 2H, HC*H* + CH), 7.21−7.33 (m, 5H, Ph). $^{13}$C NMR (50 MHz, $CD_3OD$): $\delta$ 132.0, 129.0, 127.8, 126.1 (Ph), 96.5, 85.5 (C≡C), 69.4 (bs, CH), 66.1 ($CH_2$), 15.4 ($CH_3$). IR (KBr): 3568, 3466, 2363, 2289, 2158, 1618, 1059 cm$^{-1}$. Anal. Calcd for $C_{12}H_{13}BNNaO{\cdot}H_2O$: C, 60.29; H, 6.32; N, 5.86. Found: C, 60.13; H, 6.21; N, 5.73.

**Reaction of 4b with $NaCNBH_3$ in $CH_3OH$.** The general procedure was followed by using 299 mg (0.90 mmol) of **4b** and 60 mg (0.90 mmol) of $NaCNBH_3$ (95%). After 1 h of reaction, quenching with water, and further oxidation of the reaction mixture, the boron salt **5b** was obtained as a yellow viscous oil (90 mg, 46%, pure by $^1$H NMR). The chromatography on silica gel of the crude oil (hexane/AcOEt 1:1 to AcOEt) afforded 39 mg (20%) of **5b** as a white solid. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 0.95−1.19 (m, 12H, $3CH_3 + CH_3$), 3.38 (dq, $J_1 = 9.6$ Hz, $J_2 = 7.1$ Hz, 1H, *H*CH), 3.68 (bs, 1H, CH), 3.79 (dq, $J_1 = 9.6$ Hz, $J_2 = 7.1$ Hz, 1H, HC*H*). $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ 93.7, 84.8 (C≡C), 68.5 (bs, CH), 65.4 ($CH_2$), 32.0 ($Me_3C$), 28.5 ($Me_3C$), 15.5 ($CH_3$). IR (KBr): 3420, 3018, 2253, 2104, 1065 cm$^{-1}$. This compound was unstable on silica gel and could not be obtained in analytically pure form.

**Reaction of 4c with $NaCNBH_3$ in $CH_3OH$.** The general procedure was followed by using 500 mg (1.58 mmol) of **4c** and 104 mg (1.58 mmol) of $NaCNBH_3$ (95%). After 1 h of reaction, quenching with water, and further oxidation of the reaction mixture, boron salt **5c** was obtained as a yellow viscous oil (151 mg, 47%, pure by $^1$H NMR). The chromatography on silica gel of the crude oil (hexane/AcOEt 1:1 to AcOEt) afforded 94 mg (29%) of **5c** as a white solid. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 0.91 (t, $J = 7.1$ Hz, 3H, $CH_3$), 1.20 (t, $J = 7.1$ Hz, 3H, $OCH_2CH_3$), 1.45 (sext, $J = 7.1$ Hz, 2H, $CH_2$), 2.14 (m, 2H, $CH_2C{\equiv}$), 3.44 (m, 1H, *H*CH), 3.77 (m, 2H, HC*H* + CH). IR (KBr): 3414, 3018, 2966, 2933, 2399, 2345, 2262, 2179, 1637, 1059 cm$^{-1}$. This compound was very unstable on silica gel and could not be obtained in analytically pure form.

**Reaction of 4d with $NaCNBH_3$ in $CH_3OH$.** The general procedure was followed by using 250 mg (0.72 mmol) of **4d** and 48 mg (0.72 mmol) of $NaCNBH_3$ (95%). After 1 h of reaction, quenching with water, and further oxidation of the reaction mixture, **5d** was obtained as a yellow viscous oil (88 mg, 52%, pure by $^1$H NMR). The chromatography on silica gel of the crude oil (hexane/AcOEt 1:1 to AcOEt) afforded 44 mg (26%) of **5d** as a white solid. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 0.20 (s, 9H, $3CH_3$), 1.17 (t, $J = 7.1$ Hz, 3H, $CH_3$), 3.55 (dq, $J_1 = 9.8$ Hz, $J_2 = 7.1$ Hz, 1H, *H*CH), 3.82−4.03 (m, 2H, HC*H* + CH). $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ 101.3, 90.6 (C≡C), 67.0 (bs, CH), 65.6 ($CH_2$), 15.0 ($CH_3$), −0.2 ($Si(CH_3)_3$). IR (KBr):

---

(25) Jayaprakash, K. N.; Ray, P. C.; Matsuoka, I.; Bhadbhade, M. M.; Puranik, V. G.; Das, P. K.; Nishihara, H.; Sarkar, A. *Organometallics* **1999**, *18*, 3851.

(26) Aumann, R.; Hinterding, P. *Chem. Ber.* **1993**, *126*, 421.

(27) (a) Duetsch, M.; Stein, F.; Lackmann, R.; Pohl, E.; Herbst-Irmer, R.; de Meijere, A. *Chem. Ber.* **1992**, *125*, 2051. (b) Chan, K. S.; Wulff, W. D. *J. Am. Chem. Soc.* **1986**, *108*, 5229.

(28) Fernández, I.; Sierra, M. A.; Mancheño, M. J.; Gómez-Gallego, M.; Ricart, S. *Organometallics* **2001**, *20*, 4304.

(29) Sierra, M. A.; Mancheño, M. J.; del Amo, J. C.; Fernández, I.; Gómez-Gallego, M.; Torres, M. R. *Organometallics* **2003**, *22*, 384.

(30) Complex **6** was prepared by following the method reported by Fischer for the aminolysis of alkoxychromium(0) carbene complexes: Klabunde, U.; Fischer, E. O. *J. Am. Chem. Soc.* **1967**, *89*, 7141.

(31) Carpita, A.; Rossi, R.; Veracini, C. A. *Tetrahedron* **1985**, *41*, 1919.

3416, 2349, 2260, 2177, 2152, 1647, 1250, 1051 cm$^{-1}$. This compound was very unstable on silica gel and could not be obtained in analytically pure form.

**Reaction of 4e with NaCNBH$_3$ in CH$_3$OH.** The general procedure was followed by using 310 mg (0.91 mmol) of **4e** and 60 mg (0.91 mmol) of NaCNBH$_3$ (95%). After 1 h of reaction, quenching with water, and further oxidation of the reaction mixture **5e** was obtained as a yellow viscous oil (168 mg, 81%, pure by $^1$H NMR). The chromatography on silica gel of the crude oil (hexane/AcOEt 1:1 to AcOEt) afforded 148 mg (71%) of **5e** as a white solid. $^1$H NMR (300 MHz, CD$_3$OD): $\delta$ 1.18 (t, $J = 7.0$ Hz, 3H, CH$_3$), 3.44 (dq, $J_1 = 9.5$ Hz, $J_2 = 7.0$ Hz, 1H, *H*CH), 3.75−3.90 (m, 2H, HC*H* + CH), 6.37 (dd, $J_1 =$ 3.2 Hz $J_2 = 1.8$ Hz, 1H, furyl), 6.42 (d, $J = 3.2$ Hz, 1H, furyl), 7.37 (m, 1H, furyl). $^{13}$C NMR (75 MHz, CD$_3$OD): $\delta$ 143.6, 139.7, 114.2, 111.6 (furyl), 100.6, 75.7 (C≡C), 68.2 (bs, CH), 66.3 (CH$_2$), 15.4 (CH$_3$). IR (KBr): 3566, 3402, 2347, 2272, 2181, 2110, 1624, 1059 cm$^{-1}$. Anal. Calcd for $C_{10}H_{11}BNNaO_2 \cdot H_2O$: C, 52.44; H, 5.72; N, 6.12. Found: C, 52.30; H, 5.84; N, 5.98.

**Reaction of 4f with NaCNBH$_3$ in CH$_3$OH.** The general procedure was followed by using 250 mg (0.67 mmol) of **4f** and 44 mg (0.67 mmol) of NaCNBH$_3$ (95%). After 1 h of reaction, quenching with water, and further oxidation of the reaction mixture, **5f** was obtained as a yellow viscous oil (150 mg, 85%, pure by $^1$H NMR). The chromatography on silica gel of the crude oil (hexane/AcOEt 1:1 to AcOEt) afforded 118 mg (67%) of **5f** as a white solid. $^1$H NMR (300 MHz, CD$_3$OD): $\delta$ 1.20 (t, $J = 7.1$ Hz, 3H, CH$_3$), 3.42−3.52 (m, 2H, *H*CH + HC≡), 3.81−3.91 (m, 2H, HC*H* + CH), 7.22−7.41 (m, 4H, Ph). $^{13}$C NMR (75 MHz, CD$_3$OD): $\delta$ 135.3, 132.4, 131.3, 129.4, 126.8, 123. 7 (Ph), 97.8, 84.6, 83.7, 78.8 (C≡C), 68.0 (bs, CH), 66.3 (CH$_2$), 15.5 (CH$_3$). IR (KBr): 3552, 3462, 2353, 2285, 2185, 1622, 1059 cm$^{-1}$. Anal. Calcd for $C_{14}H_{13}BNNaO \cdot H_2O$: C, 63.92; H, 5.75; N, 5.32. Found: C, 64.01; H, 5.63; N, 5.29.

**Reaction of 4g with NaCNBH$_3$ in CH$_3$OH.** The general procedure was followed by using 500 mg (0.80 mmol) of **4g** and 106 mg (1.60 mmol) of NaCNBH$_3$ (95%). After 1 h of reaction, quenching with water, and further oxidation of the reaction mixture, **5g** was obtained as a yellow viscous oil (223 mg, 70%, pure by $^1$H NMR). The chromatography on silica gel of the crude oil (hexane/AcOEt 1:1 to MeOH) afforded 205 mg (64%) of **5g** as a white solid. $^1$H NMR (300 MHz, CD$_3$OD): $\delta$ 1.20 (t, $J = 7.1$ Hz, 6H, CH$_3$), 3.53 (dq, $J_1 = 9.4$ Hz, $J_2 = 7.1$ Hz, 2H, *H*CH), 3.82−3.92 (m, 4H, HC*H* + CH), 7.15−7.31 (m, 4H, Ph). $^{13}$C NMR (75 MHz, CD$_3$OD): $\delta$ 134.5, 130.6, 128.9, 126.2 (Ph), 96.9, 85.0 (C≡C), 68.6 (bs, CH), 66.2 (CH$_2$), 15.4 (CH$_3$). IR (KBr): 3393, 2974, 2872, 2345, 2185, 1593, 1475, 1063 cm$^{-1}$. Anal. Calcd for $C_{18}H_{20}B_2N_2Na_2O_2 \cdot 2H_2O$: C, 54.05; H, 6.05; N, 7.00. Found: C, 53.86; H, 6.16; N, 6.87.

**Reaction of 4h with NaCNBH$_3$ in CH$_3$OH.** The general procedure was followed by using 250 mg (0.55 mmol) of **4h** and 36 mg (0.55 mmol) of NaCNBH$_3$ (95%). After 1 h of reaction at 0 °C the crude reaction mixture was quenched with water, concentrated under reduced pressure, and air-oxidized under sunlight. The $^1$H NMR spectrum of the crude mixture showed a mixture of ether **2b** and alcohol **7**. The products were separated by flash column chromatography on silica gel (hexane/AcOEt 100:1 to AcOEt). **2b** (24 mg, 16%) was obtained as a orange solid: mp 83−85 °C; $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 1.17 (t, $J = 7.0$ Hz, 3H, CH$_3$), 3.45 (q, $J = 7.0$ Hz, 2H, OCH$_2$), 3.93 (dd, $J_1 = 6.3$ Hz, $J_2 = 1.3$ Hz, 2H, =CHC*H*$_2$), 4.03 (s, 5H, Cp), 4.12−4.13 (m, 2H, Cp), 4.25−4.27 (m, 2H, Cp), 5.82 (dt, $J_1 = 15.7$ Hz, $J_2 = 6.3$ Hz, 1H, =C*H*CH$_2$), 6.26 (d, $J = 15.7$ Hz, 1H, =C*H*Cp); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$ 130.2, 123.7 (C=C), 82.6 (Cp), 71.4 (=CH*C*H$_2$), 69.1, 68.6, 66.8 (Cp), 65.2 (CH$_2$), 15.2 (CH$_3$); IR (film) 2247, 2166, 1952 (C−OEt) cm$^{-1}$. **7** (95 mg, 73%) was obtained as an orange solid: $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 1.71 (t, $J = 1.7$ Hz, 1H, OH), 4.12−4.14 (m, 7H, Cp + CH$_2$), 4.34−4.35 (m, 4H, Cp). $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$ 84.5, 83.7, 71.4, 69.9, 68.7, 64.4 (Cp + C≡C), 51.8 (CH$_2$); IR (KBr) 3400 (OH), 2243, 2216 (C≡C), 2185 cm$^{-1}$.

**Reaction of 1a with NaCNBH$_3$ in CH$_3$OH.** The general procedure was followed by using 352 mg (1.00 mmol) of **1a** and 66 mg (1.00 mmol) of NaCNBH$_3$ (95%). After 1 h of reaction, quenching, and further oxidation of the reaction mixture the crude mixture was purified by chromatography on silica gel (hexane/AcOEt 10:1) to afford 124 mg (92%) of (*E*)-3-phenyl-2-propenol (**8a**) as a colorless oil. The NMR data of this compound were identical with those obtained from a commercial sample (Fluka).

**Reaction of 1b with NaCNBH$_3$ in CH$_3$OH.** The general procedure was followed by using 250 mg (0.73 mmol) of **1b** and 48 mg (0.73 mmol) of NaCNBH$_3$ (95%). After 1 h of reaction the crude reaction mixture was quenched with 0.1 mL of water, concentrated under reduced pressure, and air-oxidized under sunlight. The $^1$H NMR spectrum of the reaction crude showed a mixture of (*E*)-3-(2-furyl)-2-propenol (**8b**) and (*E*)-3-(2-furyl)-2-propenal (**9a**). The products were separated by flash column chromatography on silica gel (hexane/AcOEt 10:1 to hexane/AcOEt 10:2). (*E*)-3-(2-Furyl)-2-propenal (20 mg, 22%) was obtained as a white solid, and its NMR data were identical with those obtained from a commercial sample (Aldrich). (*E*)-3-(2-Furyl)-2-propenol (40 mg, 44%) was obtained as a colorless oil, and its $^1$H NMR data were identical with those previously reported.[32]

**Reaction of 1c with NaCNBH$_3$ in CH$_3$OH.** The general procedure was followed by using 250 mg (0.54 mmol) of **1c** and 36 mg (0.54 mmol) of NaCNBH$_3$ (95%). After 1 h of reaction at 0 °C the crude reaction mixture was quenched with water, concentrated under reduced pressure, and air-oxidized under sunlight. The $^1$H NMR spectrum of the crude mixture showed a mixture of ether **2b**, alcohol **8c**, and aldehyde **9b**. The products were separated by flash column chromatography on silica gel (hexane/AcOEt 100:1 to AcOEt). **2b** (29 mg, 20%) was obtained as an orange solid. **9b** (32 mg, 25%) was obtained as a red solid (mp 90−92 °C), and **8c** (34 mg, 26%) was obtained as a yellow solid (mp 66−68 °C). In all cases the NMR data were identical with those previously reported.[33,34]

**Reaction of 1a with BH$_3$·THF.** A solution of 250 mg (0.71 mmol) of **1a** in 40 mL of anhydrous THF at −78 °C was placed in a flame-dried airless flask containing a magnetic stirring bar, degassed by evacuation/back-fill with argon (3×). Then, 1.06 mL (1.06 mmol) of a solution of BH$_3$ (1.0 M in THF) was added by syringe over a period of 10 min. This solution was warmed to −30 °C until complete disappearance of the starting material (checked by TLC). The reaction mixture was quenched with 0.1 mL of water, concentrated under reduced pressure, and air-oxidized under sunlight. The $^1$H NMR spectrum of the crude reaction mixture showed a 4:1 mixture of ethers **3a** and **2a**, which were separated by chromatography on silica gel (hexane/CH$_2$Cl$_2$ 8:1 to AcOEt.). Both **3a** (58 mg, 50%) and **2a** (12 mg, 10%) were obtained as colorless oils, and their spectroscopic data were identical with those reported previously.[12a,b]

**Reaction of 1a with K-Selectride.** To a solution of 250 mg (0.71 mmol) of **1a**, in anhydrous THF at −78 °C, was added by syringe 0.78 mL (0.78 mmol) of a solution of K-Selectride (1.0 M in THF) over a period of 10 min, and the mixture was stirred at this temperature until the complete disappearance of the starting material (checked by TLC). After 1 h of reaction, quenching with water, and further oxidation of the reaction mixture, a colorless oil (106 mg) was obtained. The $^1$H NMR spectrum of the crude reaction mixture showed the presence of ethyl 3-phenylpropionate (**10**) and (*E*)-ethyl cinnamate (**11**)

---

(32) Turnbull, M. D. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1241.

(33) Akiyama, A.; Hattori, T.; Ito, K.; Uryu, T.; Kajitani, M.; Sugimori, A. *Chem. Lett.* **1980**, 361.

(34) Catasús, M.; Bueno, A.; Moyano, A.; Maestro, M. A.; Mahía, J. *J. Organomet. Chem.* **2002**, *642*, 212.

(35) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473.

(36) Sheldrick, G. M. SHELXL-97, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.

in a 3:2 ratio. After chromatography on silica gel (hexane) 58 mg (46%) of **10** and 36 mg (29%) of **11** were obtained. Both compounds were identical with the corresponding authentic samples.

**Reaction of 4a with K-Selectride.** This reaction was carried out as described above, starting from 250 mg (0.71 mmol) of **4a** and 0.78 mL (0.78 mmol) of a solution of K-Selectride (1.0 M in THF). After 1 h of reaction, quenching with water, and further oxidation of the reaction mixture a colorless oil (121 mg) was obtained. The $^1$H NMR spectrum of the crude reaction mixture showed a 1:1 mixture of (*E*)-/(*Z*)-ethyl cinnamate (**11**) and ethyl phenylpropiolate (**12**). Trace amounts of ethyl 3-phenylpropionate were also detected. After chromatography on silica gel (hexane) 56 mg (45%) of **11** and 50 mg (40%) of **12** were obtained. Both compounds were identical with the corresponding authentic samples.

**Reaction of 1a with $LiAlH_4$ in THF.** A suspension of 28 mg (0.71 mmol) of $LiAlH_4$ (95%) in 40 mL of anhydrous THF at −78 °C was placed in a flame-dried airless flask containing a magnetic stirring bar, degassed by evacuation/back-fill with argon (3×). Then, a solution of 250 mg (0.71 mmol) of **1a** in 10 mL of anhydrous THF at −78 °C was carefully added via cannula over a period of 30 min and the mixture was stirred at this temperature until the complete disappearance of the starting material (checked by TLC). The reaction mixture was quenched with 0.1 mL of water, filtered through Celite, concentrated under reduced pressure, and air-oxidized under sunlight. The solvent was removed under vacuum, and the residue was chromatographed on silica gel (hexane/$CH_2Cl_2$ 8:1) to afford 83 mg (72%) of **3a** as colorless oil. The NMR data of **3a** were identical with those reported previously.[12a,b]

**Reaction of 1a with DIBAL-H.** To a solution of 250 mg (0.71 mmol) of **1a** in anhydrous THF at −78 °C was added by syringe 1.42 mL (1.42 mmol) of a solution of DIBAL-H (1.0 M in THF) over a period of 10 min, and the mixture was stirred at this temperature until the complete disappearance of the starting material (checked by TLC). The reaction mixture was quenched with 0.1 mL of water, filtered through Celite, concentrated under reduced presure, and air-oxidized under sunlight. The crude reaction mixture was purified by chromatography on silica gel (hexane) to afford 32 mg (39%) of (*E*,*E*,*E*)-1,6-diphenyl-1,3,5-hexatriene (**13**) as a solid. Mp: 197−199 °C (lit.[17] mp 197−200 °C). This product was identified by comparison of its $^1$H NMR,$^{13}$C NMR, and IR data with the corresponding data reported for an authentic sample.[18]

**Reaction of 4a with DIBAL-H.** The reaction was carried out as described above, starting from 250 mg (0.71 mmol) of **4a** and 2.84 mL (2.84 mmol) of a solution of DIBAL-H (1.0 M in THF). Purification of the crude reaction mixture by chromatography on silica gel (hexane) yielded 29 mg (40%) of (*E*)-1,6-diphenyl-3-hexene-1,5-diyne (**14**) as a low-melting solid. This product was identified by comparison of its $^1$H NMR,$^{13}$C NMR, and IR data with the corresponding data reported for an authentic sample.[19]

**Acknowledgment.** Financial support by the Spanish Ministerio de Ciencia y Tecnología (Grant No. BQU2001-1283) and Comunidad Autónoma de Madrid (Grant No. CAM07M-0043/2002) is gratefully acknowledged. P.R.-L. thanks the Comunidad Autónoma de Madrid for a fellowship (Programa de Incorporación de Técnicos a Grupos de Investigación).

**Supporting Information Available:** Tables giving X-ray characterization data for compound **5a**; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM034010V