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On the Reduction of α,β-Unsaturated (Group 6) Carbene Complexes by $NaBH_4$[1]

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Abstract—Chromium and tungsten styryl Fischer carbene complexes **12** and **15** were transformed into *Z*-vinyl ether **13** and *E*-allyl ether **14** by $NaBH_4$ reduction in EtOH. Deuterium labeling experiments demonstrate that the reaction occurs by the initial addition of the hydride to the carbene carbon atom, followed by a 1,3-rearrangement of the $M(CO)_5$ fragment. The process could involve the participation of an η^3-allyl chromium intermediate. The reaction is general and has been applied to a series of α,β-unsaturated alkoxy and aminocarbene complexes. In the case of chromium and tungsten alkynyl carbenes **38** and **39**, $NaBH_4$ reduction exclusively yields *E*-allyl ether **14**. The intermediacy of an allenyl complex **41** obtained after the 1,3-rearrangement of the metal center is confirmed by deuterium labeling experiments. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

Although the knowledge about the reactivity of group 6 metal carbene complexes has grown exponentially during the last 20 years,[2] our understanding of the mechanisms of the reactions involved do not parallel these results. Due to the seminal work of Bernasconi, processes like α-deprotonation,[3] or addition of nucleophiles to the carbene carbon atom on simple chromium complexes,[4] are now more intimately known. However, the reaction mechanism for other processes such as the cocyclization of an α,β-unsaturated chromium carbene complex and an alkyne (Dötz reaction),[5] in difference the most thoroughly studied reaction of this kind of complexes, is still under a passionate debate. In other cases, the well accepted mechanisms are based mainly on indirect evidence. This is the case, for example, of the photochemical carbonylation of chromium carbene complexes, that it is believed to generate metal-bounded ketenes.[2j,6a] Nevertheless, the sole reported attempt, made to detect the formation of such intermediates, occurred with no success.[6b]

The isolobal analogy principle[7] states that α,β-unsaturated alkoxychromium(0) carbenes should behave as α,β-unsaturated organic esters in processes taking place outside of the coordination sphere of the metal.[2] In consequence, such complexes may be regarded as a kind of super-esters, with their reactivity enhanced due to the presence of a metal in their structures. Processes such as Diels–Alder,[8] 1,3-dipolar,[21] and [2+2] cycloadditions[9] have been reported with no essential changes in the nature of the reaction products with respect to those described for organic esters. Logically, when the metal takes an active role in the process, (like in Dotz's benzannulation)[5], new types of products, unknown for their organic counterparts, were obtained. In this context, the behavior of α,β-unsaturated alkoxychromium(0) carbenes and α,β-unsaturated organic esters towards the addition of nucleophiles, should be similar. The competition between 1,2- and 1,4-addition of dimethylamine to alkynylcarbene complexes of chromium and tungsten, was reported in 1972 by Fischer,[10] but the factors controlling the chemoselectivity of these processes are not yet fully understood. As an example, in an early report, Casey[11] stated that the conjugate addition of enolate anions to vinyl carbene complexes is controlled mainly by steric effects, while more recent work[12] describes the preferred conjugated addition, in spite of unfavorable steric effects. On the other hand, the decisive influence of the reagent in the chemoselectivity of the reaction is exemplified by the addition of $ZnEt_2$ and ArLi to alkynyl complexes, to yield 1,2-adducts exclusively.[13] Our own findings[14] in this field have shown that heteronucleophiles may form either 1,4- or 1,2-adducts depending on the case, and that factors other than the steric hindrance may control the chemoselectivity of these processes. Among many other examples the reaction of complex **1** with phosphorous ylides **2** gave exclusively 1,2-adducts **3**, while the conjugated addition of sulfur ylides **4** to give cyclopropanes **5**, is strongly dependent on the ylide stabilization and the reaction conditions (Scheme 1).[14d]

An additional variable to be taken into consideration in the addition of nucleophiles to α,β-unsaturated carbene complexes, is the possibility of the active participation of

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Keywords: organometallic mechanism; metal carbenes; hydride reduction; 1,3-metal migration.

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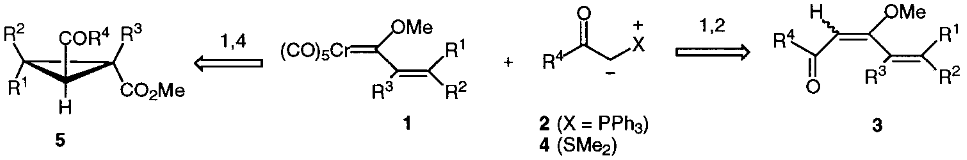
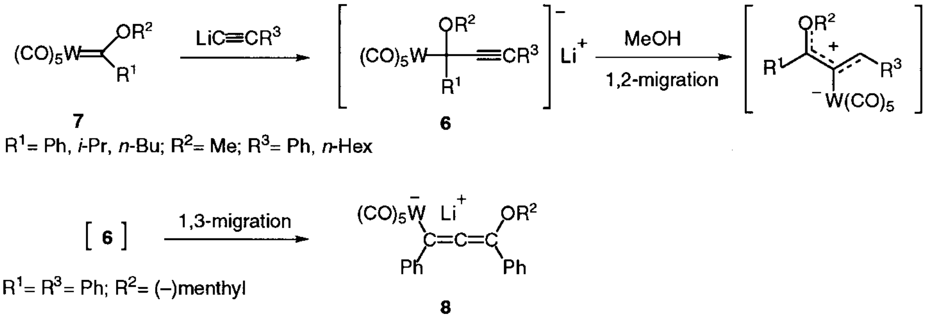


Scheme 1.

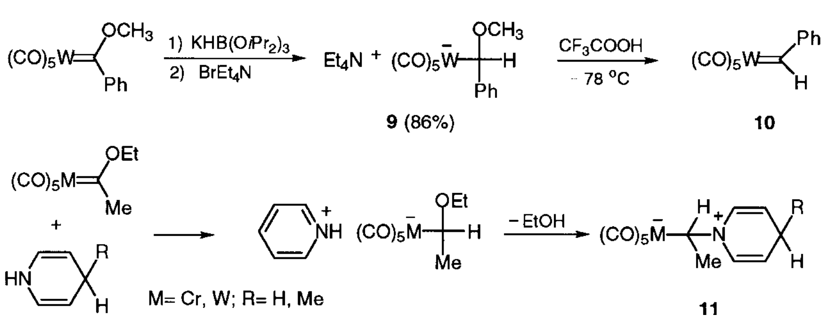
the metal in the process. Although 1,2 and 1,3-migrations of metal fragments have been reported, these processes are not frequent in Fischer carbene complexes. The 1,2-migration of a $M(CO)_5$ fragment was first proposed by Fischer to account for the cyclodimerization of ethynyl tungsten carbenes by ArLi reagents.[15] An analogous observation was made by Dötz and Knochel[13] in the reaction of such complexes and Et_2Zn. More recently, Iwasawa[16] has reported the preparation of different compounds, taking advantage of the migration of the $M(CO)_5$ in the intermediates **6** obtained by reaction of complexes **7** and alkynyllithiums. Other similar migration processes have been described by Barluenga, in the reaction of α,β-unsaturated group 6 metal carbenes with 4-amino-1-azadienes, imines, and sodium methoxide.[17] Much more unusual are 1,3 migrations of the metal fragment. The first example of one of such processes through a diazaallyl system, was found in the reaction of an alkoxy-carbene with diazobenzene.[18] This early work was followed by other analogous processes, all involving a migration through heteroatom substituted systems.[19] The first example describing the migration of the $M(CO)_5$ fragment in a fully carbonated system was reported by Barluenga while this work was in progress.[17d,20] This author described the migration of an $W(CO)_5$ moiety in an intermediate of type **6** ($R^1=R^3=Ph$; $R^2=(-)$menthyl), to yield the allenyl tungsten derivative **8**. This species led to distinct compounds upon quenching with different electrophiles (Scheme 2).

Taking into account the precedents above mentioned, it is predictable that the mechanism of the addition of simple nucleophiles to α,β-unsaturated chromium(0) carbenes, will be not as simple as in the case of their organic counterparts (namely, α,β-unsaturated esters and amides). In this context, we decided to study the reaction of group 6 α,β-unsaturated alkoxy and amino Fischer carbene complexes with $NaBH_4$. The addition of hydrides offers an exceptional opportunity to combine reagent simplicity with the possibility of isotopic labeling, (using either a reagent or a deuterated solvent). Proofs for the exclusive 1,2-addition of the hydride to the carbene carbon atom, followed by 1,3-allylic or propargylic migration of the metal moiety, will be presented.

The reactivity of group 6 metal–carbene complexes towards reducing agents has been scarcely studied. Hydrogenation of Cr– and W–carbene complexes promotes the loss of the metal moiety and the formation of the corresponding hydrocarbon, in a process thought to occur by addition of hydrogen to the C=M bond and subsequent extrusion of the metal moiety.[21] Complex $[(CO)_5WC(OMe)Ph]$ reacts sequentially with $KHB(O\textit{i}Pr_2)_3$ and $BrNEt_4$ to yield the salt **9** as a stable,

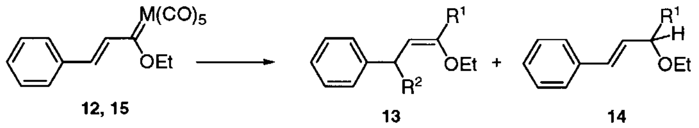


Scheme 2.



Scheme 3.

Table 1.



Complex	Reagent/Solvent	13 Yield[a] (%)	14 Yield[a] (%)	13/14[b]
12 (M=Cr)	$NaBH_4$/EtOH	**13a** R^1=R^2=H (56)	**14a** R^1=H (12)	80:20
12 (M=Cr)	$NaBD_4$/EtOH	**13b** R^1=D R^2=H (59)	**14b** R^1=D (12)	85:15
12 (M=Cr)	$NaBH_4$/CD_3OD	**13c** R^1=H R^2=D (59)	**14b** R^1=D (16)	83:17
15 (M=W)	$NaBH_4$/EtOH	**13a** R^1=R^2=H	**14a** R^1=H	89:11

[a] In pure, isolated compound.

[b] Determined by integration of well resolved signals in the reaction crude prior to any purification. The value given is the average of three separate runs.

crystalline solid.[22] This compound forms unstable carbene complex **10** upon acid treatment. The HLi reduction of $[(CO)_5MoC(OMe)SiMePh_2]$ to $[(CO)_5MoC(SiMePh_2)H]$, was observed as a competitive process during the addition of BuLi to the alkoxy carbene.[23] 1,4-Dihydropyridines reduced complexes $[(CO)_5MC(OEt)Me]$ (M=Cr, W) to ylides **11**, again through the initial addition of an hydride to the carbene carbon atom.[24] It should be noted that all of these results are fully compatible with those expected for the addition of simple nucleophiles to esters. Finally, not many data about the reactivity of hydrides and metal carbene complexes other than group 6, can be found in the literature, but they follow essentially the same patterns previously mentioned (Scheme 3).[25]

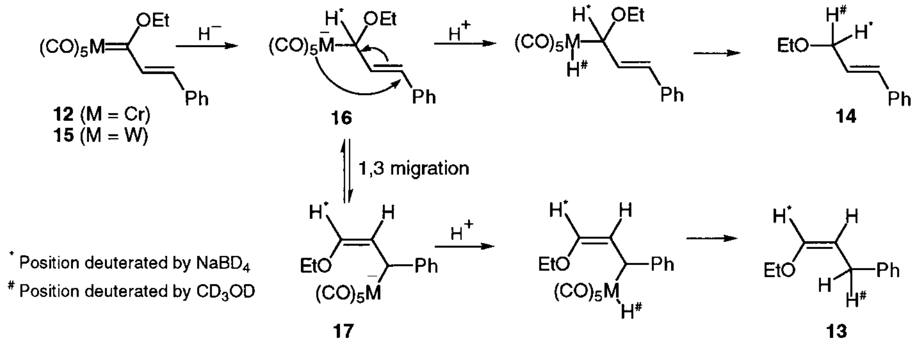
Results and Discussion

Reduction of alkoxy α,β-unsaturated (group 6) carbene complexes

We started this study by reducing a cooled (−20°C) solution of complex **12** in EtOH with the equimolar amount of $NaBH_4$. This reaction yielded, after oxidation, a mixture of *Z*-vinyl ether **13a** and *E*-allyl ether **14a** in a 80:20 ratio. The reaction was almost quantitative and except for a little oxidation product (the corresponding organic ester) obtained in some cases, no other by-products could be detected in the reaction mixtures. It was obvious that compounds **13a** and **14a** could not be derived from the standard hydride addition-alkoxide elimination sequence,[22] thus, we undertook the task of determining the possible participation of the metal in the process. Complex **12** was reduced using $NaBD_4$/EtOH and monodeuterated compounds **13b** and **14b** were obtained. On the other hand, the reaction with CD_3OD as solvent, yielded monodeuterated **13c** and **14b** (in this case, quenching was by addition of D_2O). A control experiment was done by submitting ethyl cinnamate to analogous reaction conditions, yielding unreacted material with only traces of ethyl 3-phenylpropanoate, even after prolonged reaction times. Changing the metal in the α,β-unsaturated complex does not make any relevant difference. So, the reduction of tungsten carbene **15** under the same conditions yielded a mixture of ethers **13a** and **14a** in an 89:11 ratio (Table 1).

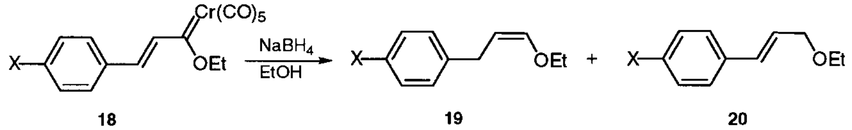
These results clearly pointed to an involvement of the $M(CO)_5$ in the reduction process. Hydride addition takes place on the carbene carbon atom to form intermediate **16**, from which the formation of *E*-**14a** is immediate. An alternative evolution for **16** could be the 1,3-migration of the $M(CO)_5$ moiety, that would lead to complex **17**. This is the key feature of the process and explains the formation of *Z*-**13a** as the main reaction product. Both pathways are consistent with the deuteration experiments. The incorporation of deuterium from the reagent takes place during the hydride addition step, whereas in the CD_3OD experiment, the deuterium transfer occurs during the protonation step (Scheme 4).

Extension of this reaction to a series of *p*-substituted pentacarbonyl[(ethoxy)(styryl)carbene]chromium(0) complexes



Scheme 4.

Table 2.



Complex	19 Yield[a] (%)	20 Yield[a] (%)	19/20[b]
18a X=Me	45	17	80:20
18b X=OMe	48	14	87:13
18c X=Cl	42	9	90:10
18d X=CN	53	–	100:0[c]

[a] In pure, isolated compound.

[b] Determined by integration of well resolved signals in the reaction crude prior to any purification.

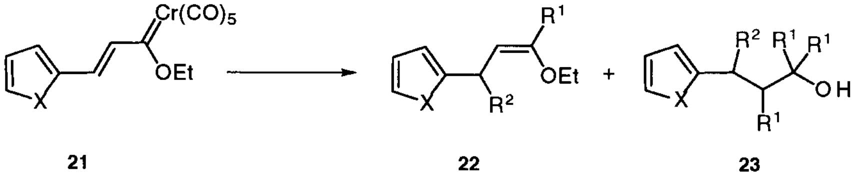
[c] 8% of Ethyl *p*-cyanocinnamate was also obtained.

18 was searched next. Exception made of **18d**, mixtures of ethers **19** and **20** were obtained. The reaction times remained essentially unaltered and neither notable modifications in the structure, nor in the stereochemistry of the reaction products were observed. However, a steady increase of the ratio of vinyl ether **19** was observed with the electron withdrawing nature of the substituents. In fact, the reaction of the cyano-substituted complex **18d** exclusively gave vinyl ether **19d** (Table 2).

α,β-Unsaturated complexes **21** having heterocyclic substituents were also studied. In these cases the presence of an electron rich aromatic ring may alter the 1,3-allylic migration step. Interestingly, a clear difference in reactivity was found depending on the nature of the heterocycle. The most reactive towards hydride reduction was the furyl complex **21a** that was instantaneously reduced with $NaBH_4$ in EtOH at −78°C, followed by the thiophene substituted complex **21b** whose reduction required several hours at the same temperature. Finally, the reduction of pyrrole substituted complex **21c** was afforded at −20°C. In the case of furyl substituted complex **21a** the analysis of the reaction crude showed a 80:20 mixture of the expected *Z*-vinyl ether **22a** together with a new compound that was identified as the saturated alcohol **23a**. In order to establish the outcome of the reaction in this case, deuterium labeling experiments were carried out. Reduction of complex **21a** with $NaBD_4$ gave the corresponding monodeuterated vinyl ether **22b** together with the trideuterated alcohol **23b**, while when the reaction was carried out with $NaBH_4/CD_3OD$, monodeuterated vinyl ether **22c** and monodeuterated alcohol **23c** were obtained (Table 3).

The major reduction product, vinyl ether **22a**, should arise from the initial 1,2-hydride addition to the carbene complex **21a**, followed by 1,3-allylic migration of the $Cr(CO)_5$ fragment and subsequent protonation, as is proposed in Scheme 5. Again, the key feature of the process is the allylic rearrangement of the metal fragment and this is supported by the deuteration experiments, in which the reagent transfers the labeling during the reduction process and the solvent in the protonation step. The formation of the secondary product, the alcohol **23a**, could be justified by alkoxide elimination[22] on intermediate **24**, that would lead to unstable carbene complex **25**. By hydrolysis, this complex would be transformed into the corresponding aldehyde,[26] but only *E*-3-(2-*N*-methylpyrrolyl)-2-propenal has been detected during the $NaBH_4$ reduction of the pyrrole substituted complex **21c**, the less reactive of the series. On the other hand, the complete reduction of an α,β-unsaturated aldehyde under these conditions does not take place,[27] therefore it could be considered that saturated alcohol **23a** is

Table 3.

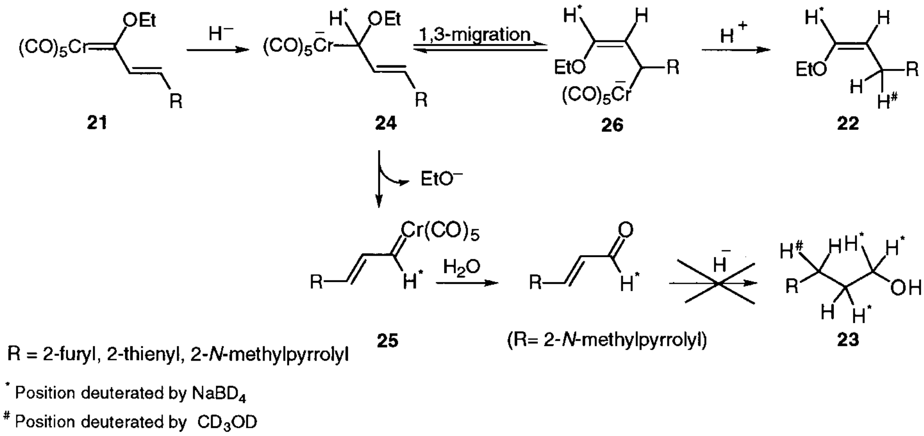


Complex	Reagent/Solvent	22 Yield[a] (%)	23 Yield[a] (%)	22/23[b]
21a (X=O)	$NaBH_4/EtOH$	**22a** $R^1=R^2=H$ (55)	**23a** $R^1=R^2=H$ (13)	80:20
21a (X=O)	$NaBD_4/EtOH$	**22b** $R^1=D$ $R^2=H$ (50)	**23b** $R^1=D$ $R^2=H$ (12)	83:17
21a (X=O)	$NaBH_4/CD_3OD$	**22c** $R^1=H$ $R^2=D$ (53)	**23c** $R^1=H$ $R^2=D$ (11)	85:15
21b (X=S)	$NaBH_4/EtOH$	**22d** $R^1=R^2=H$ (77)	–	100:0
21c (X=NMe)	$NaBH_4/EtOH$	**22e** $R^1=R^2=H$ (45)	–	[c]

[a] In pure, isolated compound.

[b] Determined by integration of well resolved signals in the reaction crude prior to any purification. The value given is the average of three separate runs.

[c] In this case, a 80:20 mixture of **22e** and *E*-3-(2-*N*-methylpyrrolyl)-2-propenal was obtained.



R = 2-furyl, 2-thienyl, 2-*N*-methylpyrrolyl

(R= 2-*N*-methylpyrrolyl)

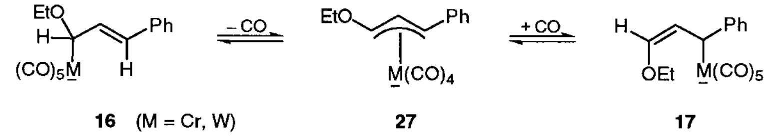
* Position deuterated by $NaBD_4$
\# Position deuterated by CD_3OD

Scheme 5.

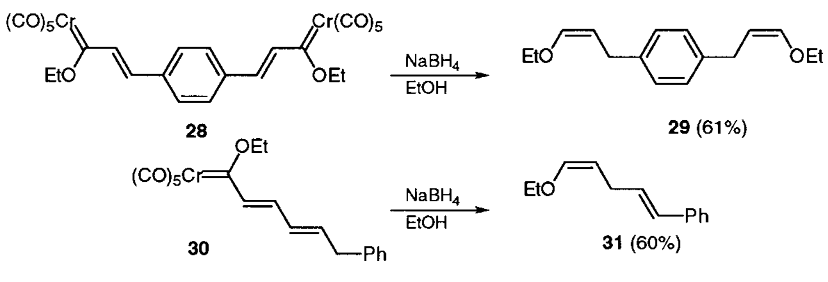
formed after overreduction and hydrolysis of **25**. The behavior of carbene complexes like **25** towards nucleophiles is currently under study in our laboratories. Thiophene derivative **21b** yields vinyl ether **22d** as the sole reaction product, indicating that the replacement of an oxygen by a sulfur atom benefits the 1,3-$M(CO)_5$ migration and perhaps, suggesting an extra stabilization of intermediate **26** by coordination of the metal and the sulfur of the thiophene ring.

Some features of the reactions previously discussed warrant additional debate. First, the exquisite *E*/*Z* selectivity observed on the newly formed C=C double bond of vinyl ethers **13**, **19** and **22**, arising from the 1,3-migration path. Second, the participation of an η^3-allyl chromium intermediate in these processes.[28] The selectivity of the process could be consequence of the chelation of the basic alkoxy oxygen to the metal center, once the 1,3-rearrangement has occurred. This chelation should impose the relative disposition of the metal and alkoxyde groups around the C=C double bond and hence the observed stereochemistry. An alternate explanation could derive from the participation of the sodium cation in the reduction process. In fact, assuming that through this paper we have depicted the more stable conformer of the different alkenyl complexes, 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 through the opposite face of the 3-carbon unit. This possibility has to be discarded because the reduction of complex **12** with Me_4NBH_4 gave the expected mixture **13a**/**14a** and again, **13a** was obtained with *Z*-stereochemistry exclusively. The participation of an η^3-allyl metal intermediate like **27** (M=Cr, W), in the 1,3-allylic rearrangement is suggested by the results obtained by effecting the reduction process under a CO atmosphere (Scheme 6).

It is clear that the migration of the $M(CO)_5$ moiety from **16** to **17** should involve a decarbonylation-carbonylation process that would be hampered under CO atmosphere. When the reduction of complex **12** was carried out in a CO-saturated EtOH solution, maintaining a positive CO pressure during the reaction, the ratio of products **13a**/**14a** decreased from 4:1 to 2.7:1, while the stereochemistry of **13a** remained unchanged. It was also observed that the reactions were dirtier when CO was present, and variable amounts of cinnamaldehyde were obtained. Clearly, a partial inhibition of the 1,3-rearrangement process occurs under such conditions, although the presence of CO does

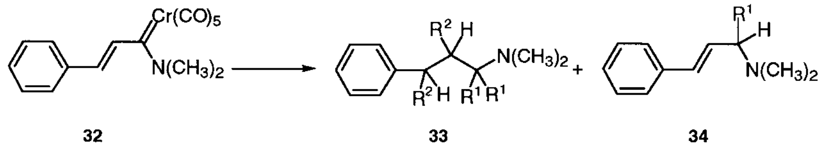


Scheme 6.



Scheme 7.

Table 4.



Reagent/Solvent	33	34	33/34[a]
$NaBH_4/EtOH$	**33a** $R^1=R^2=H$	**34a** $R^1=H$	3:2
$NaBD_4/EtOH$	**33b** $R^1=D$ $R^2=H$	**34b** $R^1=D$	3:2
$NaBH_4/CD_3OD$	**33c** $R^1=H$ $R^2=D$	**34b** $R^1=D$	3:2

[a] Determined by integration of well resolved signals in the reaction mixtures.

not interfere with the hypothetical chelation of the metal by the alkoxy group, which, as we propose, defines the vinyl ether stereochemistry.

To complete the study, carbene complexes **28** and **30** having an additional conjugated double bond, were submitted to reaction with $NaBH_4$. 1,3-Allylic migration also occurred in the case of biscarbene **28**, that exclusively gave *Z*-divinylether **29**. In the case of the conjugated complex **30** it could be expected a 1,5-$M(CO)_5$ long range rearrangement. However, only dienyl ether **31**, resulting from the usual 1,3-allylic migration process, was obtained (Scheme 7).

Reduction of α,β-unsaturated aminochromium carbene complexes

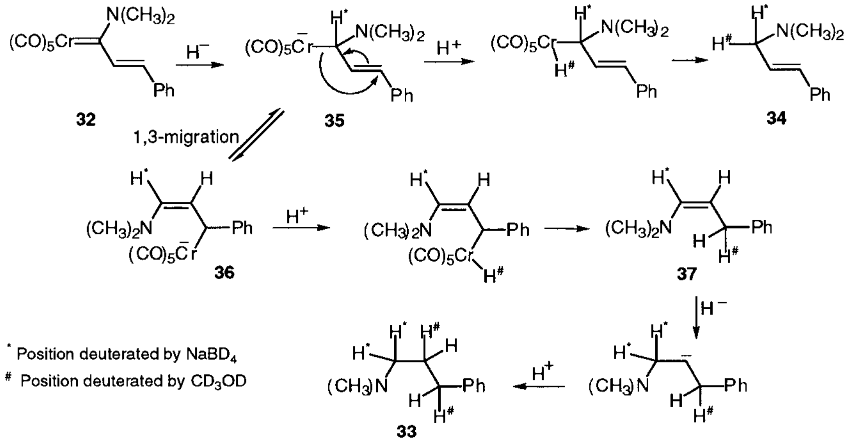
α,β-Unsaturated aminochromium carbene complex **32** was submitted to $NaBH_4$ reduction. Due to the lower reactivity of aminocarbenes towards nucleophiles the reaction required room temperature to occur, leading to an unseparable 3:2 mixture of amines **33a** and **34a**. The formation of totally reduced amine **33a** resembles the results previously obtained with furyl substituted complex **21a**, although in this case, compound **33a** is the main reaction product. Again deuteration experiments were carried out and the results are summarized on Table 4.

A mechanism analogous to the proposed for the reduction of alkenyl alkoxycarbenes, could explain the experimental results (Scheme 8). Intermediate **35** was formed as a result of the initial 1,2-addition of hydride to the aminocarbene **32**. 1,3-Allylic migration of the metallic moiety in such species yields the new complex **36** that after protonation, forms enamine **37**. The reduction of enamines by $NaBH_4$ is a known process[29] and in this case explains the formation of the totally saturated amine **33a** as the main reaction product, although all the attempts to detect the enamine **37** in the reaction mixtures have been fruitless.

Reduction of alkynyl (group 6) carbene complexes

Pentacarbonyl[(ethoxy)(phenylethynyl)carbene]chromium (0) **38** was also reactive towards $NaBH_4$ at −20°C, yielding in a few minutes ether *E*-**14a** as the sole reaction product. With $NaBD_4/EtOH$ dideuterated derivative *E*-**14c** was obtained. Finally, when CD_3OD was the solvent, the reaction yielded dideuterated compound *E*-**14d**. Again the reactions were almost quantitative and the results are summarized on Table 5. The same result was obtained starting from tungsten alkynyl carbene complex **39**, that yielded *E*-**14a** as the sole reaction product. To complete these experiments, the $NaBH_4/EtOH$ reduction of the analogous organic ester, ethyl phenylpropiolate was checked, yielding 50% of a 2:1 mixture of *E*/*Z*-ethyl cinnamates and 50% of unreacted starting material, after 48 h of reaction.

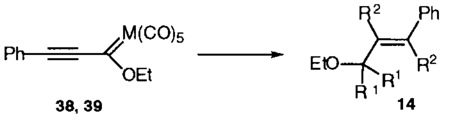
Again, it is difficult to understand the results obtained in the reduction of complexes **38** and **39** without considering the



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

Scheme 8.

Table 5.



Complex	Reagent/Solvent	14 Yield[a] (%)
38 (M=Cr)	$NaBH_4$/EtOH	**14a** $R^1=R^2=H$ (74)
38 (M=Cr)	$NaBD_4$/EtOH	**14c** $R^1=D$ $R^2=H$ (74)
38 (M=Cr)	$NaBH_4/CD_3OD$	**14d** $R^1=H$ $R^2=D$ (71)
39 (M=W)	$NaBH_4$/EtOH	**14a** $R^1=R^2=H$ (61)

[a] In pure isolated compound.

active participation of the metal in the process. The 1,3-migration of the $M(CO)_5$ fragment in the $NaBH_4$ reduction processes seems to be a general behavior for α,β-unsaturated complexes of different structures.

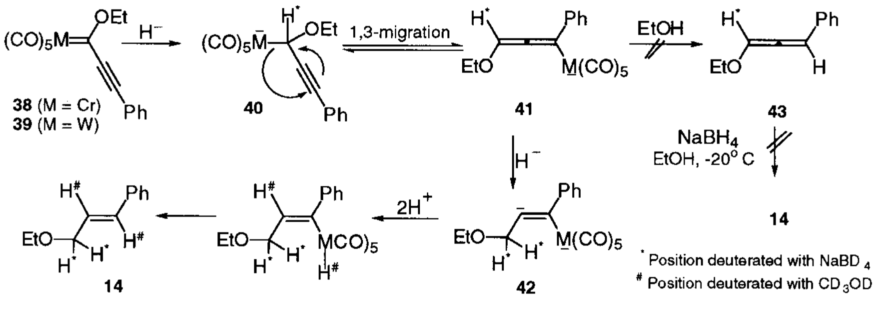
The initial 1,2-addition of hydride on the carbene carbon atom of **38** and **39** would lead to intermediate **40**. The first incorporation of deuterium occurs at this point when $NaBD_4$ is used as reagent. Alkynyl intermediate **40** may evolve to allenyl complex **41**[30] by a 1,3-propargylic rearrangement.[20] The isolation of ethers **14** from the intermediate **41** requires the addition of a new hydride ion at the end of the allenyl system and justifies the incorporation of the second deuterium atom in **14c**. This is remarkable, since the addition of nucleophiles to allenes usually takes place at the central allenic carbon.[31] Finally, diprotonation of dianion **42** would yield the allyl ethers **14** and explains the formation of dideuterated **14d** when CD_3OD was used as solvent. An alternative interpretation could be the protonation of allenyl intermediate **41** before the addition of a new hydride, to form free allene **43**. The subsequent reduction of this compound would also lead to allyl ethers **14** in a pathway fully compatible with the observed deuteration pattern. To exclude this possibility, allene **43** was prepared from 1-ethoxy-3-phenyl-2-propyne and BuLi,[32] and treated at −20°C with $NaBH_4$ in EtOH. The compound was recovered unchanged after several hours of reaction. This lack of reactivity of allenes towards $NaBH_4$ is in agreement with previous literature reports.[33] Finally, the reduction of complex **38** was carried out with $NaBH_4$ in anhydrous THF. The reaction needed higher temperatures to occur but the sole reaction product was again **14a**. Under this conditions, protonation of allenyl chromium intermediate **41** should be precluded and hence, its evolution to the final products thorough a free allene may be discarded. The conclusion from these experiments is that the second hydride transfer has to occur prior to the protonation step. The negative charge in the allenyl complex **41** should be fully delocalized across the coordination sphere of chromium, which renders the anionic complex slightly basic (Scheme 9).

In conclusion, in this paper we have described an unprecedent 1,3-migration of a $M(CO)_5$ fragment in the $NaBH_4$ reduction of α,β-unsaturated (group 6) metal carbene complexes (M=Cr, W). We propose the participation of an η^3-allyl chromium intermediate in the process, as it is suggested by the partial inhibition of the metal migration when the reduction is carried out under CO atmosphere. The exquisite *E*/*Z*-selectivity of the products obtained is also determined during the rearrangement, possibly by chelation of the metal center and the alkoxy group once the 1,3-$M(CO)_5$ migration has occurred. The process is general and can be observed either for styryl-type alkoxy and aminocarbenes, or for propargyl alkoxy carbenes. The proposed mechanisms are supported by the deuterium labeling experiments and these reduction reactions can be applied to the obtention of selectively deuterated *Z*-vinyl and *E*-allyl ethers and amines.

Experimental

General procedures

^1H NMR and ^{13}C NMR spectra were obtained in $CDCl_3$, on a Varian XL-300S (299.94 MHz for ^1H and 75.43 MHz for ^{13}C), a Bruker 250-AC (250.13 MHz for ^1H and 62.90 MHz for ^{13}C) or a Bruker 200-AC (200.132 MHz for ^1H and 50.03 MHz for ^{13}C) spectrometers. Chemical shifts are given in ppm relative to TMS (^1H, 0.0 ppm), or $CDCl_3$ (^{13}C, 76.9 ppm). IR spectra were recorded on a Perkin–Elmer 781 spectrometer. Mass spectra were carried out on a GC–MS HP-5989 (70 eV) mass spectrometer using methanol as solvent. The degree of deuteration was determinated by NMR and mass spectrometry (EI, 70 eV). Flame-dried glassware and standard Schlenck 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. TLC analyses were performed using silica plates (Kiesegel 60F-254) and were visualized using UV (254 nm) or iodine. All commercially available compounds were used without further purification. Carbene–chromiun complexes **12**,[34] **15**,[34] **21a**,[34] **21b**,[34] **21c**,[35] **28**,[34] **30**,[34] **32**,[36] **38**[37] and **39**[37]



Scheme 9.

were prepared according to literature methods. All new compounds gave satisfactory microanalytical data.

Synthesis of styryl alkoxychromium(0)carbenes. To a solution of pentacarbonyl [(ethoxy)(methyl)carbene]-chromium(0) **44**[38] (5.0 mmol) and the aldehyde (5.0 mmol) in anhydrous Et$_2$O, were added 20 mmol of Et$_3$N. Then, 15 mmol of TMSCl were added dropwise at room temperature. The mixture was stirred until disappearance of the starting material (checked by TLC). The solvent was removed under reduced pressure and the product purified by flash chromatography on silica gel.

Pentacarbonyl[(ethoxy)(*p*-tolylethenyl)carbene]chromium-(0) (18a): From 1.32 g (5.0 mmol) of **44**, 0.6 g (5.0 mmol) of *p*-methylbenzaldehyde, 2.8 mL (20 mmol) of Et$_3$N and 2.3 mL (15.0 mmol) of TMSCl. After 48 h of reaction and flash chromatography (hexane), **18a** (1.33 g, 73%) was obtained as a black crystalline solid. ^{1}H NMR δ=1.63 (t, 3H, J=7.0 Hz), 2.32 (s, 3H), 5.05 (q, 2H, J=7.0 Hz), 6.90 (d, 1H, J=15.4 Hz), 7.15 (d, 2H, J=7.8 Hz), 7.44 (d, 2H, J=7.8 Hz), 7.84 (d, 1H, J=15.4 Hz); ^{13}C NMR δ=330.4, 224.2, 216.7, 141.4, 138.7, 131.4, 130.2, 129.7, 129.3, 76.9, 21.4, 15.0; IR (CHCl$_3$): 2056, 1940, 1710 cm^{-1}.

Pentacarbonyl[(ethoxy)(*p*-methoxyphenylethenyl)carbene]-chromium(0) (18b): From 1.32 g (5.0 mmol) of **44** 0.68 g (5.0 mmol) of *p*-methoxybenzaldehyde, 2.8 mL (20.0 mmol) of Et$_3$N and 2.3 mL (15 mmol) of TMSCl. After 64 h of reaction and flash chromatography (hexane/CH$_2$Cl$_2$ 8:1), **18b** (1.24 g, 65%) was obtained as a red crystalline solid. ^{1}H NMR δ=1.61 (t, 3H, J=7.0 Hz), 3.79 (s, 3H), 5.02 (q, 2H, J=7.0 Hz), 6.86 (d, 2H, J=8.6 Hz), 6.93 (d, 1H, J=15.2 Hz), 7.49 (d, 2H, J=8.6 Hz), 7.77 (d, 1H, J=15.2 Hz); ^{13}C NMR δ=328.7, 224.2, 216.8, 162.2, 137.7, 131.2, 130.8, 126.7, 114.5, 75.6, 55.3, 15.0; IR (CHCl$_3$): 2056, 1940, 1711 cm^{-1}.

Pentacarbonyl[(*p*-chlorophenylethenyl)(ethoxy)carbene]-chromium(0) (18c): From 1.32 g (5.0 mmol) of **44**, 0.7 g (5.0 mmol) of *p*-chlorobenzaldehyde, 2.8 mL (20.0 mmol) of Et$_3$N and 2.3 mL (15.0 mmol) of TMSCl. After 66 h of reaction and flash chromatography (hexane), **18c** (1.01 g, 52%) was obtained, as a black crystalline solid. ^{1}H NMR δ=1.55 (t, 3H, J=7.0 Hz), 4.98 (q, 2H, J=7.0 Hz), 6.70 (d, 1H, J=15.4 Hz), 7.22 (d, 2H, J=8.4 Hz), 7.36 (d, 2H, J=8.4 Hz), 7.74 (d, 1H, J=15.4 Hz); ^{13}C NMR δ=331.4, 224.2, 216.6, 139.7, 136.7, 133.0, 130.3, 129.3, 127.6, 76.3, 15.1; IR (CHCl$_3$): 2057, 1942, 1711 cm^{-1}.

Pentacarbonyl[(*p*-cyanophenylethenyl)(ethoxy)carbene]-chromium(0) (18d): From 1.32 g (5.0 mmol) of **44,** 0.68 g (5.0 mmol) of *p*-cyanobenzaldehyde, 2.8 mL (20.0 mmol) of Et$_3$N and 2.3 mL (15 mmol) of TMSCl. After 96 h of reaction and flash chromatography (hexane/CH$_2$Cl$_2$ 8:1), **18d** (0.9 5g, 50%) was obtained as a green crystalline solid. ^{1}H NMR δ=1.56 (t, 3H, J=7.0 Hz), 5.02 (q, 2H, J=7.0 Hz), 6.62 (d, 1H, J=15.4 Hz), 7.51 (broad s, 4H), 7.78 (d, 1H, J=15.4 Hz); ^{13}C NMR δ=332.4, 224.0, 216.1, 141.1, 139.1, 132.4, 129.2, 124.9, 118.2, 113.1, 75.6, 15.0; IR (CHCl$_3$): 2230 (CN), 2058, 1946, 1711 cm^{-1}.

Hydride reduction: general procedure

A suspension of NaBH$_4$ in absolute EtOH at −20°C, was placed in a flame-dried airless flask containing a magnetic stirring bar, degassed by evacuation/back-fill with argon (3x). Then, a solution of the carbene in EtOH 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). After the addition of water at −20°C, the solvent was removed under reduced pressure and the mixture 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. For the deuterium experiments the same procedure was followed, using NaBD$_4$ in EtOH or NaBH$_4$ in CD$_3$OD as solvent (in these cases, the reaction was quenched by addition of D$_2$O instead of water).

Reduction of pentacarbonyl[(ethoxy)(phenylethenyl)-carbene]chromium(0) (12) with NaBH$_4$ in EtOH. From 350 mg (0.99 mmol) of **12** and 37.4 mg (0.99 mmol) of NaBH$_4$ in absolute EtOH at −20°C. After 10 min of reaction and further oxidation of the reaction mixture, a colorless oil (120 mg) was obtained. The ^{1}H NMR spectrum of the reaction crude showed a 80:20 mixture of ethers **13a** and **14a**. The products were separated by flash column chromatography (hexane/CH$_2$Cl$_2$ 8:1 to AcOEt). *Z-1-Ethoxy-3-phenyl-1-propene* (**13a**), (90 mg, 56%) was obtained as a colorless oil. ^{1}H NMR δ=1.22 (t, 3H, J=6.9 Hz), 3.37 (d, 2H, J=7.2 Hz), 3.77 (q, 2H, J=6.9 Hz), 4.50 (dt, 1H, J_1=7.2 Hz, J_2=6.0 Hz), 6.00 (d, 1H, J=6.0 Hz), 7.11–7.24 (m, 5H); ^{13}C NMR δ=145.2, 141.9, 128.3, 125.7, 105.5, 67.7, 30.2, 15.4; IR (film): 1662 (C=C), 1495, 1452 cm^{-1}; MS: *m*/*z* (%): 162 (M$^+$, 78), 133 (42), 118 (18), 117 (23), 116 (15), 105 (100), 103 (23), 91 (38), 79 (28), 78 (28), 77 (39). *E-3-Ethoxy-1-phenyl-1-propene* (**14a**), (20 mg, 12%) was obtained as a colorless oil. ^{1}H NMR δ=1.18 (t, 3H, J=6.9 Hz), 3.48 (q, 2H, J=6.9 Hz), 4.07 (d, 2H, J=6.0 Hz), 6.21 (dt, 1H, J_1=15.9 Hz, J_2=6.0 Hz), 6.54 (d, 1H, J=15.9 Hz), 7.12–7.33 (m, 5H); ^{13}C NMR δ=136.7, 132.0, 128.4, 127.5, 126.3, 126.2, 71.2, 65.7, 15.3; IR (film): 1653 (C=C), 1495, 1448 cm^{-1}; MS: *m*/*z* (%): 162 (M$^+$, 41), 133 (39), 118 (26), 117 (51), 116 (25), 115 (58), 105 (100), 103 (22), 91 (36), 79 (26).

Reduction of pentacarbonyl[(ethoxy)(phenylethenyl)-carbene]chromium(0) (12) with NaBD$_4$ in EtOH. From 200 mg (0.57 mmol) of **12** and 24 mg (0.57 mmol) of NaBD$_4$ in absolute EtOH at −20°C. After 10 min of reaction and further oxidation of the reaction crude, a colorless oil (82 mg) was obtained. The ^{1}H NMR spectrum of the reaction crude showed a 85:15 mixture of ethers **13b** and **14b**. The products were separated by flash column chromatography (hexane/CH$_2$Cl$_2$ 8:1 to AcOEt). *Z-1-Deutero-1-ethoxy-3-phenyl-1-propene* (**13b**), (55 mg, 59%) was obtained as a colorless oil. ^{1}H NMR δ=1.20 (t, 3H, J=7.0 Hz), 3.36 (d, 2H, J=7.4 Hz), 3.74 (q, 2H, J= 7.0 Hz), 4.49 (t, 1H, J=7.4 Hz), 7.06–7.24 (m, 5H); ^{13}C NMR δ=145.0 (t, $J_{\text{C–D}}$=25.6 Hz), 142.0, 128.3, 125.7, 105.4, 67.7, 30.3, 15.4; IR (film) 1683(C=C), 1506, 1473 cm^{-1}; MS: *m*/*z* (%): 163 (M$^+$, 100), 134 (44), 118 (28), 116 (24), 106 (76), 91 (22), 78 (23). *E-3-deutero-3-ethoxy-1-phenyl-1-propene*

(**14b**), (11 mg, 12%) was obtained as a colorless oil. ^{1}H NMR δ=1.21 (t, 3H, J=7.0 Hz), 3.49 (q, 2H, J=7.0 Hz), 4.10 (broad d, 1H, J=6.0 Hz), 6.23 (dd, 1H, J_1=16.0 Hz, J_2=6.0 Hz), 6.54 (d, 1H, J=16.0 Hz), 7.01–7.24 (m, 5H); ^{13}C NMR δ=136.6, 132.1, 128.4, 127.4, 126.3, 126.1, 70.6 (t, $J_{\text{C–D}}$=21.7 Hz), 65.4, 15.0; IR (film): 1652(C=C), 1506, 1448 cm^{-1}; MS: m/z (%): 163 (M$^+$, 77), 162 (14), 134 (52), 118 (63), 106 (100), 92 (22), 78 (18).

Reduction of pentacarbonyl[(ethoxy)(phenylethenyl)-carbene]chromium(0) (12) with NaBH$_4$ in CD$_3$OD. From 206 mg (0.56 mmol) of **12** and 22 mg (0.56 mmol) of NaBH$_4$ in 10 mL of CD$_3$OD at −20°C. After 10 min of reaction and further oxidation of the reaction mixture, a colorless oil (90 mg) was obtained. The ^{1}H NMR spectrum of the reaction crude showed a 83:17 mixture of ethers **13c** and **14b**. The products were separated by flash column chromatography (hexane/CH$_2$Cl$_2$ 8:1 to AcOEt). *Z-3-Deutero-1-ethoxy-3-phenyl-1-propene* (**13c**) (51 mg, 59%) was obtained as a colorless oil. ^{1}H NMR δ=1.21 (t, 3H, J=7.0 Hz), 3.35 (broad d, 1H, J=5.5 Hz), 3.74 (q, 2H, J=7.0 Hz), 4.49 (t, 1H, J=6.7 Hz), 5.90 (dd, 1H, J_1=6.2 Hz, J_2=1.1 Hz), 6.91–7.23 (m, 5H); ^{13}C NMR δ=145.2, 141.8, 128.3, 125.6, 105.4, 67.6, 29.9 (t, $J_{\text{C–D}}$=20 Hz), 15.3; IR (film): 1662 (C=C), 1495, 1448 cm^{-1}; MS: m/z (%): 163 (M$^+$, 75), 134 (39), 119 (19), 118 (24), 106 (100), 104 (20), 92 (36), 79 (20), 78 (39), 77 (26). *E-3-Deutero-3-ethoxy-1-phenyl-1-propene* (**14b**) (14 mg, 16%) was obtained as a colorless oil.

Reduction of pentacarbonyl[(ethoxy)(phenylethenyl)-carbene]tungsten(0) (15) with NaBH$_4$ in EtOH. From 200 mg (0.41 mmol) of **15** and 15.62 mg (0.41 mmol) of NaBH$_4$ in absolute EtOH at −20°C. After 1 h of reaction and further oxidation of the reaction mixture, a yellow oil (140 mg) was obtained. The ^{1}H NMR spectrum of the reaction crude showed the presence of **13a** and **14a** in a 89:11 ratio.

Reduction of pentacarbonyl[(ethoxy)(phenylethenyl)-carbene]chromium(0) (12) with Me$_4$NBH$_4$ in EtOH. From 250 mg (0.71 mmol) of **12** and 63.2 mg (0.71 mmol) of Me$_4$NBH$_4$ in absolute EtOH at 0°C. After 10 min of reaction and further oxidation of the reaction mixture, a colorless oil (85 mg) was obtained. The ^{1}H NMR spectrum of the reaction crude showed the presence of the isomers **13a** and **14a** in a 88:12 ratio.

Reduction of pentacarbonyl[(ethoxy)(phenylethenyl)-carbene]chromium(0) (12) under CO atmosphere with NaBH$_4$ in EtOH. The experiments were carried out by bubbling a CO stream through a solution of 100 mg (0.28 mmol) of **12** in absolute EtOH at −20°C, for about 30 min before the addition of 10.6 mg (0.28 mmol) of NaBH$_4$. A CO filled balloon was placed at the top of the flask to maintain the CO atmosphere during the reduction process. After 10 min of reaction and further oxidation of the reaction mixture, 85 mg of a colorless oil were obtained. The ^{1}H NMR spectrum of the reaction crude showed the presence of cinamaldehyde together with a mixture of **13a** and **14b** in a 2.7:1 ratio.

Reduction of pentacarbonyl[(ethoxy)(*p*-tolylethenyl)carbene]chromium(0) (18a) with NaBH$_4$ in EtOH. From 200 mg (0.55 mmol) of **18a** and 20.8 mg (0.55 mmol) of NaBH$_4$ in absolute EtOH at −20°C. After 10 min of reaction and further oxidation of the reaction mixture, a colorless oil (109 mg) was obtained. The ^{1}H NMR spectrum of the reaction crude showed a 80:20 mixture of **19a** and **20a**. The products were separated by flash column chromatography (hexane/CH$_2$Cl$_2$ 4:1 to AcOEt). *Z-1-Ethoxy-3-(p-tolyl)-1-propene* (**19a**), (43 mg, 45%) was obtained as a colorless oil. ^{1}H NMR δ=1.20 (t, 3H, J=7.1 Hz), 2.24 (s, 3H), 3.32 (d, 2H, J=7.4 Hz), 3.76 (q, 2H, J=7.1 Hz), 4.47 (td, 1H, J_1=7.4 Hz, J_2=6.3 Hz), 5.97 (dt, 1H, J_1=6.3 Hz, J_2=1.45 Hz), 7.00 (d, 2H, J=8.6 Hz), 7.05 (d, 2H, J=8.6 Hz); ^{13}C NMR δ=145.2, 139.0, 135.2, 129.1, 128.3, 106.0, 67.8, 29.9, 21.1, 15.5; IR (CHCl$_3$): 1685 (C=C), 1618, 1610, 1515, 1419 cm^{-1}. *E-3-Ethoxy-1-(p-tolyl)-1-propene* (**20a**), (17 mg, 17%) was obtained as a colorless oil. ^{1}H NMR δ=1.18 (t, 3H, J=7.0 Hz), 2.26 (s, 3H), 3.48 (q, 2H, J=7.0 Hz), 4.06 (dd, 2H, J_1=6.1 Hz, J_2=1.2 Hz), 6.18 (dt, 1H, J_1=15.9 Hz, J_2=6.1 Hz), 6.51 (d, 1H, J=15.9 Hz), 7.05 (d, 2H, J=8.3 Hz), 7.22 (d, 2H, J=8.3 Hz); ^{13}C NMR δ=137.5, 134.1, 132.3, 129.3, 126.4, 125.3, 71.4, 65.7, 21.2, 15.3; IR (CHCl$_3$) 1514, 1465 cm^{-1}.

Reduction of pentacarbonyl[(ethoxy)(*p*-methoxyphenyl-ethenyl)carbene]chromium(0) (18b) with NaBH$_4$ in EtOH. From 250 mg (0.66 mmol) of **18b** and 25 mg (0.66 mmol) of NaBH$_4$ in absolute EtOH at −20°C. After 10 min of reaction and further oxidation of the reaction mixture, a colorless oil (120 mg) was obtained. The ^{1}H NMR spectrum of the reaction crude showed a 87:13 mixture of **19b** and **20b**. The products were separated by flash column chromatography (hexane/CH$_2$Cl$_2$ 4:1 to AcOEt). *Z-1-ethoxy-3-(p-methoxyphenyl)-1-propene* (**19b**) (61 mg, 48%) was obtained as a colorless oil. ^{1}H NMR δ=1.20 (t, 3H, J=7.1 Hz), 3.30 (d, 2H, J=7.4 Hz), 3.71 (s, 3H), 3.76 (q, 2H, J=7.1 Hz), 4.47 (q, 1H, J=7.4 Hz), 5.99 (d, 1H, J=6.3 Hz), 6.75 (d, 2H, J=8.5 Hz), 7.07 (d, 2H, J=8.5 Hz); ^{13}C NMR δ=157.8, 145.1, 134.1, 129.3, 113.9, 106.1, 67.8, 55.4, 29.4, 15.4; IR (CHCl$_3$): 1662 (C=C), 1608, 1510, 1245 cm^{-1}. *E-3-Ethoxy-1-(p-methoxy-phenyl)-1-propene* (**20b**), (17 mg, 13%) was obtained as a colorless oil. ^{1}H NMR δ=1.17 (t, 3H, J=7.0 Hz), 3.47 (q, 2H, J=7.0 Hz), 3.77 (s, 3H), 4.05 (d, 2H, J=6.1 Hz), 6.10 (dt, 1H, J_1=16.1 Hz, J_2=6.1 Hz), 6.48 (d, 1H, J=16.1 Hz), 6.83 (d, 2H, J=8.8 Hz), 7.21 (d, 2H, J=8.8 Hz); ^{13}C NMR δ=159.3, 144.3, 132.0, 127.7, 124.1, 114.0, 71.5, 65.6, 55.3, 15.3; IR (CHCl$_3$): 1606 (C=C), 1512, 1249 cm^{-1}.

Reduction of pentacarbonyl[(*p*-chlorophenylethenyl) (ethoxy)carbene]chromium(0) (18c) with NaBH$_4$ in EtOH. From 250 mg (0.52 mmol) of **18c** and 19.6 mg (0.52 mmol) of NaBH$_4$ in absolute EtOH at −20°C. After 10 min of reaction and further oxidation of the reaction mixture, a colorless oil (84 mg) was obtained. The ^{1}H NMR spectrum of the reaction crude showed the presence of the isomers **19c** and **20c** in a ratio of 90:10. The products were separated by flash column chromatography (hexane/CH$_2$Cl$_2$ 4:1 to AcOEt). *Z-1-Ethoxy-3-(p-chlorophenyl)-1-propene* (**19c**), (40 mg, 42%) was obtained as a colorless oil. ^{1}H NMR δ=1.20 (t, 3H, J=7.1 Hz), 3.31 (dd, 2H, J_1=7.5 Hz, J_2=1.34 Hz), 3.76 (q, 2H, J=7.1 Hz), 4.44 (td, 1H, J_1=7.5 Hz, J_2=6.1 Hz), 5.99 (d, 1H, J=6.1 Hz), 7.07 (d, 2H, J=8.4 Hz), 7.16 (d, 2H, J=8.4 Hz); ^{13}C NMR

δ=145.7, 140.5, 131.4, 129.8, 128.4, 105.4, 67.9, 29.7, 15.4; IR (CHCl$_3$): 1662 (C=C), 1491 cm^{-1}. E-*3-Ethoxy-1-(p-chlorophenyl)-1-propene* (**20c**), (8 mg, 9%) was obtained as a colorless oil. ^{1}H NMR δ=1.18 (t, 3H, *J*=7.0 Hz), 3.48 (q, 2H, *J*=7.0 Hz), 4.06 (d, 2H, *J*=6.0 Hz), 6.21 (dt, 1H, J_1=15.9 Hz, J_2=6.0 Hz), 6.54 (d, 1H, *J*=15.9 Hz), 7.29 (d, 2H, *J*=8.6 Hz), 7.38 (d, 2H, *J*=8.6 Hz); ^{13}C NMR δ=143.1, 129.2, 128.7, 127.7, 127.1, 118.9, 71.0, 65.9, 15.2; IR (CHCl$_3$): 1637 (C=C), 1490 cm^{-1}.

Reduction of pentacarbonyl[(*p*-cyanophenylethenyl)(ethoxy)carbene]chromium(0) (18d) with NaBH$_4$ in EtOH. From 200 mg (0.53 mmol) of **18d** and 20 mg (0.53 mmol) of NaBH$_4$ in absolute EtOH at −20°C. After 10 min of reaction and further oxidation of the reaction mixture, a colorless oil (119 mg) was obtained. The ^{1}H NMR spectrum of the reaction crude showed a 92:8 mixture of **19d** and ethyl *p*-cyanocinnamate. These products were separated by flash column chromatography (hexane/CH$_2$Cl$_2$ 8:1 to AcOEt). *Z-1-Ethoxy-3-(p-cyanophenyl)-1-propene* (**19d**), (53 mg, 54%) was obtained as a colorless oil. ^{1}H NMR δ=1.20 (t, 3H, *J*=7.1 Hz), 3.40 (d, 2H, *J*=7.5 Hz), 3.78 (q, 2H, *J*=7.1 Hz), 4.44 (td, 1H, J_1=7.5 Hz, J_2=6.2 Hz), 6.04 (dt, 1H, J_1=6.2 Hz, J_2=1.34 Hz), 7.25 (d, 2H, *J*=8.3 Hz), 7.48 (d, 2H, *J*=8.3 Hz); ^{13}C NMR δ=147.6, 146.2, 132.0, 129.0, 119.1, 109.4, 103.2, 67.8, 30.3, 15.2; IR (CHCl$_3$): 2230 (CN), 1662 (C=C), 1608, 1505 cm^{-1}.

Reduction of pentacarbonyl[(ethoxy)[2-(2-furyl)ethenyl]-carbene]chromium(0) (21a) with NaBH$_4$ in EtOH. From 200 mg (0.58 mmol) of **21a** and 22 mg (0.58 mmol) of NaBH$_4$ in absolute EtOH at −78°C. After 10 min of reaction and further oxidation of the reaction mixture, a colorless oil (64 mg) was obtained. The ^{1}H NMR spectrum of the reaction crude showed a 80:20 mixture of **22a** and **23a**. The products were separated by flash column chromatography (hexane/CH$_2$Cl$_2$ 8:1 to AcOEt). *Z-1-Ethoxy-3-(2-furyl)-1-propene* (**22a**), (49 mg, 55%) was obtained as a colorless oil. ^{1}H NMR δ=1.15 (t, 3H, *J*=7.0 Hz), 3.37 (d, 2H, *J*=7.2 Hz), 3.74 (q, 2H, *J*=7.0 Hz), 4.47 (td, 1H, J_1=7.2 Hz, J_2=6.2 Hz), 5.92 (m, 1H), 6.01 (d,t 1H, J_1=6.2 Hz, J_2=1.55 Hz), 6.20 (m, 1H), 7.23 (m, 1H); ^{13}C NMR δ=155.3, 146.0, 140.9, 110.0, 104.5, 101.7, 67.7, 23.1, 15.4; IR (film): 1666 (C=C), 1596, 1550 cm^{-1}; MS: *m*/*z* (%): 152 (M$^+$, 100), 123 (60), 108 (18), 95 (78), 81 (32), 67 (57). *3-(2-Furyl)propanol* (**23a**), (10 mg, 13%) was obtained as a colorless oil. ^{1}H NMR δ=1.84 (m, 2H), 2.67 (t, 2H, *J*=7.4 Hz), 3.62 (t, 2H, *J*=6.2 Hz), 5.95 (m, 1H), 6.22 (m, 1H), 7.24 (m, 1H); ^{13}C NMR δ=155.5, 140.9, 110.2, 105.0, 62.1, 31.0, 24.3; IR (CHCl$_3$): 3413 (OH) cm^{-1}; MS: *m*/*z* (%): 126 (M$^+$, 84), 108 (72), 95 (18), 81 (100), 79 (58), 65 (19).

Reduction of pentacarbonyl[(ethoxy)[2-(2-furyl)ethenyl]-carbene]chromium(0) (21a) with NaBD$_4$ in EtOH. From 300 mg (0.88 mmol) of **21a** and 37 mg (0.88 mmol) of NaBD$_4$ in absolute EtOH at −78°C. After 10 min of reaction and further oxidation of the reaction mixture, a colorless oil (86 mg) was obtained. The ^{1}H NMR spectrum of the reaction crude showed a 83:17 mixture of **22b** and **23b**. The products were separated by flash column chromatography (hexane/CH$_2$Cl$_2$ 8:1 to AcOEt). *Z-1-Deutero-1-ethoxy-3-(2-furyl)-1-propene* (**22b**) (67 mg, 50%) was obtained as a colorless oil. ^{1}H NMR δ=1.19 (t, 3H, *J*=7.0 Hz), 3.37 (d, 2H, *J*=7.2 Hz), 3.74 (q, 2H, *J*=7.0 Hz), 4.47 (t, 1H, *J*=7.2 Hz), 5.92 (m, 1H), 6.20 (m, 1H), 7.23 (m, 1H); ^{13}C NMR δ=155.4, 141.0 (t, $J_{\mathrm{C-D}}$=26 Hz), 140.7, 110.0, 104.4, 101.4, 67.6, 23.0, 15.1; IR (film): 1647 (C=C), 1595, 1506 cm^{-1}; MS: *m*/*z* (%): 153 (M$^+$, 100), 124 (51), 109 (17), 96 (23), 81 (22), 68 (49). *1,1,2-Trideutero-3-(2-furyl)propanol* (**23b**) (16 mg, 12%) was obtained as a colorless oil. ^{1}H NMR δ=1.80 (m, 1H), 2.66 (d, 2H, *J*=8.1 Hz), 5.55 (m, 1H), 6.21 (m, 1H), 7.24 (m, 1H); ^{13}C NMR δ=155.7, 140.8, 110.3, 105.1, 62.1 (m, CD$_2$), 31.0 (t, $J_{\mathrm{C-D}}$=19.5 Hz), 24.3; IR (film): 3413 (OH) cm^{-1}; MS: *m*/*z* (%): 129 (M$^+$, 27), 128 (15), 111 (31), 81 (100), 68 (10).

Reduction of pentacarbonyl[(ethoxy)[2-(2-furyl)ethenyl]-carbene]chromium(0) (21a) with NaBH$_4$ in CD$_3$OD. From 300 mg (0.88 mmol) of **21a** and 34 mg (0.88 mmol) of NaBH$_4$ in 10 mL of CD$_3$OD at −78°C. After 10 min of reaction and further oxidation of the reaction mixture, a colorless oil (93 mg) was obtained. The ^{1}H NMR spectrum of the reaction crude showed a 85:15 mixture of **22c** and **23c**. The products were separated by flash column chromatography (hexane/CH$_2$Cl$_2$ 8:1 to AcOEt). *Z-3-Deutero-1-ethoxy-3-(2-furyl)-1-propene* (**22c**) (71 mg, 53%) was obtained as a colorless oil. ^{1}H NMR δ=1.18 (t, 3H, *J*=7.0 Hz), 3.38 (broad s, 1H), 3.73 (q, 2H, *J*=7.0 Hz), 4.46 (t 1H, *J*=7.31 Hz), 5.92 (m, 1H), 6.00 (dd, 1H, J_1=6.2 Hz, J_2=1.47 Hz), 6.20 (m, 1H), 7.22 (m, 1H); ^{13}C NMR δ=155.4, 146.1, 140.9, 110.2, 104.6, 101.8, 67.9, 22.4 (t, $J_{\mathrm{C-D}}$=20 Hz), 15.4; IR (film): 1662 (C=C), 1595, 1560 cm^{-1}; MS: *m*/*z* (%): 153 (M$^+$, 100), 124 (52), 109 (15), 96 (66), 82 (19), 68 (54). *3-Deutero-3-(2-furyl)propanol* (**23c**) (12 mg, 11%) was obtained as a colorless oil. ^{1}H NMR δ=1.84 (m, 2H), 2.66 (t, 1H, *J*=6.1 Hz), 3.63 (t, 2H, *J*=6.1 Hz), 5.95 (m, 1H), 6.22 (m, 1H), 7.24 (m, 1H); ^{13}C NMR δ=155.5, 140.9, 110.2, 105.0, 62.1, 31.0, 24.3 (t, $J_{\mathrm{C-D}}$=25 Hz); IR (film): 3419 (OH) cm^{-1}; MS: *m*/*z* (%): 127 (M$^+$, 42), 109 (34), 108 (33), 96 (14), 81 (100), 68 (23).

Reduction of pentacarbonyl[(ethoxy)[2-(2-thienyl)ethenyl]-carbene]chromium(0) (21b) with NaBH$_4$ in EtOH. From 175 mg (0.49 mmol) of **21b** and 18.5 mg (0.49 mmol) of NaBH$_4$ in absolute EtOH at −78°C. After 5 h of reaction and further oxidation of the reaction mixture, a colorless oil (70 mg) was obtained. The ^{1}H NMR spectrum of the reaction crude only showed product, **22d**. This product was purified by column chromatography (hexane/CH$_2$Cl$_2$ 4:1). *Z-1-Ethoxy-3-(2-thienyl)-1-propene* (**22d**) (63.1 mg, 77%) was obtained as a colorless oil. ^{1}H NMR δ=1.20 (t, 3H, *J*=7.1 Hz), 3.55 (d, 2H, *J*=7.3 Hz), 3.77 (q, 2H, *J*=7.1 Hz), 4.54 (td, 1H, J_1=7.3 Hz, J_2=6.2 Hz), 5.99 (dt, 1H, J_1=6.2 Hz, J_2=1.22 Hz), 6.74 (m, 1H), 6.84 (m, 1H), 7.03 (m, 1H); ^{13}C NMR δ=145.6, 145.1, 126.7, 123.9, 123.0, 104.8, 67.8, 24.6, 15.3; IR (CHCl$_3$): 1662 (C=C), 1438 cm^{-1}.

Reduction of pentacarbonyl[(ethoxy)[2-(2-*N*-methylpyrrolyl)ethenyl]carbene]chromium(0) (21c) with NaBH$_4$ in EtOH. From 170 mg (0.48 mmol) of **21c** and 18.1 mg (0.48 mmol) of NaBH$_4$ in absolute EtOH at −20°C. After 1 h of reaction and further oxidation of the reaction mixture, a brown oil (88 mg) was obtained. The ^{1}H NMR spectrum of the reaction crude showed a 80:20 mixture of **22e** and *E*-3-(2-*N*-methylpyrrolyl)-2-propenal. The products were separated by flash column chromatography (hexane/CH_2Cl_2 8:1 to AcOEt). *Z-1-Ethoxy-3-(2-N-methylpyrrolyl)-1-propene* (**22e**) (36 mg, 45%) was obtained as a colorless oil. ^{1}H NMR δ=1.29 (t, 3H, J=7.0 Hz), 3.36 (d, 2H, J=7.0 Hz), 3.52 (s, 3H), 3.81 (q, 2H, J=7.0 Hz), 4.47 (td, 1H, J_1=7.0 Hz, J_2=6.0 Hz), 5.87 (m, 1H), 6.02 (dt, 1H, J_1=6.0 Hz, J_2=1.4 Hz), 6.03 (m, 1H), 6.52 (m, 1H); ^{13}C NMR δ=145.0, 132.4, 121.2, 106.4, 105.6, 103.7, 67.7, 33.5, 21.5, 15.3; IR ($CHCl_3$): 1662 (C=C), 1492 cm^{-1}. *E-3-(2-N-methylpyrrolyl)-2-propenal* (11 mg, 17%) was obtained as a brown oil. ^{1}H NMR δ=3.69 (s, 3H), 6.18 (m, 1H), 6.39 (dd, 1H, J_1=15.6 Hz, J_2=7.8 Hz), 6.69 (m, 1H), 6.54 (m, 1H), 7.26 (d, 1H, J=15.6 Hz), 9.49 (d, 1H, J=7.8 Hz); ^{13}C NMR δ=193.1, 139.8, 136.9, 129.0, 123.6, 114.7, 110.2, 34.6; IR (film): 1660 (CHO) cm^{-1}.

Reduction of decacarbonyl-μ-[1,4[phenylenebis(1-ethoxy-2-propen-3-yl-1-yliden)]]di-chromium(0) (28) with NaBH$_4$ in EtOH. From 500 mg (0.8 mmol) of **28** and 60.5 mg (1.6 mmol) of $NaBH_4$ in absolute EtOH at −20°C. After 6 h of reaction and further oxidation of the reaction mixture, diene **29** (119 mg, 61%) was obtained as a colorless oil. This product was purified by vacuum distillation. ^{1}H NMR δ=1.20 (t, 3H, J=7.1 Hz), 3.32 (dd, 2H, J_1=7.4 Hz, J_2=1.35 Hz), 3.76 (q, 2H, J=7.1 Hz), 4.47 (td, 1H, J_1=7.4 Hz, J_2=6.2 Hz), 5.96 (dt, 1H, J_1=6.2 Hz, J_2=1.35 Hz), 7.06 (s, 4H); ^{13}C NMR δ=145.0, 139.1, 128.2, 105.8, 67.6, 29.8, 15.3; IR (film): 1662 (C=C), 1510 cm^{-1}.

Reduction of pentacarbonyl[(1-ethoxy)(*E,E*-5-phenyl-2,4-pentadienylidene)]chromium(0) (30) with NaBH$_4$ in EtOH. From 200 mg (0.53 mmol) of **30** and 20 mg of $NaBH_4$ in absolute EtOH at −78°C. After 3 h of reaction and further oxidation of the reaction mixture, diene **31** (87 mg (60%) was obtained as a colorless oil. This product was purified by vacuum distillation. ^{1}H NMR δ=1.20 (t, 3H, J=7.1 Hz), 2.93 (dd, 2H, J_1=7.3 Hz, J_2=6.3 Hz), 3.75 (q, 2H, J=7.1 Hz), 4.37 (td, 1H, J_1=7.3 Hz, J_2=6.2 Hz), 5.97 (d, 1H, J=6.2 Hz), 6.15 (dt, 1H, J_1=15.9 Hz, J_2=6.3 Hz), 6.34 (d, 1H, J=15.9 Hz), 6.88–7.29 (m, 5H); ^{13}C NMR δ=145.3, 137.9, 129.4, 128.4, 126.7, 126.1, 125.9, 103.9, 67.6, 27.5, 15.3; This compound was unstable and could not be obtained in analytically pure form.

Reduction of pentacarbonyl[(*N,N*-dimethylamino)-(phenylethylene)carbene]chromium(0) (32) with NaBH$_4$ in EtOH. From 143 mg (0.41 mmol) of **32** and 15.5 mg (0.41 mmol) of $NaBH_4$ in absolute EtOH at room temperature, after 3 h of reaction and further oxidation, a yellow oil (46 mg) was obtained. The ^{1}H NMR spectrum of the reaction crude showed a 60:40 mixture of **33a** and **34a**. The separation of these two products was not possible by flash column chromatography although a pure fraction of **33a** could be obtained by vacuum distillation. *N,N-Dimethyl-3-(phenyl)propanamine* (**33a**), ^{1}H NMR δ=1.91–2.01 (m, 2H), 2.49 (s, 6H), 2.54 (t, 2H, J=7.8 Hz), 2.71 (m, 2H), 7.10–7.39 (m, 5H); ^{13}C NMR δ=140.7, 126.3, 128.3, 128.6, 64.2, 51.4, 33.3, 25.5; MS: m/z (%): 163 (M$^+$, 1), 91 (11), 58 (100). *E-(3-Phenyl)-N,N-dimethyl-2-propeneamine* (**34a**), data taken from an enriched mixture: ^{1}H NMR δ=2.59 (s, 3H), 3.48 (d, 2H, J=7.0 Hz), 6.37 (dt, 1H, J_1=15.8 Hz, J_2=7.0 Hz), 6.55 (d, 1H, J=15.8 Hz), 7.10–7.39 (m, 5H); ^{13}C NMR δ=137.9, 126.7, 128.5, 128.7, 135.9, 120.3, 66.5, 50.8.

Reduction of pentacarbonyl[(1-*N,N*-dimethylamino)-(phenylethylene)carbene]chromium(0) (32) with NaBD$_4$ in EtOH. From 256 mg (0.73 mmol) of **32** and 31 mg (0.73 mmol) of $NaBD_4$ in absolute EtOH at room temperature, after 3 h of reaction and further oxidation of the reaction mixture, a yellow oil (93 mg) was obtained. The ^{1}H NMR spectrum of the reaction crude showed a 60:40 mixture of **33b** and **34b**. The separation of these products was not possible by flash column chromatography or by distillation. The spectroscopical data are listed from a pure mixture of both compounds: *1,1-Dideutero-3-phenyl-N,N-dimethylpropanamine* (**33b**), ^{1}H NMR δ=1.98 (t, 2H, J=7.6 Hz), 2.48 (s, 6H), 2.55 (t, 2H, J=7.6 Hz), 7.10–7.38 (m, 5H); ^{13}C NMR δ=140.8, 126.3, 128.4, 128.6, 64.2 (m, CD_2), 51.3, 33.3, 25.4. *E-1-Deutero-N,N-dimethyl-3-phenyl-2-propenamine* (**34b**), ^{1}H NMR δ=2.52 (s, 3H), 3.47 (d, 1H, J=7.0 Hz), 6.37 (dd, 1H, J_1=15.9 Hz, J_2=7.0 Hz), 6.55 (d, 1H, J=15.9), 7.10–7.38 (m, 5H); ^{13}C NMR δ=138.0, 135.9, 128.8, 128.5, 126.8, 120.3, 66.2 (t, J_{C-D}=20 Hz), 50.8.

Reduction of pentacarbonyl[(1-*N,N*-dimethylamino)-(phenylethylene)carbene]chromium(0) (32) with NaBH$_4$ in CD$_3$OD. From 215 mg (0.61 mmol) of **32** and 23 mg (0.61 mmol) of $NaBH_4$ in 10 mL of CD_3OD at room temperature, after 18 h of reaction and further oxidation of the reaction mixture, a yellow oil (72.6 mg) was obtained. The ^{1}H NMR spectrum of the reaction crude showed a 60:40 mixture of **33c** and **34b**. The separation of these products was not possible by flash column chromatography or distillation. The spectroscopical data are listed from a pure mixture of both compounds: *2,3-Dideutero-N,N-dimethyl-3-phenylpropanamine* (**33c**), ^{1}H NMR δ=1.91–2.01 (m, 1H), 2.49 (s, 7H), 2.71 (d, 2H, J=8.7 Hz), 7.10–7.38 (m, 5H); ^{13}C NMR δ=140.8, 128.6, 128.3, 126.3, 64.1, 51.4, 32.9 (t, J_{C-D}=19 Hz), 25.0 (t, J_{C-D}=20 Hz).

Reduction of pentacarbonyl[(ethoxy)(phenylethynyl)-carbene]chromium(0) (38) with NaBH$_4$ in EtOH. From 250 mg (0.71 mmol) of **38** and 26.8 mg (0.71 mmol) of $NaBH_4$ in absolute EtOH at −20°C. After 10 min of reaction and further oxidation of the reaction mixture, an oil (85.2 mg) was obtained. The ^{1}H NMR spectrum of the reaction crude showed product **14a** exclusively. This product was purified by flash column chromatography (hexane/CH_2Cl_2 4:1 to AcOEt) and was obtained as a colorless oil (64 mg, 56%).

Reduction of pentacarbonyl[(ethoxy)(phenylethynyl)-carbene]chromium(0) (38) with NaBD$_4$ in EtOH. From 200 mg (0.57 mmol) of **38** and 24 mg (0.57 mmol) of $NaBD_4$ in absolute EtOH at −20°C. After 10 min of reaction and further oxidation of the reaction mixture, an oil (69 mg) was obtained. The ^{1}H NMR spectrum of the reaction crude showed product **14c** exclusively. This product was purified by flash column chromatography (hexane/CH_2Cl_2 4:1 to AcOEt). *E-3,3-Dideutero-3-ethoxy-1-phenyl-1-propene* (**14c**) (49 mg, 55%), colorless oil. ^{1}H NMR

δ=1.16 (t, 3H, J=7.0 Hz), 3.44 (q, 2H, J=7.0 Hz), 6.21 (d, 1H, J=15.9 Hz), 6.53 (d, 1H, J=15.9 Hz), 7.11–7.33 (m, 5H); ^{13}C NMR δ=136.9, 132.4, 128.6, 127.6, 126.6, 126.3, 70.5 (m, CD_2), 65.6, 15.3; IR (film): 1654 (C=C), 1481, 1446 cm^{-1}. MS m/z: 164 (M$^+$, 45), 163 (12), 135 (43), 119 (62), 107 (100), 93 (22), 78 (22).

Reduction of pentacarbonyl[(ethoxy)(phenylethynyl)-carbene]chromium(0) (38) with $NaBH_4$ in CD_3OD. From 90 mg (0.26 mmol) of **38** and 9.8 mg (0.26 mmol) of $NaBH_4$ in 10 mL of CD_3OD at −20°C. After 10 min of reaction and further oxidation of the reaction mixture, an oil (30 mg) was obtained. The ^{1}H NMR spectrum of the reaction crude showed **14d** exclusively. This product was purified by flash column chromatography (hexane/CH_2Cl_2 4:1 to AcOEt). *E-1,2-Dideutero-3-ethoxy-1-phenyl-1-propene* (**14d**) (24 mg 57%), colorless oil. ^{1}H NMR δ=1.18 (t, 3H, J=6.9 Hz), 3.48 (q, 2H, J=6.9 Hz), 4.07 (s, 2H), 7.16–7.33 (m, 5H); ^{13}C NMR δ=136.7, 131.5 (m), 128.4, 127.5, 126.3, 126.2 (m), 71.0, 65.6, 15.2; IR (film): 1655 (C=C), 1492, 1446 cm^{-1}; MS: m/z (%): 164 (M$^+$, 36), 163 (12), 135 (46), 120 (38), 119 (63), 118 (37), 117 (51), 108 (28), 107 (100), 106 (25).

Reduction of pentacarbonyl[(ethoxy)(phenylethynyl)-carbene]chromium(0) (38) with $NaBH_4$ in THF. From 200 mg (0.57 mmol) of **38** and 22 mg (0.57 mmol) of $NaBH_4$ in anhydrous THF at room temperature. After 3 h of reaction and further oxidation of the reaction mixture, 53 mg (59%) of a colorless oil were obtained. The ^{1}H NMR spectrum of the reaction crude showed the presence of **14a** as the sole reaction product.

Reduction of pentacarbonyl[(ethoxy)(phenylethynyl)-carbene]tungsten(0) (39) with $NaBH_4$ in EtOH. From 200 mg (0.41 mmol) of 39 and 15.7 mg (0.41 mmol) of $NaBH_4$ in absolute ethanol at −20°C. After 1 h of reaction and further oxidation of the reaction mixture, 40 mg (61%) of **14a** were obtained as a yellow oil.

Reduction of 1-phenyl-1,2-propene (43) with $NaBH_4$ in EtOH. From 200 mg (1.25 mmol) of **43**[32] and 47.2 mg (1.25 mmol) of $NaBH_4$ in absolute EtOH at −20°C. After 4.5 h of reaction and further oxidation of the reaction mixture, 87 mg of a brown oil were obtained. The ^{1}H NMR spectrum of the reaction crude showed the starting material unaltered.

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