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1,4- to 1,5-Homologation of Alkene−Carbene and Alkyne−Carbene Complexes of Chromium and Tungsten: The Clue to Reactivity

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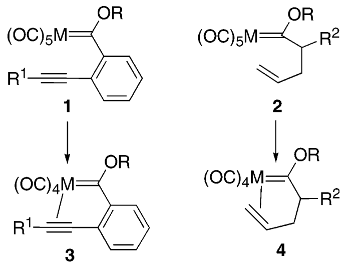
*Summary: The carbene carbon of 1,4-alkene and -alkyne carbene complexes of chromium and tungsten (**1** and **2**) reacts with nucleophiles such as hydrides originating from dihydropyridine and methyllithium to give upon CO and alkyne (or alkene) insertions polycyclic lactones **6** and **7**, cyclopentanones **10** and **11**, and cyclopentanols **12**.*

Attempts to elucidate the mechanism of metal-induced transformations of organic compounds rely very often on the synthesis and behavior of model complexes mimicking such presumed discrete intermediates and possibly their evolution. However, the isolation of such complexes occurs in general at the expense of reactivity. For example, in the chemistry of carbene complexes, the synthesis and behavior of alkene−carbene and alkyne−carbene complexes has been the subject of extensive investigations, since they were involved in benzannulation, olefin cyclopropanation, and metathesis reactions.[1−3] In that regard we focused on two such complexes, **1** and **2**, which were synthesized respectively by Dötz[2a,b] and by our group[3b] (Scheme 1).

Scheme 1



Although both complexes underwent the crucial coordination of the triple and double bonds to give complexes **3** and **4**, *neither **3** nor **4** underwent an intramolecular insertion* of the coordinated double or triple bonds.[2b,4a−d] Herein we report a very simple means to lift the lack of reactivity of the carbene function in **1** and **2** toward the tethered triple and

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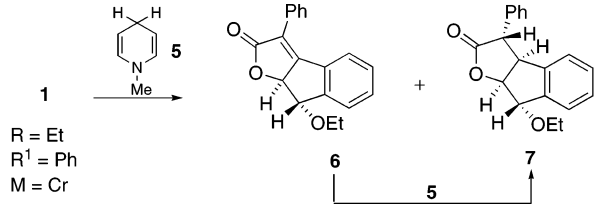
[1] (a) Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Abel, A. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 12, p 469. (b) Hegedus, L. S. In ref 1a, p 549. (c) *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, Germany, 2003.

[2] (a) Hohmann, F.; Siemoneit, S.; Nieger, M.; Kotila, S.; Dötz, K. H. *Chem. Eur. J.* **1997**, *3*, 853. (b) Dötz, K. H.; Schäfer, T.; Kroll, F.; Harms, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1236. (c) Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064.

[3] (a) Casey, C. P.; Vollendorf, N. W.; Haller, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 3754. (b) Alvarez, C.; Levisalles, J.; Rudler, M.; Rudler, H.; Daran, J. C.; Jeannin, Y. *J. Organomet. Chem.* **1982**, *228*, C7. (c) Casey, C. P.; Hornung, N. L.; Kosar. W. P. *J. Am. Chem. Soc.* **1987**, *109*, 4908. (d) Barluenga, J.; Aznar, F.; Martin, A.; Garcia-Granda, S.; Pérez-Carreno, E. *J. Am. Chem. Soc.* **1994**, *116*, 11191. (e) Soderberg, B. C.; Hegedus, L. S. *Organometallics* **1990**, *9*, 3113.

10.1021/om0491286 CCC: $30.25

Scheme 2



double bonds: their reaction with nucleophiles. This induces an increase in the distance between the carbene function and the tethered unsaturation by one unit.

Complexes **1** and **2** were synthesized according to the literature[2a,5a] and successively submitted to nucleophiles such as hydrides originating from dihydropyridines and alkylmetals such as methyllithium, which are both known to add to the carbene carbon of Fischer-type carbene complexes.[5a,b]

Thus, when a CH_2Cl_2 solution of complex **1** at −10 °C was treated with a mixture of 2,2-dihydro- and 4,4-dihydro-1-methylpyridines **5** (only one isomer shown) in the same solvent, stirred at this temperature for 15 min, and then left at room temperature for 12 h, the two new crystalline organic compounds **6** and **7** were isolated in an overall yield of 40% (Scheme 2). Their structures were established by detailed analyses of their ^{13}C and ^{1}H NMR data. Moreover, the structure of **6**, a tricyclic butenolide (34%, mp 116 °C), could be confirmed through single-crystal X-ray diffractometry[6] (Figure 1), which confirmed the reduction of the carbene function and the insertion of a first CO group, of the triple bond, and of a second CO group.

As far as **7** is concerned (6%, pale yellow crystals, mp 110 °C), it contains two extra methine groups and could thus be the result of the reduction of the carbon−carbon double bond of **5.** And indeed, mixing **6** in CH_2Cl_2 with a 3-fold excess of dihydropyridines led quantitatively after 12 h at room temperature to **7**. This is, to the best of our knowledge, the first example of the reduction of the double bond of a conjugated carbonyl group by N-substituted dihydropyridines.[7a,c]

When instead MeLi (1.6 M, 1.5 equiv) in diethyl ether was added to a THF solution of **1** at −40 °C, a deep red solution developed rapidly. Warming to room temperature followed by stirring for 12 h led to two new crystalline compounds (Scheme 3; 46% yield). The faster moving compound, obtained as deep red needles (32%, mp 150 °C), was given structure **9** on the grounds of NMR spectroscopy. Particularly diagnostic were signals present in the ^{1}H NMR spectrum of **9**, including a singlet for a methyl group at δ 2.08 ppm, four quaternary carbons besides those for the aromatic groups in the ^{13}C NMR spectrum, and the disappearance of the signals for the ethoxy group. An X-ray analysis[6] confirmed structure **9** and, thus, the addition of the methyl group to the former carbene carbon of **1** with loss of the ethoxy group. The NMR data of the second compound agreed with structure **8** (14%, mp 130 °C), a butenolide bearing a methyl group (δ 1.25 ppm), a methine group (δ 5.4 ppm), and still the ethoxy group of the starting carbene complex **1** with signals for its two stereotopic hydrogens. Its structure is thus directly linked to the structure of **6**. Interestingly, slow formation of **9** from **8** on silica gel was observed.[8]

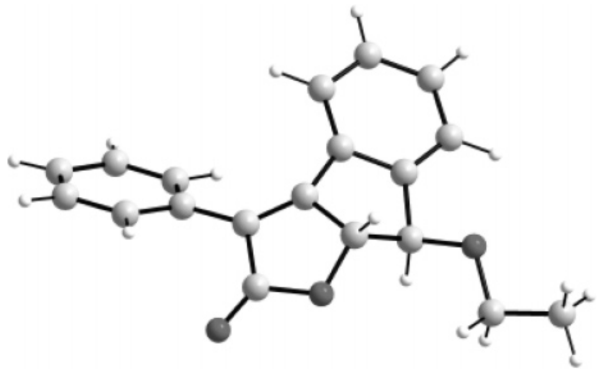
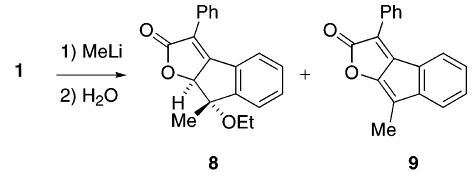
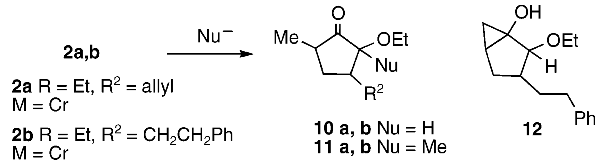


Figure 1. Diamond view of butenolide **6**.

Scheme 3



Scheme 4



The same series of reactions was then carried out on complexes **2a**,**b** (R = allyl, CH_2CH_2Ph). Under the same conditions as above, *N*-methyldihydropyridines **5** led with **2a** to the substituted cyclopentanone **10a**, isolated as a single isomer (Scheme 4; 83%), and methyllithium gave, at −70 °C, two separable diastereomers **11a** (10:1, 41%). Whereas the singlet for the methyl in an α position with respect to the carbonyl group appeared at δ 1.05 ppm in the less polar and less abundant isomer, it appeared at δ 1.18 ppm in the more polar isomer, an indication of the probable axial vs equatorial position of this substituent. Complex **2b** behaved similarly: with **5**, two compounds were isolated in 68% yield, the cyclopentanone **10b** (37%, one isomer) and **12** (31%, one isomer), a cyclopropanol, showing in the ^{1}H NMR spectrum typical high-field signals for three adjacent protons. With MeLi, the cyclopentanone **11b** was obtained as a 1:1 mixture of isomers (52%).[9]

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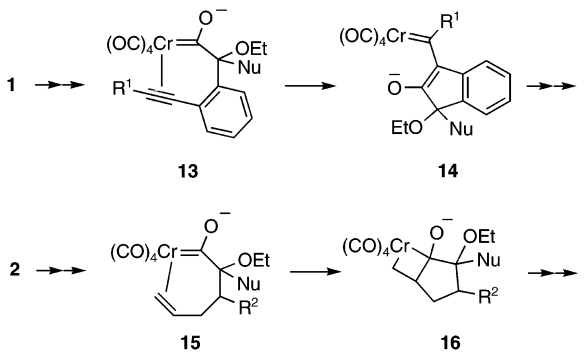
(5) (a) Rudler, H.; Parlier, A.; Durand-Réville, T.; Martin-Vacan, B.; Audouin, M.; Garrier, E.; Certal, V.; Vaissermann, J. *Tetrahedron* **2000**, *56*, 5001. (b) Rudler, H.; Parlier, A.; Certal, V.; Lastennet, G.; Audouin, M.; Vaissermann, J. *Eur. J. Org. Chem.* **2004**, 2471.

(6) Crystal data: $C_{19}H_{16}O_3$, M_w = 292.33, monoclinic, $P2_1$, a = 8.271(3) Å, b = 19.028(6) Å, c = 9.7530(12) Å, β = 102.38(2)°, V = 1499.2(7) Å^3. X-ray data for **9** can be found in the Supporting Information.

(7) (a) Braude, E. A.; Hannah, J. Linstead, R. *J. Chem. Soc.* **1960**, 3257. (b) Zhu, X.-Q.; Zou, H.-L.; Yuan, P.-W.; Liu, Y.; Cao, L.; Cheng, J.-P. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1857. (c) Garden, S. J.; Werneck Guimareas, C. R.; Corréa, M. B.; de Oliveira, C. A. F.; da Cunhia Pinto, A.; de Alencastro, R. B. *J. Org. Chem.* **2003**, *68*, 8815.

(8) A minor compound (<5%) was also isolated; its formation will be discussed elsewhere (see the Supporting Information).

Scheme 5



The formation of **6**, **8**, and **10**−**12** can be accounted for by the addition of a nucleophile (H^-, Me^-) to the carbene carbon and homologation of the starting carbene complex upon insertion of a CO group with concomitant coordination/insertion of the triple or double bonds, leading in each case to a five-membered ring (Scheme 5): **13** → **14** and **15** → **16**. This is followed by a well-documented lactonization,[5,10] for **14**. Conversely, a reductive elimination on **16** leads after protonation to the cyclopropanol **12** or, upon rearrangement, to the ketones **10** and **11**. No such products were detected, however, starting from complexes of the type **4**, a result which confirms that the presence of five CO groups is fundamental to the first CO insertion.[11]

In summary, the key point for the success of these insertion reactions is the formation of complexes **13** and **15** bearing an unsaturation now three carbons remote from the carbene carbon. It is indeed known that carbene complexes containing an unsaturation in δ with respect to the carbene carbon, which can be obtained inter alia upon *double* homologations by alkyne insertions into **1** or **2**, easily undergo intramolecular cyclopropanation reactions.[3,4] The present communication demonstrates clearly that the necessary and sufficient condition for triggering these transformations is a *single* homologation of the carbene function brought about by the interaction of the carbene carbon with a nucleophile.

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Supporting Information Available: Text and figures giving experimental procedures and spectroscopic data for the compounds prepared in this paper and X-ray crystallographic data for compounds **6** and **9** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Complex **3a** (M = W) behaved similarly.

(10) Foland, D. L.; Karlsson, J. O.; Perri, S. T.; Schwabe, R.; Xu, S. L.; Patil, S.; Moore, H. W. *J. Am. Chem. Soc.* **1989**, *111*, 975.

(11) $[(CO)_5Cr{-}R]^-$ is isoelectronic with $(CO)_5Mn{-}R$, which easily undergoes CO insertion reactions.