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[6] Neither a relevant reduced Keggin ion $[H_xPMo_{12}O_{40}]^{3-}$ nor the $\{Mo_{72}Fe_{30}\}$-type compounds containing only Mo^{VI} and Fe^{III} centers without an encapsulated Keggin ion (see ref. [4]) taken separately show this electronic absorption band at 550 nm. Using blue or green excitation lines give Raman spectra of the capsule with changing intensity only of the 830 cm^{-1} band.

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Linear Coupling of Three CO Ligands of Chromium Hexacarbonyl Leading to Functionalized Butenolides via Fischer Carbene Complexes

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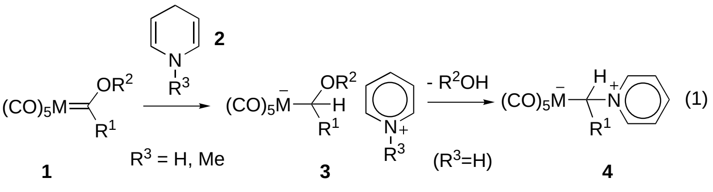
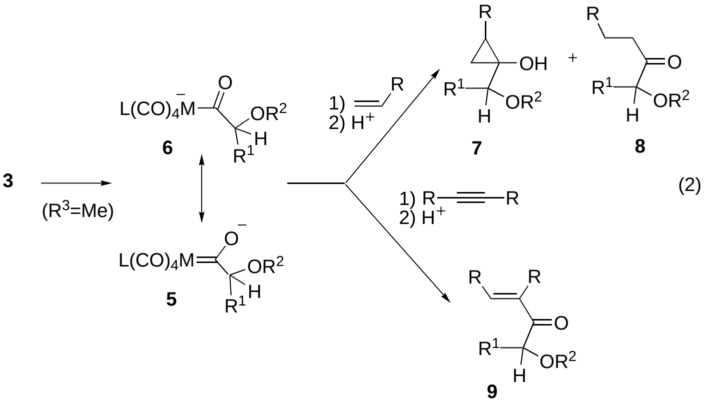
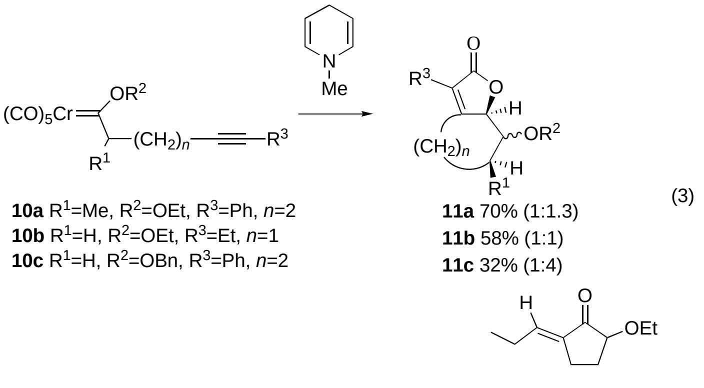
Fischer carbene complexes have been widely used for the synthesis of a broad spectrum of organic compounds.[1, 2] By far the best known applications are the formation of cyclopropanes and phenols by reaction with olefins and alkynes, respectively. Whereas in the former, besides the olefin, one CO ligand of $[Cr(CO)_6]$ is incorporated as a carbene group, in the latter, besides the alkyne, two CO ligands are included in the final product, the first one again as a carbene group. Here we describe the first general synthesis of functionalized polycyclic butenolides by incorporation of three CO groups of $[Cr(CO)_6]$, besides an alkyne. This reaction involves successive insertion reactions of a carbene complex of chromium, an alkyl chromate, an acylium chromate, and a ketene complex of chromium.

In previous papers, we have described a general dihydropyridine-induced reduction of alkoxycarbene complexes of chromium and tungsten to pyridinium metalates **3** [Eq. (1)].[3–5] When $R^3 = H$, isolable pyridinium ylide complexes **4** were formed in high yield; for $R^3 = Me$, unstable *N*-methylpyridinium metalates **3** could be characterized by NMR spectroscopy. Interestingly, the latter complexes underwent a CO insertion reaction, akin to that observed for other (carbonyl)metalates,[6–12] to give oxycarbene complexes **5**, a resonance form of the acylium metalates **6**. These complexes gave hydroxycyclopropanes **7** and/or ketones **8** with alkenes, whereas reaction with alkynes gave *α,β*-unsaturated ketones **9** [Eq. (2)].





However the most gratifying transformation occurred in the case of alkynylalkoxycarbene complexes of chromium. When complex **10a** was treated with a twofold excess of *N*-methyldihydropyridine at −10 °C and the reaction mixture warmed to room temperature overnight, the bicyclic butenolide **11a** was obtained in 70% yield as a 1/1.3 mixture of *cis*/*trans* isomers which differ in the relative configuration of the hydrogen atoms at the ring junction and on the carbon atom bearing the ethoxyl group [Eq. (3)]. Their structures were established by NMR spectroscopy.



10a R^1=Me, R^2=OEt, R^3=Ph, *n*=2
10b R^1=H, R^2=OEt, R^3=Et, *n*=1
10c R^1=H, R^2=OBn, R^3=Ph, *n*=2

11a 70% (1:1.3)
11b 58% (1:1)
11c 32% (1:4)

12 (11%)

Changing the nature of the substituents on the triple bond and the number of methylene groups in the alkynyl chain did not affect the course of the reaction: complex **10b** gave **11b** in 58% yield as a 1/1 mixture of isomers together with 11% of **12**. The alkoxyl group was modified by a known procedure, which in the case of benzyl alcohol led to **10c**.[13, 14] Reaction of **10c** with *N*-methyldihydropyridine gave the butenolide **11c**, again as a mixture of isomers (1:4), in 32% yield.

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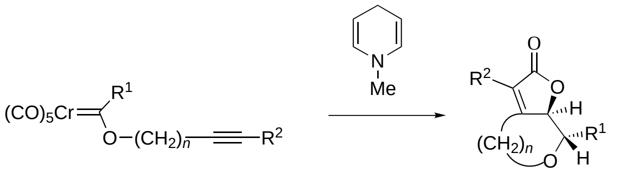
Similarly, the introduction of alkynyloxy groups led to the carbene complexes **13a–e**. In all the cases examined so far, clean conversion to the expected butenolides **14a–e**, as single isomers, was observed. Lengthening of the alkynyl chain led to the expected product **14d** containing a seven-membered ring, albeit in a much lower yield (12%) [Eq. (4)].



(4)

13a R^1=Ph, R^2=Ph, *n*=2
13b R^1=Me, R^2=Ph, *n*=2
13c R^1=cyclopropyl, R^2=Ph, *n*=2
13d R^1=Ph, R^2=Ph, *n*=3
13e R^1=cyclopropyl, R^2=H, *n*=2

14a 46%
14b 47%
14c 64%
14d 12%
14e 47%

The structure of compound **14a** was confirmed by X-ray crystallography, and a Cameron projection appears in Figure 1. It clearly shows the *trans* stereochemistry of the carbon–oxygen single bond of the lactone with respect to the phenyl group, and more importantly, the presence of the coupled three former CO groups.

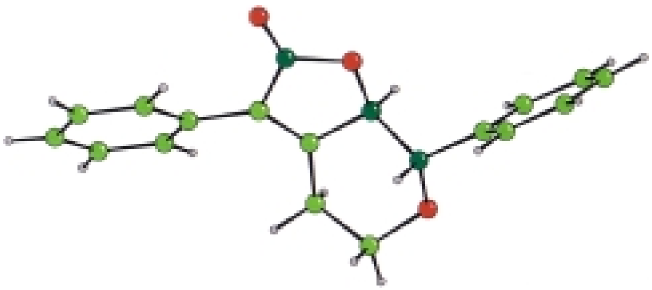
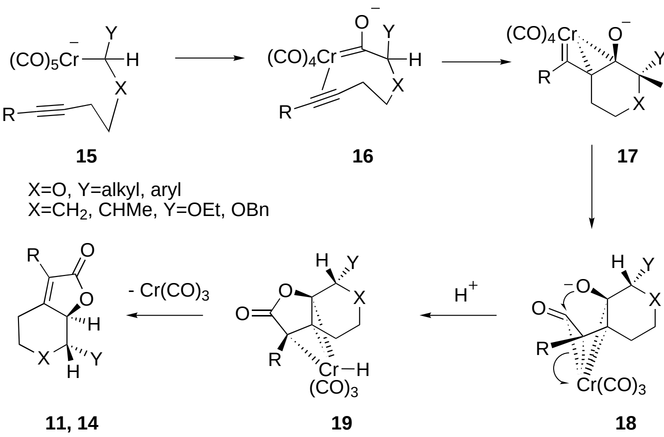


Figure 1. Molecular projection of the butenolide **14a** showing the carbon and the oxygen atoms of the incorporated carbonyl groups. Color code: C green, O red, H gray.

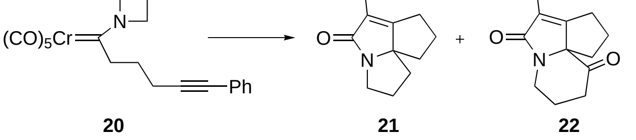
Although the exact structures of the intermediates are unknown as yet, a mechanism can be suggested on the basis of previous observations. The reduction of the starting carbene complexes with *N*-methyldihydropyridine leads first to the chromate **15** [Eq. (5)]. A straightforward transformation into an oxycarbene complex **16** by migration of the (alkoxy)alkyl group to an adjacent CO ligand then occurs with concomitant coordination of the triple bond. A classical transformation of **16** leads to **17**, a new carbene complex, then to ketene complex **18**. The close proximity of a nucleophile to the central carbon atom of the ketene, a situation which was already encountered in the insertion of alkynes into alkoxy- and aminocarbene complexes of chromium, promotes the formation of an oxygen–carbon bond, the last step of a linear oligomerization of three CO groups of $[Cr(CO)_6]$.[15, 17, 18]



(5)

The general stereochemical outcome of these cascade insertions is linked to two determining steps: the transfer of a hydride to the carbene carbon atom and the addition of a proton to the carbon atom α to the former carbene carbon atom in the ketene complex **18**. The exact mechanism of these processes is still a matter of speculation. Three cases must be considered: first, when the alkynyl chain is linked to the oxygen atom as in **15** (X = O, Y = alkyl or aryl), then the reaction led specifically to a single isomer in which Y is *trans* with respect to the carbon–oxygen single bond of the lactone. This might be indicative of a metal-assisted stereospecific protonation:[16] for steric reasons, the cycloaddition between the triple bond and the carbene moiety in **16** is likely to lead to **17** and then to **18**, in which the alkoxide is *trans* to Y and to the metal center. Protonation at the metal atom would then lead to **19**, which might deliver hydride *cis* to Y and give **14**. For less bulky substituents, as in **15** (Y = OEt, X = CH_2), the selectivity of the protonation step is obviously less marked, and both the *cis* and *trans* isomers are formed. The behavior of complexes of the type **15** (Y = OEt, OBn, X = CHMe) was peculiar, since only two isomers, in which the carbon–oxygen single bond of the lactone and the methyl groups adopt a *cis* configuration, were detected. Three contiguous asymmetric carbon centers are present in **11a**, two of which are formed during the insertion reactions. In these cases, the lack of complete diastereosectivity may be due to a lack of stereoselectivity in the hydride-transfer step.

Although we had already observed during the thermolysis of aminocarbene complexes of the type **20**, besides the expected product **21**, a product of structure **22**, in which three CO groups have been incorporated, its structure, and thus the mode of its formation is fundamentally different, since the CO groups are not linearly coupled in the tricyclic nitrogen-containing compound.[17, 18] [Eq. (6)]



(6)

Taken together, the transformations described here lead to butenolides in which three former CO ligands of $[Cr(CO)_6]$ are linked together by carbon–carbon or carbon–oxygen bonds.

Experimental Section

Reaction of *N*-methyldihydropyridine with carbene complexes (general procedure): A solution of *N*-methyldihydropyridine (3 equiv) in CH_2Cl_2 (0.5 mL per mmol of amine) was added dropwise to a solution of carbene complex (1 equiv) in CH_2Cl_2 (25 mL per mmol of carbene) at −10 °C under argon . After 15 min, the ice bath was removed and the mixture was stirred at room temperature for 24 h. The solution slowly turned dark red. The solvent was evaporated under vacuum, and the residue purified by chromatography on silica gel with petroleum ether (PE)/Et_2O as eluent.

The general procedure was followed with carbene complex **10a** (2.03 g, 5 mmol). Elution with PE/Et_2O (70/30) gave a 4:3 mixture of two isomers (0.953 g, 70 %). **11a** (*trans*): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.49-7.24$ (m, 5H; ArH), 4.74 (d, ^3J (H,H) = 8.4 Hz, 1H; H^{7a}), 4.06 (m, 1H; OCH_2), 3.60 (m, 1H; OCH_2), 2.81 (dd, ^3J(H,H) = 10.2, 8.4 Hz, 1H; H^7), 2.32 (m, 1H; H^4), 1.90 (m, 1H; H^4), 1.56 (m, 1H; H^5), 1.75 (m, 1H; H^6), 1.24 (t, ^3J (H,H) = 7 Hz, 3H; CH_3), 1.08 (d, ^3J (H,H) = 6.3 Hz, 1H; H^8), 0.84 (m, 1H; H^5); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 172.6$ (CO), 161.2 (C^3), 129.5, 128.8, 128.5, 128.3, 128.1 (Ar), 124.4 (C^{3a}), 87.8 (C^{7a}), 85.9 (C^7), 67.9 (OCH_2), 35.9 (C^6), 32.3 (C^4), 25.7 (C^5), 17.4 (C^8), 15.5 (CH_3). **11a** (*cis*): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.49-7.24$ (m, 5H; ArH), 4.82 (d, ^3J(H,H) = 3.4 Hz, 1H; H^{7a}), 3.82 (br s, 1H; H^7), 3.72 (m, 1H; OCH_2), 3.57 (m, 1H; OCH_2), 3.01 (m, 1H; H^4), 2.30 (m, 1H; H^4), 1.80 (m, 1H; H^6), 1.58 (m, 2H; H^5), 1.08 (d, ^3J (H,H) = 6.3 Hz, 3H; H^8), 1.05 (t, 3H; ^3J(H,H) = 9 Hz, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 173.3$ (CO), 161.0 (C^3), 130.5, 129.2, 128.9, 128.8, 128.6 (Ar), 125.7 (C^{3a}), 83.0 (C^{7a}), 80.9 (C^7), 69.8 (OCH_2), 34.5 (C^6), 26.7 (C^4), 26.1 (C^5), 17.8 (C^8), 15.9 (CH_3); HR-MS (positive EI) calcd. for $C_{17}H_{21}O_3$: 273.1491; found: 273.1495.

The general procedure was followed with carbene complex **13a** (2 g, 4.69 mmol). Elution with PE/Et_2O (80/20) gave **14a** as a white solid (0.631g, 46 %), m.p. 59 °C. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.58-7.35$ (m, 10H; ArH), 4.75 (d, ^3J(H,H) = 8.8 Hz, 1H; H^{7a}), 4.38 (dd, ^3J(H,H) = 11.4 Hz, 1H; H^5), 4.15 (d, 1H; ^3J(H,H) = 8.8 Hz, 1H; H^7), 3.52 (td, 1H; ^3J(H,H) = 11.4, 3 Hz, 1H; H^5), 3.15 (dd, 1H; ^3J(H,H) = 2.5, 14 Hz, H^4), 2.91 (ddd, ^3J(H,H) = 14, 11.8, 6 Hz, 1H; $H^{4'}$); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 171.9$ (CO), 159.4 (C^3), 138.0 (C^{3a}), 129.3, 128.9, 128.8, 128.6, 126.3, 124.8 (Ar), 85.0 (C^7), 81.1 (C^{7a}), 67.8 (C^5), 29.3 (C^4); elemental analysis calcd for $C_{19}H_{16}O_3$: C 78.08, H 5.49; found: C 77.93, H 5.49. HR-MS (positive EI) calcd for $C_{19}H_{17}O_3$: 293.1178; found: 293.1174.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137062. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Spectroscopy of the Formation of Microporous Transition Metal Ion Containing Aluminophosphates under Hydrothermal Conditions**

Bert M. Weckhuysen,* David Baetens, and
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One of the greatest challenges of experimentalists working in the field of molecular sieve science is the understanding of the principles that determine how porous crystalline materials are formed starting from a precursor gel under hydrothermal conditions.[1] This is far from easy because hydrothermal crystallizations take place in a closed vessel, where many interactions, equilibria, and chemical processes continuously change with crystallization time.[2] The lack of knowledge about these phenomena means that a rational a priori design of novel molecular sieves is still impossible and, consequently to date, the synthesis of such materials requires a systematic and intelligent screening of the *n*-dimensional reaction. Recently, the concepts of combinatorial chemistry[3] and experimental design[4] have been successfully explored in order to speed up this screening process. Clearly, a more detailed understanding of the processess occurring during the synthesis of these materials is required, which can lead to a more rational approach towards zeolite syntheses.

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