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Reactions of complex ligands Part 91☆. Application of ring closing metathesis to Fischer-type carbene complexes: synthesis and structure of medium-sized chromium oxacycloalkenylidenes

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Abstract

Six- and seven-membered pentacarbonyl(2-oxacycloalkenylidene) chromium complexes **17** and **6** have been synthesized in moderate to good yields from alkenyloxy(methyl)carbene complex precursors applying an α-alkylation/ruthenium based ring closing metathesis sequence. The ring-closure is hampered for β-alkylated vinylcarbene complexes which may undergo competing intermolecular cross metathesis at the alkenyloxy terminus in low yield.

Keywords: Carbene complexes; Crotonates; Ring closing metathesis; Cross-metathesis

1. Introduction

Within a few years ring closing metathesis (RCM) has been developed to a flexible and efficient methodology for the synthesis of small, medium and large homo- and heterocycles [2]. The easy to handle ruthenium-based catalyst introduced by Grubbs [3] and more recent variations thereof [4] tolerate various functional groups including heteroatoms and, thus, find increasing application in the synthesis of macrocycles as convincingly demonstrated in examples of biological importance [5]. We became interested in whether the Grubbs catalyst is compatible with another metal alkylidene moiety as provided by a Fischer-type metal carbene bearing alkene termini in both carbene side chains. Carbonyl carbene complexes [6] provide a variety of more conventional or unique methodologies for stereoselective carbon–carbon bond formation; they may be based on the α-CH acidity [7] of alkyl carbene ligands as exploited in aldol reactions [8], on α,β-unsaturated carbene ligands activated for Michael-type addition [9], on $[n+2]$ cycloaddition reactions [10], or on metal-centered three-component cycloaddition reactions such as the chromium-mediated benzannulation reaction [11]. We now report on the synthesis of alkenyl(alkenyloxy)carbene complexes of chromium and on their potential for ring closing metathesis.

2. Synthesis of 2-oxacyclohept-4-enylidene complexes

The synthesis of suitable RCM precursors follows a two-step sequence based on the alcoholysis of the acetoxy(methyl)carbene complex [12], generated in situ from tetramethylammonium acetyl(pentacarbonyl)-chromate (**1**) and acetyl bromide [13], and subsequent tandem deprotonation/alkylation of the alkenyloxy(methyl)carbene complexes **2**, **3** [14]. This protocol afforded alkenyloxy(butenyl)carbene complexes **4**, **5** in 63 and 56% overall yields (Scheme 1). The number of methylene spacers in the alkenyloxycarbene side chain turned out to be crucial for ring closing

☆ For Part 90, see Ref. [1].

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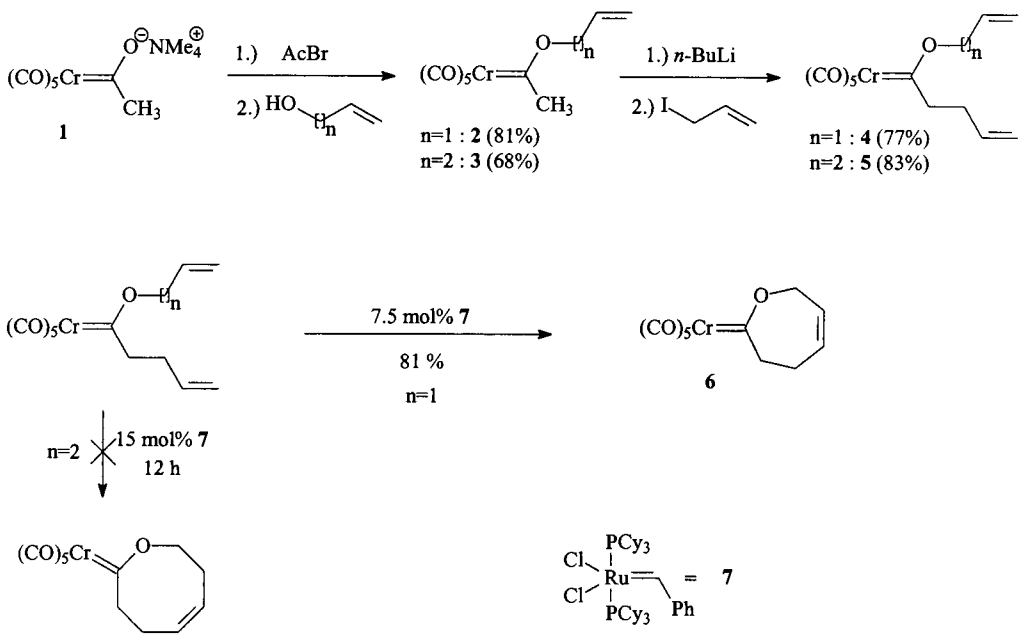
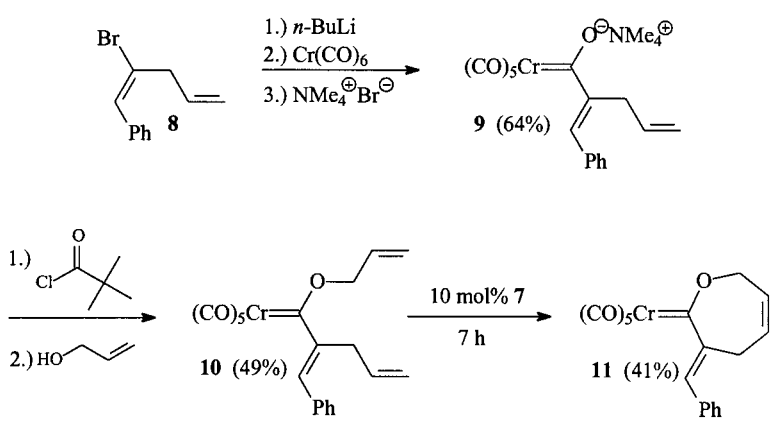
metathesis. The allyloxycarbene complex **4** underwent clean cyclization in dichoromethane at room temperature in the presence of 7.5 mol% Grubbs catalyst **7** to give a 81% yield of chromium 2-oxacyclo-4-heptenylidene **6**. The butenyloxycarbene complex analogue **5**, however, eluded ring closure even under more forcing or high dilution conditions. This result is consistent with the well-documented reluctance along the formation of eight-membered rings by RCM [15] reflecting severe transannular repulsive interactions in the transition state [16].

The α-CH acidity of oxacycloheptenylidene complex **6** was expected to allow for an exocyclic modification as required for ligand-centered conjugate addition, $[n+2]$ cycloaddition or metal-centered benzannulation reactions. The standard deprotonation/*exo*-methylenation protocol applying a methyleneiminium electrophile [17], however, failed to give satisfactory yields. Thus, we persued an alternative approach which started from 2-bromo-1,4-diene **8** [18]; lithiation and addition to hexacarbonyl chromium followed by metathesis with tetramethylammonium bromide afforded acyl chromate **9**; activation for nucleophilic attack by acylation with pivaloyl chloride and alcoholysis using allyl alcohol gave metal carbene triene **10**. At room temperature it slowly undergoes decarbonylation and chelation via the allyloxy side chain to form a stable five-membered carbene chelate complex [19]. In order to avoid this unfavourable process and to retain the uncoordinated terminal alkene moiety, the ring closing metathesis was performed at 0°C, which finally afforded red crystals of *exo*-benzylidene complex **11** as a single *E*-isomer after chromatographic workup in moderate yield (Scheme 2).



Scheme 1. Synthesis and ring closing metathesis of alkenyloxy(butenyl)carbene complexes.



Scheme 2. Synthesis of *exo*-benzylidene complex **11**.

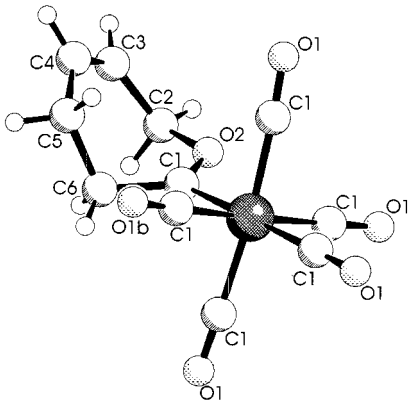


Fig. 1. Molecular structure of 2-oxacycloheptenylidene complex **6**.

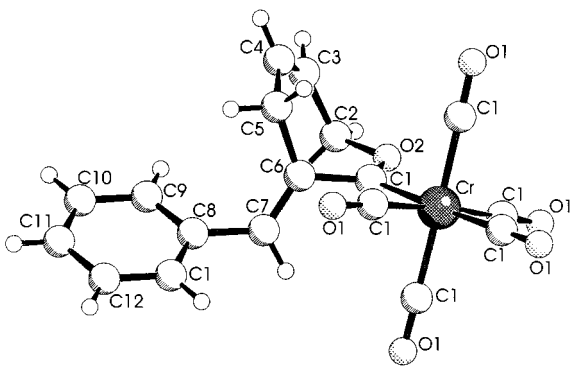


Fig. 2. Molecular structure of *exo*-benzylidene complex **11**.

Table 1
Selected bond lengths (Å) in 2-oxacycloheptenylidene complexes **6** and **11**

Bond	**6**	**11**
Cr–C(1a)	1.895(2)	1.901(2)
Cr–C(1b)	1.900(1)	1.914(2)
Cr–C(1c)	1.902(2)	1.896(2)
Cr–C(1d)	1.908(1)	1.909(2)
Cr–C(1e)	1.902(2)	1.912(2)
Cr–C(1)	2.014(1)	2.006(2)
C(1)–O(2)	1.313(2)	1.319(2)
C(1)–C(6)	1.499(2)	1.488(2)
C(3)–C(4)	1.320(2)	1.324(3)
C(6)–C(7)		1.337(2)

3. Molecular structure of 2-oxacycloheptenylidene complexes 6 and 11

In order to elucidate the conformation of the unsaturated medium-sized oxacycloalkylidene ring the molecular structure of complexes **6** and **11** was established by X-ray analysis (Figs. 1 and 2, Tables 1–3). Suitable crystals have been grown from saturated solutions in *n*-hexane at −28°C. In both cases the oxacycloheptenylidene ring adopts similar half-chair conformations irrespective of the substitution of the α-sp^2 carbon center in **11** for the sp^3 carbon atom in **6**; the angle between the C(3)–C(4)–C(5) plane and the C(2)–O(2)–C(1)–C(6) plane is nearly identical for both complexes (121.7 (3) for **6**, 121.4 (3) for **11**). The

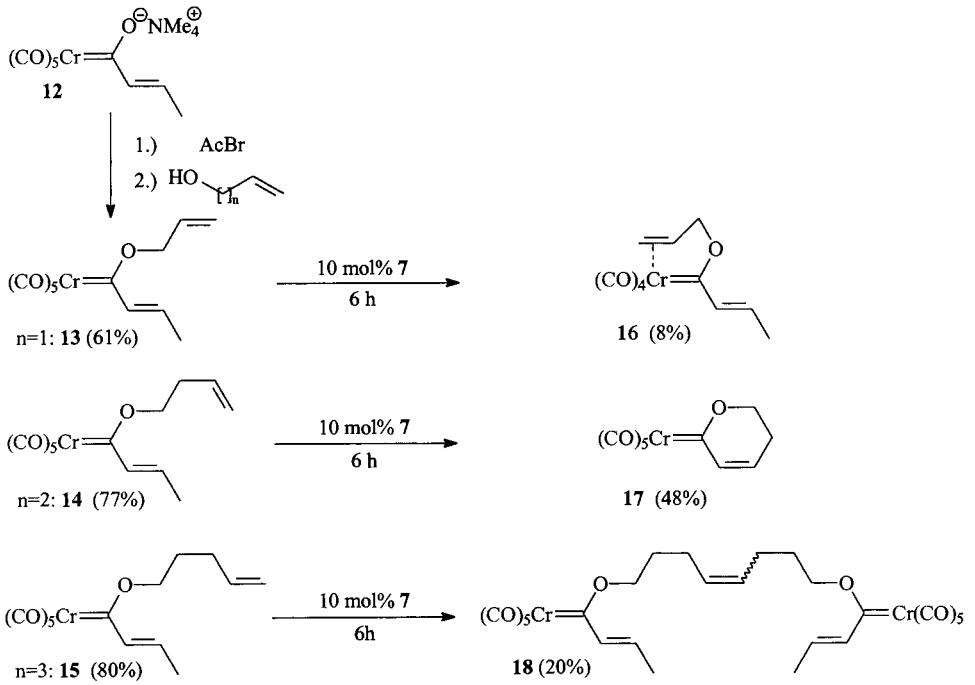
Table 2
Bond angles and torsion angles (°) in 2-oxacycloheptenylidene complexes **6** and **11**

Angle	**6**	**11**
Cr–C(1)–C(6)	125.0(9)	123.6(1)
Cr–C(1)–O(2)	119.6(9)	121.7(1)
O(2)–C(1)–C(6)	115.3(1)	114.4(1)
O(2)–C(2)–C(3)	113.0(1)	112.5(2)
C(1)–C(6)–C(5)	110.1(1)	113.6(1)
C(1b)–Cr–C(1)–C(6)	−23.3(1)	−8.7(2)
C(1c)–Cr–C(1)–O(2)	−24.3(1)	−19.6(2)
C(6)–C(1)–O(2)–C(2)	−2.1(2)	−5.1(2)
C(2)–C(3)–C(4)–C(5)	−2.8(3)	0.0(3)
C(3)–C(4)–C(5)–C(6)	−9.7(2)	−6.5(3)
Cr–C(1)–C(6)–C(7)		−73.8(2)
C(1)–C(6)–C(7)–C(8)		179.6(2)
C(6)–C(7)–C(8)–C(9)		50.1(3)

Table 3
Crystallographic and data collection parameters for complexes **6** and **11**

	6	**11**
Empirical formula	$C_{11}H_8O_6Cr$	$C_{18}H_{12}O_6Cr$
Formula weight	288.17	376.28
Temperature (K)	123(2)	123(2)
Wavelength (Å)	0.71073 (Mo–K_α)	0.71073 (Mo–K_α)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$ (no.2)	$P\bar{1}$ (no.2)
a (Å)	7.4188(5)	9.3914(4)
b (Å)	9.3844(7)	9.8758(4)
c (Å)	9.5291(6)	10.0074(5)
α (°)	99.417(3)	91.289(3)
β (°)	111.380(3)	90.405(2)
γ (°)	94.540(3)	114.127(2)
V (Å^3)	602.45(7)	846.73(7)
Z	2	2
$D_{calc.}$ (g cm^{-3})	1.589	1.476
μ (mm^{-1})	0.965	0.706
Crystal dimension (mm)	0.50 × 0.35 × 0.20	0.30 × 0.20 × 0.10
$2\theta_{max}$ (°)	28.30	28.27
Number of reflections recorded	7322	12839
Number of non-equivalent reflections recorded	2775	4004
R_{merg}	0.0363	0.0416
Number of parameters refined	163	226
R_1[a]; wR[b]	0.0257; 0.0738	0.0358; 0.0933
Goodness-of-fit[c]	1.10	1.04
Final max, min $\Delta\rho$ (e Å^{-3})	0.312/−0.373	0.443/−0.827

[a] $R_1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$ (for $I>2\sigma(I)$).
[b] $wR = [\Sigma w|F_o^2|_2]^{1/2}$
[c] Goodness-of-fit $= \{\Sigma[w|F_o^2|-|F_c^2|)^2]/(N_{obs}-N_{params})\}^{1/2}$.



Scheme 3. Reactions of chromium alkenyloxy(2-propenyl)carbenes under RCM-conditions.

majority of the pentacarbonyl carbene complexes adopt solid state conformations in which the carbene ligand bisects the angle of the *cis*-$M(CO)_2$ fragment [20]. In complexes **6** and **11,** however, the bisecting angle is reduced to 23.3° (for **6**) and 8.7° (for **11**), which is probably due to a rather flat potential for the rotation around the metal–carbene bond and intermolecular interactions between the hydrogen atoms of the seven-membered ring and oxygen atoms of the CO-ligands.

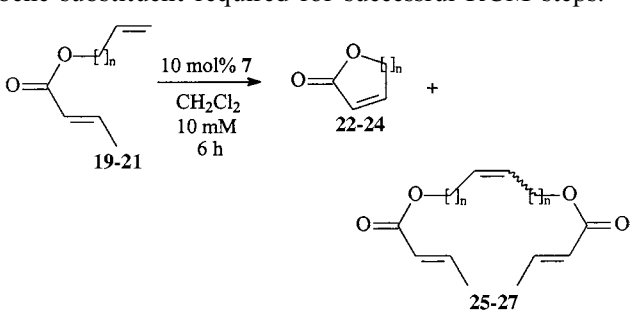
4. Cyclization of α,β-unsaturated carbene complexes

In order to probe the influence of the electron-acceptor properties of the metal carbene moiety on the propensity of adjacent C=C bonds for ring closing metathesis, we extended our studies to a serie of *E*-propenylcarbene complexes. Alkenyloxycarbene complexes **13**–**15** were synthesized by alcoholysis of the acetoxycarbene complex intermediate generated from 2-butenoylchromate **12**. Their tendency to undergo ring closing metathesis turned out to depend on the length of the methylene spacer separating the alkene terminus and the oxycarbene functionality. Allyloxycarbene complex **13** failed to undergo cyclization under our standard conditions due to a competing decarbonylation/chelation sequence which blocked the terminal alkene and produced the stable five-membered carbene chelate **16** in low yield (Scheme 3) with 81% of the starting material recovered. The reluctance of chromium allyloxycarbene for ring closing metathesis may be rationalized in terms of a carbonylation of the catalyst resulting in its deactivation. Experimental support for this idea was provided by the isolation of dicarbonyl (dichloro) bis (tricyclohexylphosphine) ruthenium as a byproduct in the metathesis of an allylhexonate-6-oxy carbene complex under similar conditions. The undesired chelation is suppressed if another methylene spacer is incorporated into the alkenyloxycarbene side chain as observed for the butenyloxycarbene complex **14**; this result reflects the reduced propensity to form homologous six-membered carbene chelates [21]. Instead, the desired ruthenium-catalyzed cyclization occurs to give chromium 2-oxacyclohexenylidene **17** in fair yield; obviously, the driving force for the ring closure overrules the complications which may be expected for the electron-deficient vinylcarbene moiety bearing an additional alkyl substituent [22]. This reaction indicates that RCM may be applied to electron deficient double bonds under mild conditions using catalyst **7**, and refines earlier reports on *N*-allyl lactam acrylates [23] or α-methylene γ-lactones [24], which required cyclization temperatures above 100°C or even refuse to undergo ring closure. Surprisingly, no RCM-product was detected from the reaction of the homologous 4-pentenyloxycarbene complex **15** under identical conditions; instead, the 4-octenyldioxy bridged biscarbene complex **18** was isolated as a mixture of *E*/*Z*-isomers in low yield; 67% of the starting material were recovered. An additional experiment carried out with a 3 mM solution of complex **15** in dichloromethane further indicated that cross-metathesis overrules ring closing metathesis even under high dilution conditions.

Table 4
Competetive metathesis reactions of alkenyl *E*-crotonates

Crotonate	Lacton (%)	Dimer (%)
$n = 1$:**19**	**22**:8	**25**:40
$n = 2$:**20**	**23**:15	**26**:60
$n = 3$:**21**	**24**:0	**27**:69

To further evaluate the unexpected preference of cross-metathesis over ring closing metathesis observed for **15** we included alkenyl *E*-crotonates **19**–**21** which represent the isolobal analogues [25] of the aforementioned propenylcarbene complexes into a comparative study under similar conditions. The results outlined in Table 4 demonstrate that cross-metathesis is the favoured reaction path leading to bisesters **25**–**27**. The unsaturated lactones **22**–**24** resulting from competitive ring closing metathesis were isolated only as minor products. This trend indicates that RCM is hampered for alkenes conjugated with potent electron-acceptor groups especially when additional substituents increase their steric bulk. The results obtained for pairs of analogous metal carbenes **14/15** and esters **20/21** appear inconsistent at first glance. However, the straightforward cyclization of chromium butenyloxycarbene **14**, which contrasts the poor selectivity observed for its crotonate analogue **20**, may reflect the steric bulk of the pentacarbonylchromium fragment which forces the butenyl side chain in a conformation allowing a closer proximity of both alkene moities which is an obvious requisite for RCM. This behaviour could be described as an organometallic variant of the Thorpe–Ingold effect [26]. On the other hand, the reluctance of the homologous carbene complex **15** towards ring closing metathesis suggests that the pentenyloxy side chain is too long to adjust the proper distance to the vinylcarbene substituent required for successful RCM steps.



5. Experimental

5.1. General reaction conditions

All reactions were carried out under dry argon using Schlenk techniques. The solvents used for reactions and chromatography were dried by distillation from calcium hydride (methylene chloride), lithium aluminium hydride (petroleum ether, b.p. 40–60°C; diethyl ether) and saturated with argon. Silica gel [(E. Merck silica gel 60 (0.63–0.200)] was degassed at high vacuum and stored under argon prior to use for chromatography.

5.2. Single-crystal X-ray diffraction analysis of *6* and *11*

Crystals of **6** and **11** were grown at −28°C in hexane. Selected structural parameters are summarized in Tables 1 and 2, crystallographic data are given in Table 3. Data were collected on a Nonius Kappa-CCD diffractometer. An empirical absorption correction was applied for complex **11** (minimum/maximum transmissions 0.8161/0.9119). The structures of **6** and **11** were solved by direct methods (SHELXS-97) [27] and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically on F^2 and hydrogen atoms were localized by difference electron density determination and refined using a riding model (SHELXL-97) [28]. For better comparison of the molecular structures the original atom labeling given in the Cambridge Data Center has been changed in this article.

5.3. Instruments

IR: Nicolet Magna 550 FT-IR. NMR: Bruker DRX-500, AM-400, AM-250. MS (EI): Kratos MS 50 (70 eV). Elemental analysis: Elementaranalysesysteme Vario EL.

5.4. Reagents

The following chemicals were prepared according to literature procedures: tetramethylammonium[acetyl-(pentacarbonyl)]chromate(−I) (**1**) [29], pentacarbonyl-[allyloxy(methyl)carbene]chromium(0) (**2**) [12], pentacarbonyl[3-butenyloxy(methyl)carbene]chromium(0) (**3**) [12], 4-bromo-5-phenyl-1,4-pentene (**8**) [18] and alkenyl crotonates (**19**–**21**) [30].

5.4.1. Synthesis of the metathesis precursors

*5.4.1.1. Synthesis of acyl(pentacarbonyl)chromates **9** and **12**.* Tetramethylammonium[(2 - *E* - benzylidene - 4 - pentenoyl)pentacarbonyl]chromate(-I): (**9**) 2.2 Equivalents (10.1 mmol, 5.94 ml) of *tert*-butyllithium (1.7 M solution in hexane) were added at −78°C to a solution of 1.03 g (4.6 mmol) 4-bromo-5-phenyl-1,4-pentene in 100 ml of diethyl ether. The solution was stirred at this temperature for 2 h, one equivalent (4.6 mmol, 1.01 g) hexacarbonyl chromium was added and the reaction mixture was allowed to warm to room temperature (r.t.) over 2 h. The solvent was evaporated and the residue was dissolved in 50 ml of argon-saturated wa-

ter. 1.5 Equivalents (1.06 g) of tetramethylammonium bromide were added, and the orange solution was stirred for 30 min at r.t. The mixture was extracted 3 times with 30 ml of CH_2Cl_2, the organic layers were dried over $MgSO_4$ and the solvent was evaporated to give 1.3 g (2.9 mmol, 64%) of a deep red oil. The crude product was not further purified. IR (CH_2Cl_2): ν(CO) = 2031 w, 1898 vs cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 3.09 (d, $^3J = 5.1$ Hz, 2H, CCH_2CHCH_2), 3.23 (s, 12H, $N(CH_3)_4$), 4.97 (d, $^3J_Z = 9.9$ Hz, 1H, $CHCH_2$), 5.02 (d, $^3J_E = 16.8$ Hz, 1H, $CHCH_2$), 5.86 (ddt, $^3J_E = 16.8$, $^3J_Z = 9.9$, $^3J = 5.1$ Hz, 1H, $CHCH_2$), 6.98 (s, 1H, CHPh), 7.21–7.40 (m, 5H, Ar–H) ppm. ^{13}C-NMR (31.25 MHz, $CDCl_3$): δ 31.4 ($N(CH_3)_4$), 56.6 (CH_2CHCH_2), 114.8 ($CHCH_2$), 128.2 (*meta*-Ar–C), 18.8 (*ortho*-Ar–C), 136.8 (*ipso*-Ar–C), 138.0 (CCHPh), 155.5 (CCHPh), 223.1 (*cis*-CO), 228.0 (*trans*-CO), 297.3 (Cr=C) ppm.

Tetramethylammonium[(*E* - but - 2 - enoyl)pentacarbonyl]chromate **(12)**: 2.2 Equivalents (90.86 mmol, 53.3 ml) of *tert*-butyllithium (1.7 M solution in hexane) were added dropwise at −78°C to a solution of 5 g (41.3 mmol) 1-bromo-propene in 200 ml of diethyl ether. After the solution was stirred at this temperature for 2.5 h, one equivalent (41.3 mmol, 9.09 g) hexacarbonyl chromium was added and the reaction mixture was allowed to warm to r.t. over 2 h. The solvent was evaporated and the residue was dissolved in 120 ml of argon-saturated water. Then 1.5 equivalents (6.99 g) of tetramethylammonium bromide were added and the orange solution was stirred for 30 min at r.t. The mixture was extracted three times with 50 ml of CH_2Cl_2, the organic layers were dried over $MgSO_4$, filtered and concentrated. After addition of 100 ml of petroleum ether the precipitate was filtered and dried in vacuo to yield 9.45 g (28.2 mmol, 68%) of a red solid. Recrystallization from water afforded dark red crystals. IR (CH_2Cl_2): ν(CO) = 2030 w, 1897 vs cm^{-1}. ^{1}H-NMR (250 MHz,CD_2Cl_2): δ 1.70 (d, $^3J = 6.3$ Hz, 3H, CH_3), 3.34 (s, 12H, $N(CH_3)_4$), 5.75 (dq, $^3J = 15.1$; 6.3 Hz, 1H, $CH{=}CHCH_3$), 6.43 (d, $^3J = 15.1$ Hz, 1H, $CH{=}CHCH_3$) ppm. ^{13}C-NMR (31.25 MHz, CD_2Cl_2): δ 14.17 (CH_3), 55.97 ($N(CH_3)_4$), 111.59 ($CH{=}CHCH_3$), 147.88 ($CH{=}CHCH_3$), 224.72 (*cis*-CO), 229.68 (*trans*-CO), 292.73 (Cr=C) ppm. MS (EI): m/z (%): 220 (21) [$M^+ - 4CO$], 192 (3) [$M^+ - 5CO$]. Anal. Found: C, 46.50; H, 5.00; N, 4.19. $C_{13}H_{17}O_6NCr$ (335.289) Calc.: C, 46.57; H, 5.11; N, 4.18%.

*5.4.1.2. [(Alkenyloxy)3-butenylcarbene]pentacarbonylchromium complexes **4**, **5** and **10**.* General procedure for C-allylation of (alkenyloxy)methylcarbene complexes **2**, **3:** 1.1 Equivalents (0.63 ml) *n*-butyllithium were added dropwise at −78°C to a solution of 1 mmol of the alkenyloxy(methyl)carbene complex **2** or **3** in 50 ml of diethyl ether. The solution was stirred for 1 h at this temperature. 1.5 Equivalents (252 mg, 0.14 ml) allyl iodide were added dropwise, and the reaction mixture was allowed to warm to r.t. over 2 h. Removal of the solvent and chromatographic work-up using petroleum ether/dichloromethane (3:1) afforded complexes **4** or **5** as yellow oils.

Pentacarbonyl[allyloxy(3-butenyl)carbene]chromium-(0) (**4**): Yield: 243 mg (0.77 mmol, 77%). $R_f = 0.4$ (petroleum ether). IR (petroleum ether): ν(CO) = 2064 m, 1961 s, 1948 vs cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.25 (td, $^3J = 7.5$, 6.9 Hz, 2H, $CH_2CH_2CHCH_2$), 3.4 (t, $^3J = 7.5$ Hz, 2H, $CH_2CH_2CHCH_2$), 4.99 (d, $^3J_Z =$ 10.5 Hz, 1H, $CH_2CH_2CHCH_2$), 5.02 (d, $^3J_E = 18.1$ Hz, 1H, $CH_2CH_2CHCH_2$), 5.46 (d, $^3J_Z = 10.6$ Hz, 1H, OCH_2CHCH_2), 5.51 (d, $^3J = 4.7$ Hz, 2H, OCH_2CHCH_2), 5.53 (d, $^3J_E = 16.7$ Hz, 1H, OCH_2CHCH_2), 5.74 (ddt, $^3J_E = 18.1$, $^3J_Z = 10.5$, $^3J = 6.9$ Hz, 1H, $CH_2CH_2CHCH_2$), 6.15 (ddt, $^3J_E = 16.7$, $^3J_Z = 10.6$, $^3J = 4.7$ Hz, 1H, OCH_2CHCH_2) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ 30.39 ($CH_2CH_2CHCH_2$), 61.9 ($CH_2CH_2CHCH_2$), 82.01 (OCH_2), 115.81 ($CH_2CH_2CHCH_2$), 120.46 (OCH_2CHCH_2), 130.70 (OCH_2CHCH_2), 136.27 ($CH_2CH_2CHCH_2$), 216.20 (*cis*-CO), 223.02 (*trans*-CO), 360.23 (Cr=C) ppm. MS (EI): m/z (%): 316 (13) [M^+], 232 (19) [$M^+ - 3CO$], 176 (34) [$M^+ - 5CO$], 135 (22) [$M^+ - 5CO$, $-C_3H_5$], 94 (21). HRMS: Calc. for M^+: 316.0039; Found 316.0032. Anal. Found: C, 49.45; H, 3.72. $C_{13}H_{12}O_6Cr$ (316.23). Calc.: C, 49.38; H, 3.82%.

Pentacarbonyl[3-butenyl-(3-butenyloxy)carbene]chromium(0) (**5**): Yield: 274 mg (0.83 mmol, 83%). $R_f = 0.4$ (petroleum ether). IR (petroleum ether): ν(CO) = 2064 m, 1948 vs cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.21 (td, $^3J = 7.5$, 6.8 Hz, 2H, $CCH_2CH_2CHCH_2$), 2.74 (td, $^3J = 6.5$ Hz, 2H, $OCH_2CH_2CHCH_2$), 3.40 (t, $^3J = 7.5$ Hz, 2H, $CCH_2CH_2CHCH_2$), 4.98 (d, $^3J_Z = 10.2$ Hz, 1H, $CCH_2CH_2CHCH_2$), 5.02 (d, $^3J_E = 16.8$ Hz, 1H, $CCH_2CH_2CHCH_2$), 5.05 (t, $^3J = 6.5$ Hz, 2H, OCH_2), 5.19 (dd, $^3J_Z = 10.2$, $^2J = 1.3$ Hz, 1H, $OCH_2CH_2CHCH_2$), 5.23 (dd, $^3J_E = 17.1$, $^2J = 1.3$ Hz, 1H, $OCH_2CH_2CHCH_2$), 5.74 (ddt, $^3J_E = 16.8$, $^3J_Z = 10.2$, $^3J = 6.8$ Hz, 1H, $CCH_2CH_2CHCH_2$), 5.89 (ddt, $^3J_E =$ 17.1, $^3J_Z = 10.2$, $^3J = 6.5$ Hz, 1H, $OCH_2CH_2CHCH_2$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ 30.28 ($CCH_2CH_2CHCH_2$), 33.66 (OCH_2CH_2), 61.95 (CCH_2), 80.68 (OCH_2), 115.72 ($OCH_2CH_2CHCH_2$), 118.47 ($CCH_2CH_2CHCH_2$), 132.78 ($OCH_2CH_2CHCH_2$), 136.38 ($CCH_2CH_2CHCH_2$), 216.31 (*cis*-CO), 223.08 (*trans*-CO), 359.68 (Cr=C) ppm. MS (EI): m/z (%): 330 (8) [M^+], 302 (5) [$M^+ - CO$], 246 (12) [$M^+ - 3CO$], 218 (8) [$M^+ - 4CO$], 190 (62) [$M^+ - 5CO$], 107 (22), 55 (100). HRMS: Calc. for $M^+ - 5CO$: 190.0449, Found: 190.0434%.

Pentacarbonyl[allyloxy(2-*E*-benzylidene-3-butenyl)-carbene]chromium(0) (**10**): One equivalent (153 mg, 0.16 ml) of pivaloyl chloride was added at −20°C to a solution of 557 mg (1.27 mmol) tetramethylammonium[(2-*E*-benzylidene-4-pentenoyl)pentacarbonyl]-chromate(−I) (**7**) in 70 ml of CH_2Cl_2. The mixture was stirred for 30 min at this temperature and two equivalents of allyl alcohol were added dropwise to the dark brown solution. The solution was allowed to warm to 0°C over 2 h. The solvent was evaporated and the residue was purified by chromatography at −5°C using petroleum ether/dichloromethane (3:1) to give 272 mg (0.62 mmol, 49%) of a red oil. IR (petroleum ether): ν(CO) = 2059 m, 1945 vs cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 3.37 (d, ^3J = 6.1 Hz, 2H, CCH_2CHCH_2), 5.09 (d, ^3J_E = 18.0 Hz, 1H, CCH_2CHCH_2), 5.12 (d, ^3J_Z = 10.3 Hz, 1H, CCH_2CHCH_2), 5.45–5.49 (m, 2H, OCH_2), 5.51 (d, ^3J_Z = 10.4 Hz, 1H, OCH_2CHCH_2), 5.59 (d, ^3J_E = 17.2 Hz, 1H, OCH_2CHCH_2), 5,85 (ddt, ^3J_E = 18.0, ^3J_Z = 10.3, ^3J = 6.1 Hz, 2H, CCH_2CHCH_2), 6.22 (ddt, ^3J_E = 17.2, ^3J_Z = 10.4, ^3J = 5.7 Hz, 2H, OCH_2CHCH_2), 7.03 (s, 1H, CCHPh), 7.32-7.43 (m, 5H, Ar–H) ppm. ^{13}C-NMR (125 MHz,$CDCl_3$): δ 33.91 (CCH_2CHCH_2), 80.97 (OCH_2), 117.29 ($CHCH_2$), 120.39 (CH CH_2), 126.66, 128.12, 128.26, 128.48, 129.09, 130.81 (all CH), 134.24 (*ipso*-ArC), 134.24 (Cr=C*C*), 216.33 (*cis*-CO), 223.72 (*trans*-CO), 350.62 (Cr=C) ppm. MS (EI): *m*/*z* (%): 404 (20) [M^+], 376 (40) [$M^+ - CO$], 348 (8) [$M^+ - 2CO$], 320 (12) [$M^+ - 3CO$], 292 (20) [$M^+ - 4CO$], 264 (20) [$M^+ - 5CO$], 236 (40) [$M^+ - 6CO$], 212 (40) [$M^+ - 5CO$, –Cr], 194 (100), 171 (62) [$M^+ - 5CO$, –Cr, $-C_3H_5$], 141 (35), 128 (95), 115 (52), 91 (39), 69 (50), 52 (87). HRMS: Calc. for [$M^+ - 5CO$]: 264.0606, Found: 264.0607%.

5.4.1.3. [Alkenyloxy(E - 1 - propenyl)carbene]pentacarbonylchromium complexes ***13–15***. General procedure: One equivalent (246 mg, 0.15 ml) of acetyl bromide was added at −40°C to a solution of 670 mg (2 mmol) **12** in 100 ml of dichloromethane. After stirring the mixture for 10 min at this temperature, two equivalents of the alcohol were added dropwise to the dark brown solution, which subsequently was allowed to warm to room temperature over a period of 2 h. Removal of the solvent and chromatographical work-up using petroleum ether/dichloromethane (3:1) as eluent afforded complexes **13**–**15** as red oils.

Pentacarbonyl [allyloxy(*E*-1-propenyl)carbene]chromium(0) (**13**): Yield: 369 mg (1.22 mmol, 61%). R_f = 0.7 (petroleum ether/CH_2Cl_2 3/1). IR (petroleum ether): ν(CO) = 2059 m, 1942 vs) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.88 (dd, ^3J = 6.9, ^4J = 1.5 Hz, 3H, CH_3), 5.42 (dd, ^3J_Z = 10.5, ^2J = 1.1 Hz, 1H, CH=CH_2), 5.47 (dd, ^3J = 5.7, ^4J = 1.0 Hz, 2H, OCH_2CHCH_2), 5.49 (ddt, ^3J_E = 16.6, ^2J = 1.1, ^4J = 1.0 Hz, 1H, OCH_2CHCH_2), 6.15 (ddt, ^3J_E = 16.6, ^3J_Z = 10.5, ^3J = 5.7 Hz, 1H, OCH_2CHCH_2), 6.39 (dq, ^3J_E = 14.9, ^3J = 6.9 Hz, 1H, $CHCHCH_3$), 7.33 (dq, ^3J_E = 14.9, ^4J = 1.5 Hz, 1H, $CHCHCH_3$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ 18.15 (CH_3), 80.26 (OCH_2), 119.83 ($CHCH_2$), 131.32 ($CHCH_2$), 132.87 ($CHCHCH_3$), 145.73 ($CHCHCH_3$), 216.62 (*cis*-CO), 223.92 (*trans*-CO), 333.99 (Cr=C) ppm. MS (EI): *m*/*z* (%): 302 (7) [M^+], 274 (4) [$M^+ - CO$], 246 (14) [$M^+ - 2CO$], 218 (6) [$M^+ - 3CO$], 190 (26) [$M^+ - 4CO$], 162 (17) [$M^+ - 5CO$], 121 (18), 52 (100). HRMS: Calc. for M^+: 301.9883; Found: 301.9885.

Pentacarbonyl [3-butenyloxy(*E*-1-propenyl)carbene]-chromium(0) (**14**): Yield: 487 mg (1.54 mmol, 77%). R_f = 0.7 (petroleum ether/CH_2Cl_2 3/1). IR (petroleum ether): ν(CO) = 2059 m, 1945 vs cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.86 (d, ^3J = 6.8 Hz, 3H, CH_3), 2.73 (m, 2H, OCH_2CH_2), 5.00 (t, ^3J = 6.0 Hz, 2H, OCH_2), 5.18 (d, ^3J_Z = 10.4 Hz, 1H, $CHCH_2$), 5.22 (d, ^3J_E = 17.3 Hz, 1H, $CHCH_2$), 5.90 (dq, ^3J_Z = 14.8, ^3J = 6.8 Hz, 1H, $CHCHCH_3$), 5.34 (ddt, ^3J_E = 17.3, ^3J_Z = 10.4, ^3J = 6.4 Hz, 1H, $CHCH_2$), 7.31 (d, ^3J_Z = 14.8 Hz, $CHCHCH_3$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ 18.08 (CH_3), 33.81 (OCH_2CH_2), 78.87 (OCH_2), 118.15 ($CHCH_2$), 132.43 ($CHCHCH_3$), 133.27 ($CHCH_2$), 145.80 ($CHCHCH_3$), 216.73 (*cis*-CO), 223.96 (*trans*-CO), 333.57 (Cr=C) ppm. MS (EI): *m*/*z* (%): 319 (60) [M^+], 288 (5) [$M^+ - CO$], 260 (12) [$M^+ - 2CO$], 232 (50) [$M^+ - 3CO$], 204 (22) [$M^+ - 4CO$], 176 (55) [$M^+ - 5CO$], 93 (20), 52 (70). HRMS: Calc. for M^+: 316.0024; Found: 316.0032%.

Pentacarbonyl [4-pentenyloxy(*E*-1-propenyl)carbene]chromium(0) (**15**): Yield: 528 mg (0.16 mmol, 80%). R_f = 0.7 (petroleum ether/CH_2Cl_2 3/1). IR (petroleum ether) ν(CO) = 2059 m, 1934 vs cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 1.88 (dd, ^3J = 6.6, ^4J = 1.4 Hz, 3H, CH_3), 2.08 (tt, ^3J = 6.5 Hz, 2H, OCH_2CH_2), 2.29 (dt, ^3J = 6.6, 6.5 Hz, 2H, $OCH_2CH_2CH_2$), 4.95 (t, ^3J = 6.5 Hz, 2H, OCH_2), 5.05 (dd, ^3J_Z = 10.4, ^2J = 1.6 Hz, 1H, $CHCH_2$), 5.09 (dd, ^3J_E = 17.0, ^2J = 1.6 Hz, 1H, $CHCH_2$), 5.87 (ddt, ^3J_E = 17.0, ^3J_Z = 10.4, ^3J = 6.6 Hz, 1H, $CHCH_2$), 6.34 (dq, ^3J_E = 14.9 Hz, 1H, $CHCHCH_3$), 7.29 (dq, ^3J_E = 14.9, ^2J = 1.4 Hz, 1H, $CHCHCH_3$) ppm. ^{13}C-NMR (31.25 MHz, $CDCl_3$): δ 18.12 (CH_3), 28.64 (CH_2), 30.12 (CH_2), 79.42 (OCH_2), 115.97 ($CHCH_2$), 132.61 ($CHCHCH_3$), 136.84 ($CHCH_2$), 145.73 ($CHCHCH_3$), 216.79 (*cis*-CO), 224.01 (*trans*-CO), 333, 75 (Cr=C) ppm. MS (EI): *m*/*z* (%): 330 (9) [M^+], 302 (2) [$M^+ - CO$], 374 (6) [$M^+ - 2CO$], 246 [$M^+ - 3CO$], 218 (30) [$M^+ - 4CO$], 190 (79) [$M^+ - 5CO$], 148 (23) [$M^+ - 5CO$, –OCH_2], 93 (34 [$M^+ - 5CO$, –OCH_2, $-C_4H_7$], 52 (100). HRMS: Calc. for $M^+ - 5CO$: 190.0450; Found: 190.0447. Anal. Found: C, 50.78; H, 4.34. $C_{14}H_{14}O_6Cr$ (330.26) Calc.: C, 50.92; H, 4.27%.

5.4.2. Metathesis reactions

Pentacarbonyl[(2-oxacyclohept-4-enyl)carbene]chromium(0) (**6**): 69 mg (5 mol%) of catalyst **7** were added at r.t. to a solution of 528 mg (1.67 mmol) of complex **4** in 55 ml of dichloromethane. The reaction mixture was stirred for 3 h and additional 35 mg (2.5 mol%) **7** were added. After additional 3 h the solvent was evaporated and chromatographic work-up at −5°C using petroleum ether/dichloromethane (3:1) afforded 390 mg (1.36 mmol, 81%) **6** a as yellow solid along with 110 mg (0.35 mmol, 17%) of the starting compound **4**. Recrystallization from hexane afforded yellow crystals. R_f = 0.5 (petroleum ether/dichloromethane (3:1)). IR (petroleum ether): ν(CO) = 2065 m, 1963 s, 1950 vs cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.50 (m, 2H, Cr=CH_2CH_2), 3.72 (t, ^3J = 6.6 Hz, 2H, Cr=CCH_2CH_2), 5.21 (m, 2H, OCH_2), 5.68 (m, 1H, OCH_2CHCH), 5.8 (dt, ^3J_Z = 10.9, ^3J = 3.5 Hz, 1H, OCH_2CH) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ 24.16 (Cr=CCH_2CH_2), 52.03 (Cr=CCH_2CH_2), 71.21 (OCH_2), 122.61 (=CH), 133.67 (=CH), 216.46 (*cis*-CO), 223.96 (*trans*-CO), 361.76 (Cr=C) ppm. MS (EI): *m*/*z* (%): 288 (25) [M^+], 260 (12) [$M^+ - CO$], 232 (11) [$M^+ - 2CO$], 204 (12) [$M^+ - 3CO$], 176 (38) [$M^+ - 4CO$], 148 (95) [$M^+ - 5CO$], 120 (20) [$M^+ - 5CO$, $-C_2H_4$], 80 (30), 52 (100). HRMS: Calc. for M^+: 287.9726; Found: 287.9719%.

Pentacarbonyl[(7-*E*-benzylidene-2-oxacyclohept-4-enyl)carbene]chromium(0) (**11**)*:* 10 mg (5 mol%) catalyst **7** were added at 0°C to a solution of 271 mg (0.62 mmol) of complex **10** in 20 ml of dichloromethane. The reaction mixture was stirred for 3 h at this temperature before additional 10 mg (5 mol%) **7** were added. After 4 additional hours the solvent was evaporated and chromatographic work-up at −5°C using petroleum ether/dichloromethane (3:1) afforded 95.6 mg (0.25 mmol, 41%) **11** as yellow solid along with 57.0 mg (0.13 mmol, 21%) of starting material **10**. Recrystallization from hexane afforded red crystals. R_f = 0.6 (petroleum ether/dichloromethane (3:1)). IR (petroleum ether): ν(CO) = 2065 m, 1965 s, 1955 vs cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 3.24 (d, ^3J = 3.2 Hz, 2H, $OCH_2CHCHCH_2$), 5.16 (d, ^3J = 4.7 Hz, 2H, OCH_2), 5.82 (dt, ^3J_Z = 10.2, ^3J = 4.7 Hz, 1H, OCH_2CH), 5.88 (dt, ^3J_Z = 10.2, ^3J = 3.2 Hz, 1H, OCH_2CHCHC), 6.45 (s, 1H, CCHPh), 7.25–7.4 (m, 5H, H–Ar) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ 27.54 ($CH_2CHCHCH_2O$), 71.46 (OCH_2), 123.18 (CHCH), 127.46 (CCH), 127.94 (*para*-Ar–C), 128.62 (*meta*-Ar–C), 128.98 (*ortho*-Ar–C), 132.23 (CH=CH), 134.33 (*ipso*-Ar–C), 150.39 (Cr=CC), 216.19 (*cis*-CO), 224.39 (*trans*-CO), 354.89 (Cr=C) ppm. MS (EI): *m*/*z* (%): 376 (3) [M^+], 348 (10) [$M^+ - CO$], 320 (2) [$M^+ - 2CO$], 292 (13) [$M^+ - 3CO$], 264 (20) [$M^+ - 4CO$], 236 (30) [$M^+ - 5CO$], 182 (33) [$M^+ - 5CO$, $-C_4H_6$]. HRMS: Calc. for M^+: 376.0039; Found 376.0039%. Anal. Calc.: C, 57.46. H, 3.21. Found: C, 57.51; H, 3.31. $C_{18}H_{12}O_6Cr$ (376.0)%.

General procedure for the metathesis of alkenyloxy(propenyl)carbene complexes **13**–**15***:* 20 mg (5 mol%) of catalyst **7** were added at r.t. to a solution of 0.5 mmol of the complexes **13**–**15** in 50 ml of dichloromethane. The reaction mixture was stirred for 3 h at this temperature before additional 20 mg (5 mol%) **7** were added. After 3 h the solvent was evaporated and chromatographic work-up at −5°C using petroleum ether/dichloromethane (3:1) afforded complexes **16**–**18**.

Cis-Tetracarbonyl[η^2-allyloxy(*E*-1-propenyl)carbene]chromium(0) (**16**)*:* Yield 11 mg (0.04 mmol, 8%) as a red oil. R_f = 0.6 (petroleum ether/dichloromethane (3:1)). IR (petroleum ether): ν(CO) = 2054 w, 2023 m, 1942 s cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.93 (d, ^3J = 6.4 Hz, 3H, CH_3), 3.08 (d, ^3J_Z = 8.8 Hz, 1H, $CHCH_2$), 3.29 (d, ^3J_E = 13.3 Hz, 1H, $CHCH_2$), 4.75 (dd, ^2J = 11.9, ^3J = 4.7 Hz, 1H, OCH_2), 4.89 (dddd, ^3J_E = 13.3, ^3J_Z = 8.8, ^3J = 4.7; 4.3 Hz, 1H, $CHCH_2$), 5.12 (dd, ^2J = 11.9, ^3J = 4.3 Hz, 1H, OCH_2), 6.75 (dq ^3J_Z = 15.4, ^3J = 6.4 Hz, 1H, $CHCHCH_3$), 6.84 (d, ^3J_Z = 15.4 Hz, 1H, $CHCHCH_3$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ 18.96 (CH_3), 65.67 ($CHCH_2$), 81.95 (OCH_2), 95.56 ($CHCH_2$), 141.34 ($CHCHCH_3$), 142.57 ($CHCHCH_3$), 221, 35, 221.75, 227.40, 231.17 (CO), 335.62 (Cr=C) ppm. MS (EI): *m*/*z* (%): 274 (2) [M^+], 246 (4) [$M^+ - CO$], 190 (6) [$M^+ - 3CO$], 162 (5) [$M^+ - 4CO$], 149 (10) [$M^+ - 3CO$, $-C_3H_5$], 108 (14) [$M^+ - 3CO$, $-C_3H_5$, $-C_3H_5$], 80 (50), 52 (90). 122 mg (0.4 mml, 81%) of starting material **13** were reisolated.

Pentacarbonyl[(2-oxacyclohex-5-enyl)carbene]chromium(0) (**17**)*:* Yield: 66 mg (0.24 mmol, 48%) as red crystals. R_f = 0.4 (petroleum ether/dichloromethane (3:1)). IR (petroleum ether): ν(CO) = 2061 m, 1946 vs cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.35 (td, ^3J = 6.8; 5.0 Hz, 2H, OCH_2CH_2), 4.42 (t, ^3J = 6.8 Hz, 2H, OCH_2), 5.95 (dt, ^3J_Z = 9.8, ^3J = 5.0 Hz, 1H, $CHCHCH_2$), 7.57 (d, ^3J_Z = 9.8 Hz, 1H, $CHCHCH_2$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ 23.02 (OCH_2CH_2), 68.01 (OCH_2), 124.73 ($CHCHCH_2$), 138.74 ($CHCHCH_2$), 216.61 (*cis*-CO), 225.05 (*trans*-CO), 324.36 (Cr=C) ppm. MS (EI): *m*/*z* (%): 274 (14) [M^+], 246 (9) [$M^+ - CO$], 218 (6) [$M^+ - 2CO$], 190 (13) [$M^+ - 3CO$], 162 (20) [$M^+ - 4CO$], 134 (97) [$M^+ - 5CO$], 80 (21), 52 (100). HRMS: Calc. for $M^+ - 5CO$: 133.9824; Found: 133.9826. 53 mg (0.16 mml, 33%) of starting material **14** were reisolated.

4-Octen-1,8-dioxy-{bis-[pentacarbonyl(*E*-1-propenylcarbene)chromium(0)]} (**18**)*:* Yield: 31.6 mg (0.05 mmol, 20%) as a red oil; *E*/*Z*-ratio: 3:1. R_f = 0.6 (petroleum ether/dichloromethane (3:1)). IR (petroleum ether): ν(CO) = 2061 m, 1946 vs cm^{-1}. *E*-isomer: ^{1}H-NMR (500 MHz, C_6D_6): δ 1.33 (dd, ^3J = 7.0, ^4J = 1.6 Hz, 6H, CH_3, CH_3'), 1.63 (tt, ^3J = 6.5 Hz, 4H, OCH_2CH_2, OCH_2CH_2'), 1.98–2.06 (m, 4H, $OCH_2CH_2CH_2$, $OCH_2CH_2CH_2'$), 4.64 (t, ^3J = 6.4 Hz, 4H, OCH_2, OCH_2'), 5.30 (tt, ^3J = 3.7, ^4J = 1.5 Hz, 2H,

$OCH_2CH_2CH_2CH$, $OCH_2CH_2CH_2CH'$), 6.15 (dq, $^3J_E = 14.8$, $^3J = 7.0$ Hz, 2H, $CHCHCH_3$, $CHCHCH_3'$), 7.19 (d, $^3J_E = 14.8$, 2H, $CHCHCH_3$) ppm. ^{13}C-NMR (125 MHz, C_6D_6): δ 17.70 (CH_3, CH_3'), 28.91 ($2 \times CH_2$), 29.03 ($2 \times CH_2$), 79.44 (CH_2O, CH_2O'), 128.29 ($CHCHCH_3$, $CHCHCH_3'$), 130.09 ($OCH_2CH_2CH_2CH$, $OCH_2CH_2CH_2CH'$), 145.63 ($CHCHCH_3$, $CHCHCH_3$‘), 217.23 (*cis*-CO, *cis*-CO′), 224.14 (*trans*-CO, *trans*-CO′), 333.80 (Cr=C, Cr=C′) ppm. *Z*-isomer: ^{1}H-NMR (500 MHz, C_6D_6): δ 1.36 (dd, $^3J = 7.0$, $^4J = 1.6$ Hz, 6H, CH_3, CH_3'), 1.63 (tt, $^3J = 6.5$ Hz, 4H, OCH_2CH_2, OCH_2CH_2'), 1.98–2.06 (m, 4H, $OCH_2CH_2CH_2$, $OCH_2CH_2CH_2'$), 4.61 (t, $^3J = 6.4$ Hz, 4H, OCH_2, OCH_2'), 5.35 (tt, $^3J = 4.8$, $^4J = 1.2$ Hz, 2H, $OCH_2CH_2CH_2CH$, $OCH_2CH_2CH_2CH'$), 6.15 (dq, $^3J_E = 14.8$, $^3J = 7.0$ Hz, 2H, $CHCHCH_3$, $CHCHCH_3'$), 7.17 (d, $^3J_E = 14.8$, 2H, $CHCHCH_3$) ppm. ^{13}C-NMR (125 MHz, C_6D_6): δ 17.70 (CH_3, CH_3'), 23.69 ($2 \times CH_2$), 29.13 ($2 \times CH_2$), 79.34 (CH_2O, CH_2O'), 128.29 ($CHCHCH_3$, $CHCHCH_3'$), 129.48 ($OCH_2CH_2CH_2CH$, $OCH_2CH_2CH_2CH'$), 145.71 ($CHCHCH_3$, $CHCHCH_3'$), 217.36 (*cis*-CO, *cis*-CO′), 224.17 (*trans*-CO, *trans*-CO′), 333.93 (Cr=C, Cr=C′) ppm. FABMS: m/z: 632 [M^+], 492 [$M^+ - 5CO$], 408 [$M^+ - 8CO$], 380 [$M^+ - 9CO$], 352 [$M^+ - 10CO$]. 110 mg (0.34 mml, 67%) of starting material **15** were reisolated.

General procedure for the metathesis of the alkenyl crotonates **19**–**21**: 41 mg (5 mol%) of catalyst **7** were added at r.t. to a solution of 1 mmol alkenyl crotonate in 100 ml dichloromethane. The reaction mixture was stirred for 3 h before additional 41 mg (5 mol%) **7** were added. After 3 h the solvent was evaporated, and chromatographic work-up using petroleum ether/diethyl ether (3:1) afforded the products as colourless oils.

Metathesis of allylcrotonate (**19**): 1,4-bis-*E*-crotonyloxy-but-2-ene (**25**): Yield: 90 mg (0.4 mmol, 40%); *E*/*Z*-ratio: 5:1. $R_f = 0.6$ (petroleum ether/diethyl ether (3:1)). *E*-isomer: ^{1}H-NMR (500 MHz, C_6D_6): δ 1.34 (dd, $^3J = 7.0$, $^4J = 1.5$ Hz, 6H, CH_3, CH_3'), 4.50 (dd, $^3J = 3.0$, $^4J = 1.5$ Hz, 4H, OCH_2, OCH_2'), 5.66 (tt, $^3J = 3.0$, $^4J = 1.5$ Hz, 2H, OCH_2CH_2, OCH_2CH_2'), 5.79 (dq, $^3J_E = 15.0$, $^4J = 1.5$ Hz, 2H, CCH, CCH'), 6.93 (dq, $^3J_E = 15.0$, $^3J = 7.0$ Hz, 2H, $OCCHCH$, $OCCHCH'$) ppm. ^{13}C-NMR (125 MHz, C_6D_6): δ 17.68 (CH_3, CH_3'), 63.75 (OCH_2 OCH_2'), 122.95 ($OCCHCH$, $OCCHCH'$), 128.43 (OCH_2CH, OCH_2CH'), 144.89 ($OCCHCH$, $OCCHCH'$), 165.72 (CO,CO′) ppm. *Z*-isomer: ^{1}H-NMR (500 MHz, C_6D_6): δ 1.34 (dd, $^3J = 7.0$, $^4J = 1.5$ Hz, 6H, CH_3, CH_3'), 4.67 (dd, $^3J = 4.0$, $^4J = 1.2$ Hz, 4H, OCH_2, OCH_2'), 5.62 (tt, $^3J = 4.0$, $^4J = 1.2$ Hz, 2H, OCH_2CH_2, OCH_2CH_2'), 5.79 (dq, $^3J_E = 15.0$, $^4J = 1.5$ Hz, 2H, CCH, CCH'), 6.93 (dq, $^3J_E = 15.0$, $^3J = 7.0$ Hz, 2H, $OCCHCH$, $OCCHCH'$) ppm. ^{13}C-NMR (125 MHz, C_6D_6): δ 17.68 (CH_3, CH_3'), 69.92 (OCH_2 OCH_2'), 122.95 ($OCCHCH$, $OCCHCH'$), 128.58 (OCH_2CH, OCH_2CH') 144.89 ($OCCHCH$, $OCCHCH'$), 165.72 (CO,CO′) ppm. FABMS: m/z: 225 [$M^+ + H$]. *5H-furan-2-one* **22**. Yield: 7 mg (0,08 mmol, 8%). The analytical data for **22** correspond to the data given in literature [31].

Metathesis of butenylcrotonate (**20**): 1,6-bis-*E*-crotonyloxy-hex-3-ene (**26**): Yield: 151 mg (0.6 mmol, 60%); *E*/*Z*-ratio: 1.8:1. $R_f = 0.6$ (petroleum ether/diethyl ether (3:1)). *E*-isomer: ^{1}H-NMR (250 MHz, C_6D_6): δ 1.40 (dd, $^3J = 6.9$, $^4J = 1.5$ Hz, 6H, CH_3, CH_3'), 2.20 (m, 4H, OCH_2CH_2, OCH_2CH_2'), 4.07 (t, $^3J = 6.7$ Hz, 4H, OCH_2, OCH_2'), 5.31 (tt, $^3J = 4.0$, $^4J = 1.5$ Hz, 2H, OCH_2CH_2CH, OCH_2CH_2CH'), 5.83 (dq, $^3J_E = 15.0$, $^4J = 1.5$ Hz, 2H, $CCHCH$, $CCHCH$‘), 6.95 (dq, $^3J_E = 15.0$, $^3J = 6.9$ Hz, 2H, $CCHCH$, $CCHCH'$) ppm. ^{13}C-NMR (62.5 MHz, C_6D_6): δ 17.53 (CH_3, CH_3'), 32.41 (OCH_2CH_2, OCH_2CH_2'), 63.49 (OCH_2, OCH_2'), 123.12 ($CCHCH$, $CCHCH'$), 128.56 (OCH_2CH_2CH, OCH_2CH_2CH'), 144.28 ($CCHCH$, $CCHCH'$), 165.92 (CO, CO′) ppm. *Z*-isomer: ^{1}H-NMR (250 MHz, C_6D_6): δ 1.40 (dd, $^3J = 6.9$, $^4J = 1.5$ Hz, 6H, CH_3, CH_3'), 2.20 (m, 4H, OCH_2CH_2, OCH_2CH_2'), 4.07 (t, $^3J = 6.7$ Hz, 4H, OCH_2, OCH_2'), 5.39 (tt, $^3J = 5.0$, $^4J = 1.2$ Hz, 2H, OCH_2CH_2CH, OCH_2CH_2CH'), 5.83 (dq, $^3J_E = 15.0$, $^4J = 1.5$ Hz, 2H, $CCHCH$, $CCHCH'$), 6.95 (dq, $^3J_E = 15.0$, $^3J = 6.9$ Hz, 2H, $CCHCH$, $CCHCH'$) ppm. ^{13}C-NMR (62.5 MHz, C_6D_6): δ 17.53 (CH_3, CH_3'), 27.21 (OCH_2CH_2, OCH_2CH_2'), 63.38 (OCH_2, OCH_2'), 123.12 ($CCHCH$, $CCHCH'$), 128.56 (OCH_2CH_2CH, OCH_2CH_2CH'), 144.36 ($CCHCH$, $CCHCH'$), 165.92 (CO, CO′) ppm. FABMS: m/z: 253 [$M^+ + H$], 167 [$M^+ + H$, $-C_4O_2H_6$]. 5,6-Dihydro-pyran-2-one (**23**). Yield: 15 mg (0.15 mmol, 15%). The analytical data for **23** correspond to the data given in literature [32]

Metathesis of butenylcrotonate (**21**): 1,8-bis-*E*-crotonyloxy-oct-4-ene (**27**): Yield: 193 mg (0.69 mmol, 69%); *E*/Z-ratio: 3:1. $R_f = 0.6$ (petroleum ether/diethyl ether (3:1)). *E*-isomer: ^{1}H-NMR (500 MHz, C_6D_6): δ 1.38 (dd, $^3J = 6.7$, $^4J = 1.5$ Hz, 6H, CH_3, CH_3'), 1.57 (tt, $^3J = 6.8$ Hz, 4H, OCH_2CH_2, OCH_2CH_2'), 1.94 (td, $^3J = 6.8$, 4.0 Hz, 4H, $OCH_2CH_2CH_2$, $OCH_2CH_2CH_2'$), 4.13 (t, $^3J = 6.8$ Hz, 4H, OCH_2, OCH_2'), 5.29 (tt, $^3J = 4.0$, $^4J = 1.5$ Hz, 2H, $OCH_2CH_2CH_2CH$, $OCH_2CH_2CH_2CH'$), 5.85 (dq, $^3J_E = 15.5$, $^4J = 1.5$ Hz, 2H, $CCHCH$, $CCHCH'$), 6.97 (dq, $^3J_E = 15.5$, $^3J = 6.7$ Hz, 2H, $CCHCH$, $CCHCH'$) ppm. ^{13}C-NMR (125 MHz, C_6D_6): δ 17.5 (CH_3, CH_3'), 28.84 ($2 \times CH_2$), 29.15 ($2 \times CH_2$), 63.51 (OCH_2, OCH_2'), 123.21 ($CCHCH$, $CCHCH'$), 130.07 ($OCH_2CH_2CH_2CH$, $OCH_2CH_2CH_2CH'$), 144.20 ($CCHCH$, $CCHCH'$), 166.01 (CO, CO′) ppm. *Z*-isomer: ^{1}H-NMR (500 MHz, C_6D_6): δ 1.39 (dd, $^3J = 6.7$, $^4J = 1.5$ Hz, 6H, CH_3, CH_3'), 1.57 (tt, $^3J = 6.8$ Hz, 4H, OCH_2CH_2, OCH_2CH_2'), 1.20 (td, $^3J = 6.8$, 4.8 Hz, 4H, $OCH_2CH_2CH_2$, $OCH_2CH_2CH_2'$), 4.11 (t, $^3J = 6.8$ Hz, 4H, OCH_2, OCH_2'), 5.31 (tt, $^3J = 4.8$, $^4J = 1.2$ Hz, 2H, $OCH_2CH_2CH_2CH$, $OCH_2CH_2CH_2CH'$), 5.85 (dq, $^3J_E =$

15.5, $^4J = 1.5$ Hz, 2H, CC*H*CH, CC*H*CH′), 6.97 (dq, $^3J_E = 15.5$, $^3J = 6.7$ Hz, 2H, CCHC*H*, CCHC*H*′) ppm. ^{13}C-NMR (125 MHz, C_6D_6): δ 17.5 (CH_3, CH_3'), 23.79 ($2 \times CH_2$), 28.90 ($2 \times CH_2$), 63.48 (OCH_2, OCH_2'), 123.17 (C*C*HCH, C*C*HCH′), 129.59 ($OCH_2CH_2CH_2$*C*H, $OCH_2CH_2CH_2$*C*H′), 144.13 (CCH*C*H, CCH*C*H′), 166.01 (CO, CO′) ppm. FABMS: m/z: 281 [$M^+ + H$], 195 [$M^+ + H$, $-C_4O_2H_6$], 167 [$M^+ + H$, $-C_4O_2H_6$, $-C_2H_4$].

6. Conclusions

We have demonstrated, in principle, that the metal carbene moiety in the Grubbs ruthenium-based RCM catalyst is compatible with another electrophilic metal carbene functionality as present in Fischer-type carbonyl carbene complexes. The propensity for ring closing metathesis within the alkenyl(alkenyloxy)carbene ligand depends on both the length of the spacers separating the alkene termini and the carbene carbon atom and the alkene substitution pattern. Whereas the allyloxy complex **13** prefers intramolecular chelation resulting in a stable tetracarbonyl carbene chelate complex **16**, its homoallyl analogue **14** undergoes ring closing metathesis probably assisted by the bulky $Cr(CO)_5$ fragment which may favour the proximity of both alkene termini required for RCM. The conformative assistance of the metal carbonyl group decreases with insertion of another methylene spacer as suggested by the pentenyloxycarbene complex **15** which prefers the formation of a dinuclear cross-metathesis product **18** over RCM. The pronounced selectivity observed for the alkenyloxy(alkenyl)carbene complex homologues obviously requires the use of tailored RCM catalysts. Recent advances in this direction have been reported by Herrmann who has developed promising imidazolylidene–phosphine complexes for application in RCM [4a].

7. Supplementary material

Crystallographic data (excluding structure factors) for complexes **6** and **11** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no CCDC-137307 (complex **6**) and CCDC-137306 (complex **11**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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