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Spirocyclobutanes via Metal Carbene Facilitated Diastereoselective [2+2]Cycloaddition Reactions of *exo*-Methylene Oxacyclopentylidene Complexes of Chromium and Tungsten[1]

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Dedicated to Prof. Dirk Walther on the occasion of his 60th birthday

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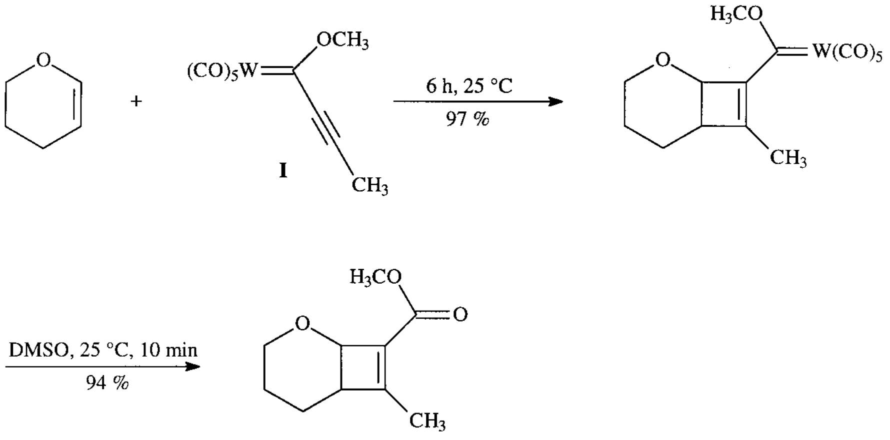
Abstract—Upon reaction with enol ethers α-*exo*-methylene-2-oxacyclopentylidene complexes of chromium and tungsten **3** and **4** undergo [2+2]cycloaddition under mild thermal conditions to give spirocyclobutanes **5**–**12** in good yields as single diastereomers. The relative stereochemistry (as established by X-ray analysis for **9** and **10** to be 5*R**,2′*S**) results from a combined *re*-*si* approach of both π-systems. The propensity for [2+2]cycloaddition depends on both the substitution pattern and the ring size of the enol ether; 1,1-disubstituted enol ethers and enamines undergo a formal conjugate addition resulting in side-chain elongation. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

The [2+2]cycloaddition is the most versatile and most popular method for the construction of four-membered rings.[2] It is widely applied to the synthesis of both heterocyclic and isocyclic skeletons; it may, in general, occur under thermal, photochemical or metal-catalyzed conditions, and may proceed either by a concerted or a stepwise mechanism involving diradical or zwitterionic intermediates.[3] In terms of orbital symmetry conservation rules the photo-induced [2+2]cycloaddition of alkenes is compatible with a concerted process.[4] The analogous reaction



Scheme 1. Thermal [2+2]cycloaddition of enolethers and alkynylcarbene tungsten complexes.

Keywords: carbenes and carbenoids; chromium/tungsten and compounds; cycloaddition reactions; cyclobutanes; spirocycles.

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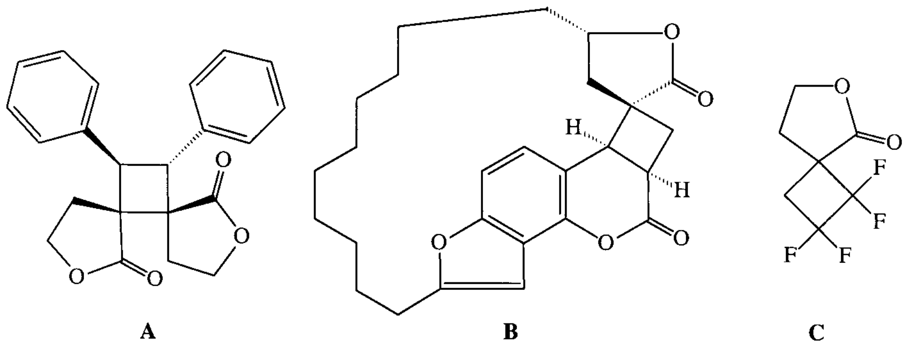


Scheme 2. Thermal and photochemical [2+2]cycloaddition products derived from α-methylene-γ-butyrolactone.

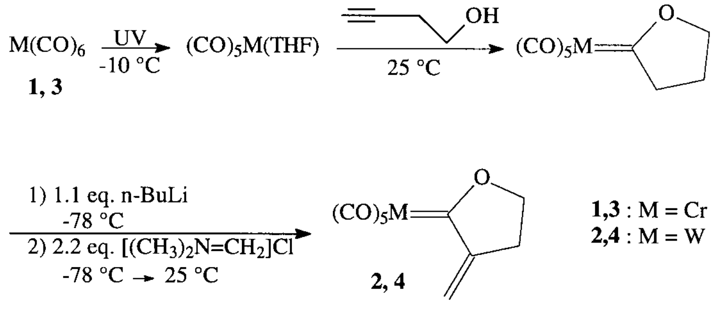
under thermal conditions appears less straightforward; it requires either strained alkenes or alkenes bearing isolated C=C bonds activated by electron-withdrawing or electron-donating substituents such as polycyanoethenes,[5] ketenes[6] or enamines, enol ethers and ketene acetals.[7] Thermal [2+2]cycloaddition reactions proceed readily under mild conditions when polycyanoethenes are used as acceptor-alkenes; in the absence of strong electron-withdrawing substituents, however, high-temperature (>100°C) and pressure conditions are required whereas the yields remain still only moderate.[8] Two alternative pathways have been reported for the reaction of enamines with acceptor-type alkenes: The formation of four-membered rings is sensitive to steric and electronic effects both in the enamine and the acceptor-alkene substitution pattern and, moreover, has to compete with a β-alkylation of the enamine (*Stork* reaction) which is favoured at higher temperature and, after hydrolysis, may be exploited as an alternative route for the alkylation of ketones.[9] Less potent carbon nucleophiles such as enol ethers require strong alkene acceptors[10] or Lewis acid catalysts[11] to undergo thermal [2+2]cycloaddition reactions. These examples reveal that the nature of the acceptor-type alkene is crucial.

Pentacarbonyl metal carbene fragments are excellent electron-acceptor auxiliaries in Diels–Alder and 1,3-dipolar cycloaddition reactions; in some cases, they are even superior to Lewis acid-coordinated carbonyl oxygen moities.[12] They have been equally applied to [2+2]cycloaddition reactions of alkynyl carbene complexes with enol ethers and ketene acetals.[13] Since the metal carbene bond is readily cleaved upon oxidation,[14] alkoxycarbene complexes serve as synthons for the corresponding esters (Scheme 1).[13a]

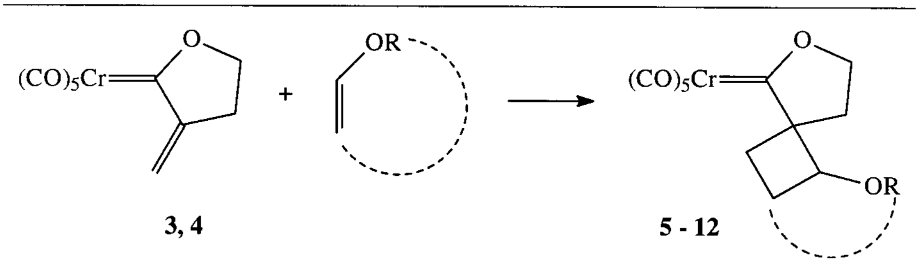
Recently, we have developed a one-pot synthesis of 2-oxacycloalkylidene complexes based on the cycloisomerization of alkynols at low-valent metal carbonyl templates.[15] Their *exo*-methylene analogues have been applied to [3+2] and [4+2]cycloaddition reactions using diazoalkanes[16] and 1,3-dienes[17]. They turned out to be surprisingly reluctant towards [3+2+1]cycloaddition upon reaction with alkynes under the thermal standard conditions but, instead, underwent photoinduced benzannulation in moderate yields.[18] We speculated that the metal carbene fragment is suited to activate the exocyclic C=C bond for [2+2]cycloaddition with electron-rich alkenes. In the resulting spirocyclobutanes the metal carbene functionality is retained, and thus available for subsequent transformations. [2+2]Spirocyclization of *exo*-alkylidene lactones, the isolobal analogues[19] of the 2-oxacycloalkylidene complexes, has been reported previously in some isolated examples. α-Benzylidene-γ-butyrolactone underwent photodimerization to give bisspirolactone **A**, [20] and a similar photoapproach was applied to the synthesis of the more complex spirolactone **B** by intramolecular [2+2]cycloaddition of a α-methylene-γ-butyrolactone-psoralen heterodimer. [21] The only example of a thermal [2+2]cycloaddition of an *exo*-methylene-γ-butyrolactone that came to our attention led to tetrafluorospirocyclobutane **C** (Scheme 2).[22]

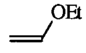
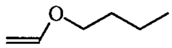
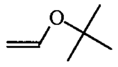
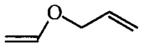
Results and Discussion

The *exo*-methylene-2-oxacyclopentylidene complexes of chromium **3** and tungsten **4** were synthesized in a two-step sequence. The cycloisomerization of 1-butynol at low-valent pentacarbonyl chromium and tungsten templates led to the metal 2-oxacyclopentylidene skeleton.[15a,c]

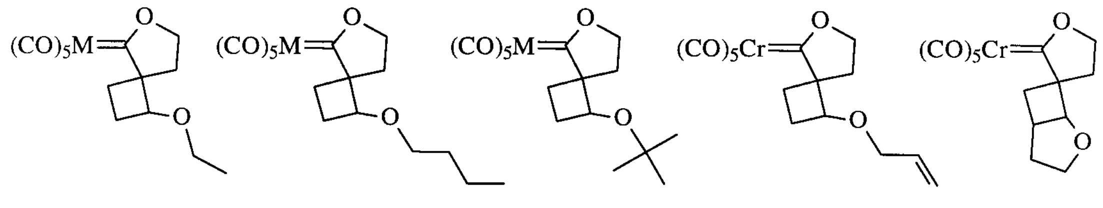


Scheme 3. Synthesis of pentacarbonyl(5-*exo*-methylene-2-oxacyclopentylidene) complexes **3** and **4**.



entry	carbene complex[a]	enol ether[b]	time	[2+2] product	Yield [%]
1	**3** (0.05)		7 d	**5**	43
2	**3** (0.09)		4.5 d		67
3	**4** (0.05)		28 h	**6**	68
4	**3** (0.05)		29 h	**7**	66
5	**3** (0.09)		19 h		46
6	**4** (0.05)		3.5 h	**8**	46
7	**3** (0.05)		6 h	**9**	73
8	**3** (neat)		3 h		81
9	**4** (0.05)		100 min	**10**	71
10	**3** (0.05)		2.5 d	**11**	26
11	**3** (0.07)		1.5 d		55
12	**3** (0.04)		36 h	**12**	30

[a] Concentration (mol/l) of starting carbene complex in THF-solution given in brackets. [b] 40 equivalents



5 : M = Cr
6 : M = W

7 : M = Cr
8 : M = W

9 : M = Cr
10 : M = W

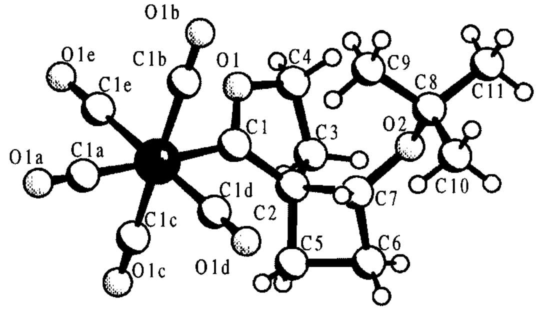
11

12

Scheme 4. Thermal [2+2]spirocycloaddition of *exo*-methylene complexes **3** and **4** with enol ethers.

α-Deprotonation followed by addition of *N*,*N*-dimethylmethyleneiminium chloride[23] afforded the α-*exo*-methylene derivatives **3** and **4** (Scheme 3). The pentacarbonyl metal fragment activates the *exo*-methylene C=C double bond for thermal [2+2]cycloaddition reactions with electron-rich alkenes. Complexes **3** and **4** react with acyclic and cyclic enol ethers under mild conditions at room temperature or 50°C, respectively, to give four-membered spirobicyclic metal carbenes **5–12** as single diastereomers in moderate to good yields. As expected from the polarization within both C=C bonds the cycloaddition is regioselective in terms of a head-to-head coupling (Scheme 4). A comparative study of reactions involving pairs of chromium and tungsten homologues reveals that under the same conditions the tungsten complex **4** reacts faster than its chromium counterpart (entries 1/3, 4/6 and 7/9) indicating that the tungsten fragment is more efficient in the activation of the exocyclic double bond than the chromium moiety. A similar trend has been previously observed for the addition of enol ethers to alkynylcarbene ligands.[13a,e]

The isolation of single diastereomers **5–12** is compatible with either a concerted mechanism or a two-step process in which ring closure is fast in comparison with rotation

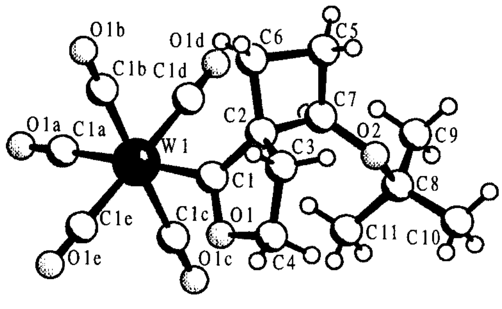


Selected Bond Lengths [Å] and Bond Angles [deg]

Cr-C(1a)	1.9167(17)	Cr-C(1)-C(2)	134.08(11)
Cr-C(1b)	1.8819(17)	Cr-C(1)-O(1)	118.87(10)
Cr-C(1c)	1.8880(17)	O(1)-C(1)-C(2)	107.06(12)
Cr-C(1d)	1.9219(19)	C(1)-O(1)-C(4)	113.33(11)
Cr-C(1e)	1.9106(19)	C(1)-C(2)-C(3)	104.20(12)
Cr-C(1)	2.0547(15)	C(1)-C(2)-C(5)	122.73(13)
O(1)-C(1)	1.3114(18)	C(1)-C(2)-C(7)	116.70(12)
C(1)-C(2)	1.514(2)	C(2)-C(5)-C(6)	88.62(12)
C(2)-C(3)	1.538(2)	C(5)-C(6)-C(7)	87.30(11)
C(2)-C(5)	1.531(2)	C(2)-C(7)-C(6)	88.36(12)
C(2)-C(7)	1.603(2)	C(5)-C(2)-C(7)	86.18(11)
C(7)-O(2)	1.4120(18)		

Scheme 5. Molecular structure of spirocyclobutane complex **9**.

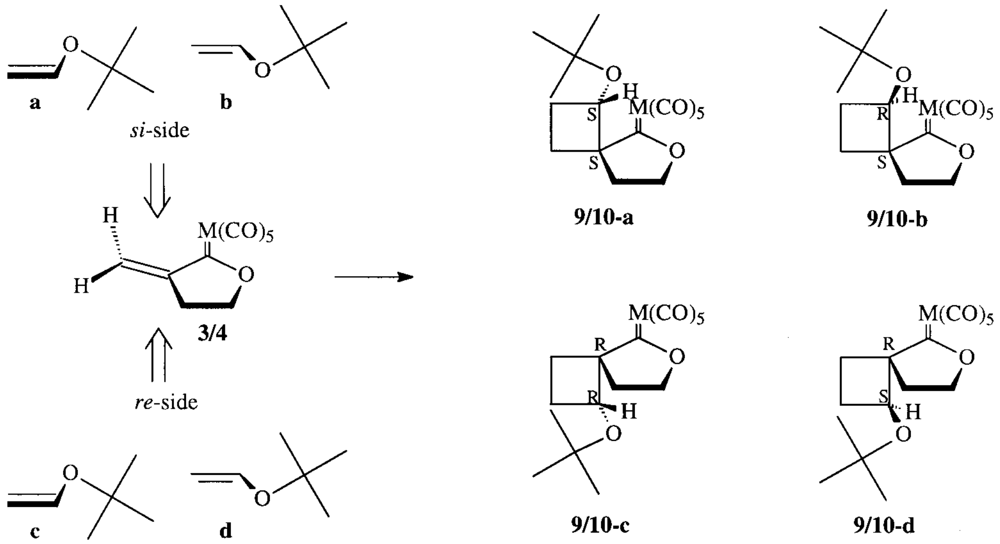
around the new C–C bond formed in the first step. The stereochemical outcome of the spirocyclobutane formation depends on whether the *re* or *si* face of the enol ether approaches the *re* or *si* face of the exocyclic double bond of the cycloalkylidene complex. In order to elucidate which face of the C=C bonds is operative in the cycloaddition the molecular structures of the *tert*-butyl substituted chromium and tungsten homologues were established by X-ray. The analysis of yellow single crystals as grown from pentane (**9**, Scheme 5) or hexane (**10**, Scheme 6) confirmed the relative configuration to be 5*R**,2′*S** in both cases. These consistent results suggest that the cycloaddition involves a combined *re-si* approach of both π-systems. The observed relative stereochemistry may be rationalized in terms of minimizing steric interactions along the cycloaddition. In the more favoured transition state the bulky alkoxy substituent of the enol ether is expected to point away from the sterically demanding pentacarbonyl metal fragment leading to the preferred 5R*,2′ S*-stereochemistry as outlined in the pair of enantiomers **9/10-b** and **9/10-d** (Scheme 7). Under the conditions of EI-mass spectrometry the spirocyclobutane complexes **5**–**12** undergo a [2+2]cycloreversion; the fragmentation of either the molecular ions or the ions generated upon subsequent loss of the pentacarbonyl metal unit is



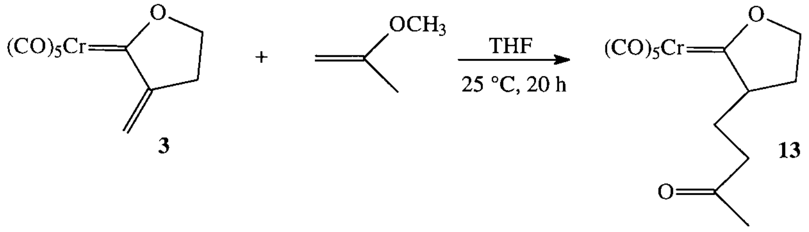
Selected Bond Lengths [Å] and Bond Angles [deg]

W-C(1a)	2.032(3)	W-C(1)-C(2)	132.90(17)
W-C(1b)	2.041(3)	W-C(1)-O(1)	119.14(17)
W-C(1c)	2.038(3)	O(1)-C(1)-C(2)	108.0(2)
W-C(1d)	2.046(3)	C(1)-O(1)-C(4)	112.90(19)
W-C(1e)	2.055(3)	C(1)-C(2)-C(3)	104.3(2)
W-C(1)	2.167(3)	C(1)-C(2)-C(5)	123.10(2)
O(1)-C(1)	1.319(3)	C(1)-C(2)-C(7)	114.50(2)
C(1)-C(2)	1.507(3)	C(2)-C(5)-C(6)	88.8(2)
C(2)-C(3)	1.526(3)	C(5)-C(6)-C(7)	87.88(19)
C(2)-C(5)	1.546(3)	C(2)-C(7)-C(6)	87.9(2)
C(2)-C(7)	1.590(4)	C(5)-C(2)-C(7)	86.08(18)
C(7)-O(2)	1.392(3)		

Scheme 6. Molecular structure of spirocyclobutane complex **10**.

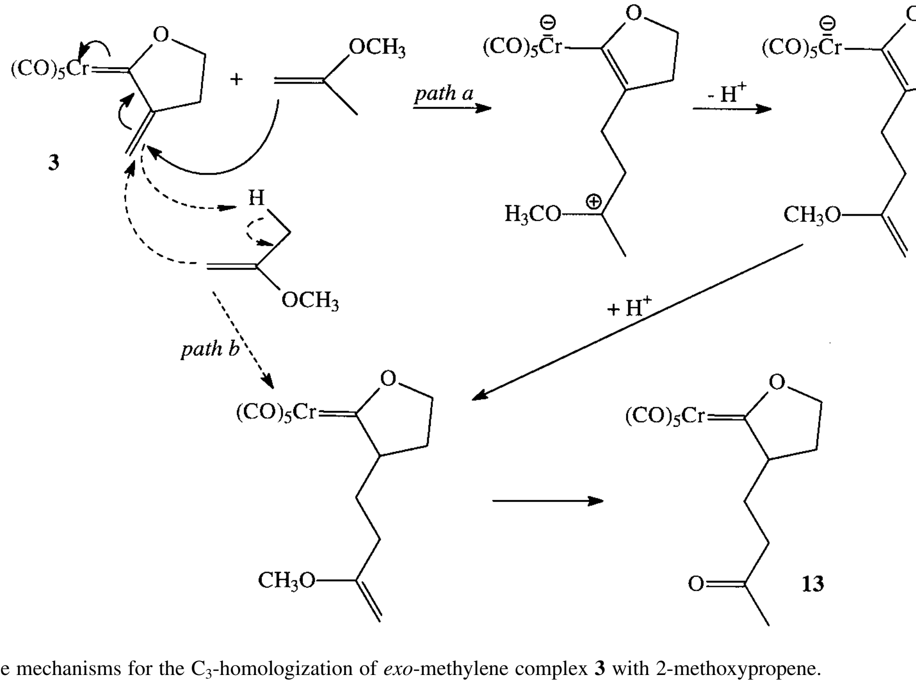


Scheme 7. Possible stereoisomers **9/10 a-d** arising from the [2+2]cycloaddition of *exo*-methylene complexes **3/4** and *tert*-butyl vinyl ether.

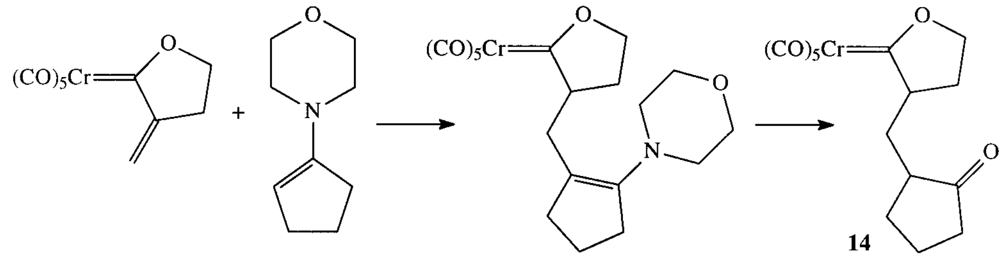


Scheme 8. Formal conjugate addition of 2-methoxypropene to *exo*-methylene complex **3**.

dominated by the cleavage of the enol ether moiety. The propensity of the enol ethers to spirocyclization depends on their ring size and their substitition pattern. The six-membered enol ether 3,4-dihydro-2H-pyran failed to undergo cycloaddition with *exo*-methylene complex **3** under our standard conditions; instead, a slow decomposition of the organometallic starting material was observed. Similary, 1,1-disubstitution within the enol ether precluded spirocyclization; the addition of 2-methoxypropene to chromium carbene **3** afforded a 93% yield of the formal conjugate addition product **13**; no concomitant [2+2]cycloaddition was observed (Scheme 8).



Scheme 9. Alternative mechanisms for the C_3-homologization of *exo*-methylene complex **3** with 2-methoxypropene.



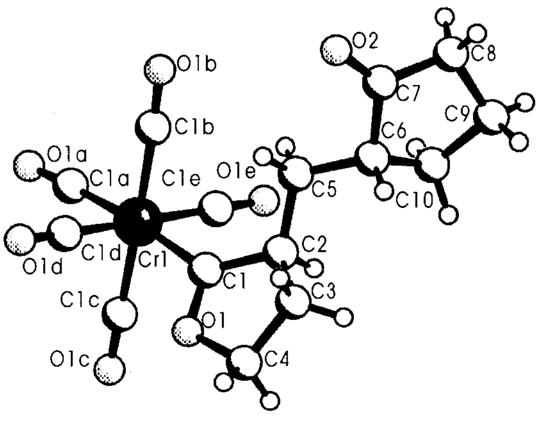
Scheme 10. Diastereoselective conjugate enamine addition to *exo*-methylene complex **3**.

Two mechanistic alternatives may be considered for the formation of 3′-oxobutyl-oxacyclopentylidene complex **13** (Scheme 9). It may arise *(path a)* from a *Michael* type addition of the enol ether to the *exo*-methylene bond activated for nucleophilic attack by the pentacarbonyl chromium fragment; a subsequent deprotonation/reprotonation sequence followed by hydrolysis of the enol ether is expected to give the homologization product **13**. An alternative mechanism may involve an *ene*-type sigmatropic rearrangement (*path b*); *ene* reactions involving alkynylcarbene complexes have been previously reported.[24]

A similar side chain elongation occurred upon addition of 1-(4-morpholino)cyclopentene to *exo*-methylene complex **3**. This reaction is distinctly faster than with 2-methoxypropene, and is completed within a few seconds at room temperature to afford the formal conjugate addition product **14** as a single diastereomer after chromatographic workup in 85% yield (Scheme 10). Obviously, hydrolysis of the intermediate enamine addition product was accompanied by a diastereoselective protonation to give a relative 5R*,2′S* configuration as established by single crystal X-ray analysis (Scheme 11).

Conclusion

The potent pentacarbonyl metal electron-acceptor auxiliary allows for diastereoselective [2+2]cycloaddition reactions of enol ethers to *exo*-methylene-2-oxacyclopentylidene complexes of chromium and tungsten. It provides a novel access to spirocyclobutane skeletons under mild conditions at room temperature combined with virtually complete diastereoselectivity. This route is compatible with acyclic vinyl ethers and five-membered endocyclic enol ethers such as dihydropyran. It fails, however, with 1,1-disubstituted enol ethers and enamines which, instead, undergo a formal conjugate addition to give side chain elongation products; chromatographic workup results in diastereoselective protonation.



Selected Bond Lengths [Å] and Bond Angles [deg]

Cr-C(1a)	1.892(3)	Cr-C(1)-C(2)	132.59(15)
Cr-C(1b)	1.898(2)	Cr-C(1)-O(1)	118.79(15)
Cr-C(1c)	1.905(2)	O(1)-C(1)-C(2)	108.40(18)
Cr-C(1d)	1.898(2)	C(1)-C(2)-C(5)	115.91(18)
Cr-C(1d)	1.898(2)	C(3)-C(2)-C(5)	115.20(2)
Cr-C(1)	2.030(2)	C(2)-C(5)-C(6)	114.17(19)
O(1)-C(1)	1.310(2)	C(5)-C(6)-C(7)	111.70(19)
C(1)-C(2)	1.514(3)	C(5)-C(6)-C(10)	118.70(2)
C(2)-C(5)	1.517(3)	C(6)-C(7)-O(2)	125.60(2)
C(5)-C(6)	1.521(3)		
C(6)-C(7)	1.517(3)		
C(7)-O(2)	1.220(3)		

Scheme 11. Molecular structure of enamine addition product **14**.

Experimental

All transformations were performed under argon using Schlenk techniques. Tetrahydrofuran was dried by destillation from potassium/sodium alloy and saturated with argon. Enol ethers and 1-(4-morpholino)-cyclopentene were degassed and saturated with argon by the freeze-pump-thaw method (−196/25°C, three cycles). Chromatography was carried out with degassed solvents on silica gel (Merck 60 (0.063–0.200 mm)) at 10°C. ^{1}H and ^{13}C NMR-spectra were recorded on either Bruker DRX-500 or AM-250 spectrometers. Chemical shifts refer to those of residual solvent signals based on δ_{TMS}=0.00 ppm. Infrared spectra were recorded in petroleum ether solution using a Nicolet Magna 550 Fourier transform infrared spectrometer. Electron impact mass spectra were recorded on a Kratos MS 50 spectrometer. Elemental analyses were obtained from a Heraeus CHN-O-Rapid. Reflections were collected on an Nonius Kappa CCD diffractometer. Structures were solved by Patterson methods (**9**, **10**) or direct methods (**14**)[25] and refined by full-matrix least-squares on F^2.[26] Non-hydrogen atoms were refined anisotropically, H atoms localized by difference electron density and refined using a riding model. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-136878 (**9**), CCDC-136879 (**10**) and CCDC-136880 (**14**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

General procedure for the preparation of 5–12

The concentration of metal carbene starting materials **3** and **4** in THF, reaction times and yields are listed in Scheme 4.

Enol ether (40 equiv.) was added by syringe to a dry THF solution (0.1 mmol) of **3** or **4**, respectively. The reaction mixture was stirred at the temperature given below for the products until the end of the reaction was indicated by TLC and IR spectroscopy. The solvent was removed in vacuo, and the crude product was purified by column chromatography on silica gel at 10°C using petroleum ether/dichloromethane (1:1 unless indicated otherwise) as eluent to give analytically pure samples of the spirocyclic oxacyclopentylidene complexes **5**–**12** as single diastereomers.

Pentacarbonyl{(2′-ethoxy)-spiro[2-oxacyclopent-5,1′-cyclobutane]-1-ylidene}chromium (5). Reaction at room temperature. Yellow solid. R_f (petroleum ether/dichloromethane: 1/1): 0.58; ^{1}H NMR (250 MHz, CDCl$_3$): δ=1.13 (t, ^3J=7.02 Hz, 3H, CH$_3$), 1.72 (m, 1H, H-4′a), 1.81 (dpt, ^2J=12.69, ^3J=8.18 Hz, 1H, H-4-a), 2.07 (dpq, ^2J=10.48 Hz, ^3J=10.48 Hz, ^3J=8.51 Hz, 1H, H-3′a), 2.42–2.64 (m, 2H, H-4b and H-3′b), 2.64 (ddd, ^2J=11.08 Hz, ^3J=10.38 Hz, ^3J=8.58 Hz, 1H, H-4′b), 3.20 (dq, ^2J=9.47 Hz, ^3J=7.01 Hz, 1H, C*H*HCH$_3$), 3.40 (dq, ^2J=9.46 Hz, ^3J=6.94 Hz, 1H, CH*H*CH$_3$), 4.62 (pt, ^3J=7.69, 1H, H-2′), 4.70 (dpt, ^2J=9.60 Hz, ^3J=7.91 Hz, 1H, H-3a), 4.85 (ddd, ^2J=9.65 Hz, ^3J=8.67 Hz, ^3J=5.56 Hz, 1H, H-3b); ^{13}C NMR (125 MHz, CDCl$_3$): δ=15.10 (CH$_3$), 24.54 (C-4′), 27.36 (C-3′), 27.68 (C-4), 64.95 (*C*H$_2$CH$_3$), 76.57 (C-2′), 78.86 (C-5), 83.78 (C-3), 216.57 (*cis*-CO), 223.04 (*trans*-CO), 345.35 (C-1); FT-IR (cm^{-1}): $\tilde{\nu}_{CO}$ = 2064 (w), 1989 (w), 1960 (sh), 1952 (vs), 1931 (s); EI-MS (70 eV): *m/z* (%)=346 (26) [M$^+$], 318 (3) [M$^+$−CO], 290 (12) [M$^+$−2CO], 262 (15) [M$^+$−3CO], 234 (42) [M$^+$−4CO], 218 (21), 206 (67) [M$^+$−5CO], 160 (68), 134 (71) [M$_{206}$−C$_4$H$_8$O], 96 (36), 52 (100) [Cr$^+$]; HR-MS calcd for M$^+$: 346.0145; found: 346.0143; Anal. calcd for C$_{14}$H$_{14}$O$_7$Cr: C 48.56; H 4.08; found: C 48.73; H 4.32.

Pentacarbonyl{(2′-ethoxy)-spiro[2-oxacyclopent-5,1′-cyclobutane]-1-ylidene}tungsten (6). Reaction at room temperature. Yellow solid. R_f (petroleum ether/dichloromethane: 1/1): 0.65; ^{1}H NMR (500 MHz, CDCl$_3$): δ=1.14 (t, ^3J=7.00 Hz, 3H, CH$_3$), 1.71 (m, 1H, H-4′a), 1.85 (ddd, ^2J=12.77 Hz, ^3J=8.18 Hz, ^3J=7.50 Hz, 1H, H-4-a), 2.10 (dpq, ^2J=10.12 Hz, ^3J=10.12 Hz, ^3J=8.49 Hz, 1H, H-3′a), 2.44–2.57 (m, 3H, H-4b, H3′b and H-4′b), 3.18 (dq, ^2J=9.49 Hz, ^3J=7.03 Hz, 1H, C*H*HCH$_3$), 3.39 (dq, ^2J=9.46 Hz, ^3J=7.03 Hz, 1H, CH*H*CH$_3$), 4.59 (dpt, ^3J=8.05 Hz, ^4J=1.04 Hz, 1H, H-2′), 4.71 (dpt, ^2J=9.84 Hz, ^3J=7.85 Hz, 1H, H-3a), 4.82 (ddd, ^2J=9.81 Hz, ^3J=8.67 Hz, ^3J=5.94 Hz, 1H, H-3b); ^{13}C NMR (125 MHz, CDCl$_3$): δ=15.19 (CH$_3$), 25.12 (C-4′), 27.12 (C-3′), 27.23 (C-4), 64.95 (*C*H$_2$CH$_3$), 76.92 (C-2′), 80.32 (C-5), 84.32 (C-3), 197.16 (*cis*-CO), 203.13 (*trans*-CO), 320.75 (C-1); FT-IR (cm^{-1}): $\tilde{\nu}_{CO}$ = 2072 (w), 1985 (w), 1950 (vs), 1926 (s); EI-MS (70 eV): *m/z* (%)=478 (9) [M$^+$], 406 (7), 378 (39) [M$_{406}$−CO], 350 (23) [M$_{406}$−2CO], 322 (35) [M$_{406}$−3CO], 294 (20) [M$_{406}$−4CO], 266 (19) [M$_{406}$−5CO], 109 (100); HR-MS calcd for $^{12}\mathrm{C}_{14}^{1}\mathrm{H}_{14}^{182}\mathrm{W}^{16}\mathrm{O}_7$ [M$^+$]: 476.0222; found: 476.0223; Anal. calcd for C$_{14}$H$_{14}$O$_7$W: C 35.17; H 2.95; found: C 35.62; H 3.26.

Pentacarbonyl{(2′-*n*-butoxy)-spiro[2-oxacyclopent-5,1′-cyclobutane]-1-ylidene}chromium (7). Reaction temperature: 50°C. Yellow–orange oil. R_f (petroleum ether/dichloromethane: 1/1): 0.78; ^{1}H NMR (500 MHz, CDCl$_3$): δ=0.85 (t, ^3J=7.40 Hz, 3H, CH$_3$), 1.30 (m, 2H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 1.47 (pqui, ^3J=6.62 Hz, 2H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.72 (dddd, ^2J=11.75 Hz, ^3J=10.21 Hz, ^3J=2.01 Hz, ^4J=0.92 Hz, 1H, H-4′a), 1.80 (dpt, ^2J=12.65 Hz, ^3J=8.37 Hz, 1H, H-4a), 2.06 (ddpt, ^2J=11.29 Hz, ^3J=10.41 Hz, ^3J=8.55 Hz, 1H, H-3′a), 2.48 (dddd, ^2J=11.30 Hz, ^3J=8.52 Hz, ^3J=7.65 Hz, ^3J=2.16 Hz, 1H, H-3′b), 2.57 (ddd, ^2J=12.77 Hz, ^3J=7.80 Hz, ^3J=5.12 Hz, 1H, H-4b), 2.64 (ddd, ^2J=11.75 Hz, ^3J=11.66 Hz, ^3J=8.52 Hz, 1H, H-4′b), 3.12 (dt, ^2J=9.40 Hz, ^3J=6.63 Hz, 1H, C*H*HCH$_2$CH$_2$CH$_3$), 3.32 (dt, ^2J=9.40 Hz, ^3J=6.51 Hz, 1H, CH*H*CH$_2$CH$_2$CH$_3$), 4.59 (ddd, ^3J=8.55 Hz, ^3J=7.65 Hz, ^4J=0.90 Hz, 1H, H-2′), 4.70 (dpt, ^2J=9.64 Hz, ^3J=8.00 Hz, 1H, H-3a), 4.85 (ddd, ^2J=9.64 Hz, ^3J=8.74 Hz, ^3J=5.26 Hz, 1H, H-3b); ^{13}C NMR (125 MHz, CDCl$_3$): δ=13.79 (CH$_3$), 19.22 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 24.57 (C-4′), 27.34 (C-3′), 27.70 (C-4), 31.72 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 69.48 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 76.75 (C-2′), 78.87 (C-5), 83.85 (C-3), 216.60 (*cis*-CO), 223.06 (*trans*-CO), 345.32 (C-1); FT-IR (cm^{-1}): $\tilde{\nu}_{CO}$ = 2070 (w), 1989 (w), 1962 (sh), 1952 (vs), 1931 (s); EI-MS (70 eV): *m/z* (%)=374 (19) [M$^+$], 346 (4) [M$^+$−CO], 318 (14) [M$^+$−2CO], 290 (15) [M$^+$−3CO], 262 (45) [M$^+$−4CO], 234 (100) [M$^+$−5CO], 218 (39), 162 (73) [M$_{262}$−C$_6$H$_{12}$O], 134 (80) [M$_{234}$−C$_6$H$_{12}$O], 124 (57), 52

(86) [Cr$^+$]; HR-MS calcd for M$^+$: 374.0458; found: 374.0458; Anal. calcd for $C_{16}H_{18}O_7Cr$: C 51.34; H 4.85; found: C 51.07; H 5.05.

Pentacarbonyl{(2′-*n*-butoxy)-spiro[2-oxacyclopent-5,1′-cyclobutane]-1-ylidene}tungsten (8). Reaction temperature: 50°C. Yellow–orange oil. R_f (petroleum ether/dichloromethane: 1/1): 0.68; ^{1}H NMR (500 MHz, $CDCl_3$): δ=0.88 (t, ^3J=7.35 Hz, 3H, CH_3), 1.31 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.48 (pqui, ^3J=7.10 Hz, 2H, $CH_2CH_2CH_2CH_3$), 1.68–1.74 (m, H-4′a), 1.83 (dpt, ^2J=12.75 Hz, ^3J=8.17 Hz, 1H, H-4a), 2.09 (dpq, ^2J=10.24 Hz, ^3J=10.42 Hz, ^3J=8.75 Hz, 1H, H-3′a), 2.44–2.58 (m, 3H, H-3′b, H-4b, H-4b′), 3.12 (dt, ^2J=9.34 Hz, ^3J=6.66 Hz, 1H, $CHHCH_2CH_2CH_3$), 3.32 (dt, ^2J=9.39 Hz, ^3J=6.51 Hz, 1H, $CHHCH_2CH_2CH_3$), 4.56 (dt, ^3J=7.65 Hz, ^4J=0.79 Hz, 1H, H-2′), 4.71 (dpt, ^2J=9.71 Hz, ^3J=7.97 Hz, 1H, H-3a), 4.83 (ddd, ^2J=9.61 Hz, ^3J=8.89 Hz, ^3J=5.71 Hz, 1H, H-3b); ^{13}C NMR (125 MHz, $CDCl_3$): δ=13.82 (CH_3), 19.25 ($CH_2CH_2CH_2CH_3$), 25.21 (C-4′), 27.10 (C-3′), 27.21 (C-4), 31.74 ($CH_2CH_2CH_2CH_3$), 69.40 ($CH_2CH_2CH_2CH_3$), 77.12 (C-2′), 80.19 (C-5), 84.41 (C-3), 197.17 (*cis*-CO), 203.17 (*trans*-CO), 320.73 (C-1); FT-IR (cm^{-1}): $\tilde{\nu}_{CO}$ = 2070 (w), 1985 (w), 1950 (vs), 1927 (s); EI-MS (70 eV): *m/z* (%)=506 (47) [M$^+$], 478 (45) [M$^+$−CO], 450 (15) [M$^+$−2CO], 422 (8) [M$^+$−3CO], 406 (16) [M$^+$−$C_6H_{12}O$], 378 (46) [M_{406}−CO], 366 (4) [M$^+$−5 CO], 350 (18) [M_{406}−2CO], 322 (25) [M_{406}−3CO], 294 (13) [M_{406}−4CO]; 266 (12) [M_{366}−$C_6H_{12}O$], 182 (16), 109 (100), 81 (28), 56 (22); HR-MS calcd for $^{12}C_{16}{}^{1}H_{18}{}^{16}O_7{}^{182}W$ [M$^+$]: 504.0535; found: 504.0547.

5*R**,2′*S**-Pentacarbonyl{(2′-*tert*-butoxy)-spiro[2-oxacyclopent-5,1′-cyclobutane]-1-ylidene}chromium (9). Reaction temperature: 50°C. Yellow crystals (mp 74–75°C) obtained from recrystallization from pentane. R_f (petroleum ether/dichloromethane: 1/1): 0.78; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.10 (s, 9H, $C(CH_3)_3$, 1.64–1.80 (m, 2H, H-4a and H-4′a), 2.10 (dpq, ^2J=10.63 Hz, ^3J=10.63 Hz, ^3J=8.36 Hz, 1H, H-3′a), 2.40 (dddd, ^2J=10.99 Hz, ^3J=8.51 Hz, ^3J=7.40 Hz, ^3J=2.17 Hz, 1H, H-3′b), 2.78 (ddd, ^2J=12.46 Hz, ^3J=6.84 Hz, ^3J=2.57 Hz, 1H, H-4b), 2.81 (ddd, ^2J=11.66 Hz, ^3J=10.56 Hz, ^3J=8.67 Hz, 1H, H-4′b), 4.54 - 4.68 (m, 2H, H-3a and H-2′), 4.86 (dpt, ^2J=9.19 Hz, ^3J=9.19 Hz, ^3J=2.48 Hz, 1H, H-3b); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ=24.04 (C-4′), 28.12 ($C(CH_3)_3$, C-4), 31.08 (C-3′), 69.93 (C-2′), 74.65 ($C(CH_3)_3$), 79.78 (C-5), 84.61 (C-3), 216.71 (*cis*-CO), 223.11 (*trans*-CO), 345.18 (C-1); FT-IR (cm^{-1}): $\tilde{\nu}_{CO}$ = 2064 (w), 1989 (w), 1959 (sh), 1952 (vs), 1931 (s); EI-MS (70 eV): *m/z* (%)=374 (12) [M$^+$], 318 (2) [M$^+$−2CO], 290 (3) [M$^+$−3CO], 262 (15) [M$^+$−4CO], 234 (35) [M$^+$−5CO], 190 (18), [M_{290}−$C_6H_{12}O$], 160 (33), 134 (39) [M_{234}−$C_6H_{12}O$], 109 (21), 95 (27), 57 (100) [$C_4H_9^+$], 52 (66) [Cr$^+$]; HR-MS calcd for M$^+$: 374.0458; found: 374.0469; Anal. calcd for $C_{16}H_{18}O_7Cr$: C 51.34; H 4.85; found: C 51.15; H 4.97.

Crystal data for **9**: $C_{16}H_{18}CrO_7$, M_r=374.30, triclinic, space group *P*-1 (No. 2), crystal size 0.18×0.12×0.06 mm^3, *a*=9.3467(6), *b*=9.7391(8), *c*=9.8541(8) Å, α=86.853(4)°, β=88.012(4)°, γ=76.640(4)°, *V*=871.19(12) Å^3, ρ_{calcd}= 1.427 Mg m^{-3}, *Z*=2, μ(MoKα)=0.689 mm^{-1}, *T*= 123(2) K, *F*(000)=388; 14491 measured reflections, 4147 symmetry-independent reflections (R_{int}=0.040), 217 refined parameters, *wR*2=0.091 [R_1=0.033 for $I>2\sigma(I)$].

5*R**,2′*S**-Pentacarbonyl{(2′-tert-butoxy)-spiro[2-oxacyclopent-5,1′-cyclobutane]-1-ylidene}tungsten (10). Reaction temperature: 50°C. Yellow crystals (mp 76–78°C) obtained from recrystallization from hexane. R_f (petroleum ether/dichloromethane: 1/1): 0.79; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.10 (s, 9H, $C(CH_3)_3$), 1.65–1.84 (m, 2H, H-4a and H-4′a), 2.11 (dpq, ^2J=10.64 Hz, ^3J=10.64 Hz, ^3J= 8.42 Hz, 1H, H-3′a), 2.40 (dddd, ^2J=10.80 Hz, ^3J= 8.43 Hz, ^3J=7.51 Hz, ^3J=2.08 Hz, 1H, H-3′b), 2.70 (dpt, ^2J=11.11 Hz, ^3J=11.11 Hz, ^3J=8.61 Hz, 1H, H-4′b), 2.77 (ddd, ^2J=12.27 Hz, ^3J=7.14 Hz, ^3J=2.81 Hz, 1H, H-4b), 4.53–4.66 (m, 2H, H-3a and H-2′), 4.85 (dpt, ^2J=9.34 Hz, ^3J=9.34 Hz, ^3J=2.89 Hz, 1H, H-3b); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ=24.68 (C-4′), 27.48 (C-4), 28.15 ($C(CH_3)_3$), 30.82 (C-3′), 70.00 (C-2′), 74.73 ($C(CH_3)_3$), 81.27 (C-5), 85.24 (C-3), 197.26 (*cis*-CO), 203.18 (*trans*-CO), 320.86 (C-1); FT-IR (cm^{-1}): $\tilde{\nu}_{CO}$ = 2070 (w), 1985 (w), 1950 (vs), 1927 (s); EI-MS (70 eV): *m/z* (%)=506 (2) [M$^+$], 450 (1) [M$^+$−2CO], 422 (1) [M$^+$−3CO], 394 (1) [M$^+$−4CO], 366 (2) [M$^+$−5CO], 266 (2) [M_{366}−$C_6H_{12}O$], 109 (27), 57 (100) [$C_4H_9^+$]; HR-MS calcd for $^{12}C_{16}{}^{1}H_{18}{}^{16}O_7{}^{184}W$ [M$^+$]: 506.0562; found: 506.0570; Anal. calcd for $C_{16}H_{18}O_7W$: C 37.97; H 3.58; found: C 37.22; H 3.96.

Crystal data for**10**: $C_{16}H_{18}WO_7$, M_r=506.15, triclinic, space group *P*-1 (No. 2), crystal size 0.20×0.10×0.03 mm^3, *a*=9.4791(3), *b*=9.8800(3), *c*=9.9688(3) Å, α=86.671(2)°, β=74.254(2)°, γ=88.897(2)°, *V*=897.06(5) Å^3, ρ_{calcd}= 1.874 Mg m^{-3}, Z=2, μ(MoKα)= 6.471 mm^{-1}, *T*= 193(2) K, *F*(000)=488; 13089 measured reflections, 4391 symmetry-independent reflections (R_{int}= 0.045), 217 refined parameters, *wR*2=0.044 [R_1=0.020 for $I>2\sigma(I)$]. A semi-empirical absorption correction (min./max. transmission 0.6143/0.7716) was applied.

Pentacarbonyl{(2′-allyloxy)-spiro[2-oxacyclopent-5,1′-cyclobutane]-1-ylidene}chromium (11). Reaction temperature: 50°C. Column chromatography (SiO_2, petroleum ether/dichlormethane: 1/2) afforded a yellow oil. R_f (petroleum ether/dichloromethane: 1/2): 0.88; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.74 (dddd, ^2J=11.67 Hz, ^3J= 9.94 Hz, ^3J=1.30 Hz, ^4J=0.77 Hz, 1H H-4′a), 1.82 (dpt, ^2J=12.7 Hz, ^3J=8.36 Hz, 1H, H-4-a), 2.10 (dpq, ^2J= 8.35 Hz, ^3J=10.47 Hz, ^3J=8.35 Hz, 1H, H-3′a), 2.43–2.66 (m, 2H, H-3b and H-3′b), 2.64 (ddd, ^2J=11.48 Hz, ^3J=10.19 Hz, ^3J=8.67 Hz, 1H, H-4′b), 3.73 (ddpt, ^2J= 12.85 Hz, ^3J=5.43 Hz, ^4J=1.53 Hz, 1H, $CHHCH{=}CH_2$), 3.86 (ddpt, ^2J=12.82 Hz, ^3J=5.52 Hz, ^4J=1.53 Hz, 1H, $CHHCH{=}CH_2$), 4.65 (pt, ^3J=8,30 Hz, 1H, H-2′), 4.70 (dpt, ^2J=9.76 Hz, ^3J=8.00 Hz, 1H, H-3a), 4.85 (ddd, ^2J=9.67 Hz, ^3J=8.64 Hz, ^3J=5.16 Hz, 1H, H-3b), 5.17 (dpq, ^2J=1.48 Hz, ^3J=10.48 Hz, ^4J=1.48 Hz, 1H, $-CH{=}CHH$), 5.24 (dpq, ^2J=1.62 Hz, ^3J=17.29 Hz, ^4J= 1.62 Hz, 1H, $-CH{=}CHH$), 5.80 (ddpt, ^3J=17.23 Hz, ^3J= 10.49 Hz, ^3J=5.30 Hz, 1H, $-CH{=}CH_2$); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ=24.40 (C-4′), 27.41 (C-3′), 27.84 (C-4), 70.23 ($CH_2CH{=}CH_2$), 76.16 (C-2′), 78.64 (C-5), 83.79 (C-3), 117.40 ($-CH{=}CH_2$), 133.69 ($-CH{=}CH_2$), 216.56 (*cis*-CO), 223.02 (*trans*-CO), 345.35 (C-1); FT-IR (cm^{-1}): $\tilde{\nu}_{CO} = 2064$ (w), 1952 (vs), 1931 (s); EI-MS (70 eV): *m*/*z* (%)=358 (19) [M^{+}], 330 (1) [M^{+}−CO], 302 (3) [M^{+}−2CO], 274 (13) [M^{+}−3CO], 246 (38) [M^{+}−4CO], 218 (50) [M^{+}−5CO], 176 (100), 134 (29) [M$_{218}$−C$_5$H$_8$O], 52 (53) [Cr^{+}]; HR-MS calcd for M^{+}: 358.0145; found: 358.0150.

Pentacarbonyl{spiro[2-oxacyclopent-5,7′-[2′]oxabicyclo-[3.2.0]heptane]-1-ylidene}chromium (12). Reaction temperature: 50°C. Yellow oil. *R*$_f$ (petroleum ether/dichloromethane: 1/1): 0.48; ^{1}H NMR (500 MHz, CDCl$_3$): δ=0.60 (dpt, ^{2}J=12.62 Hz, ^{3}J=8.81 Hz, 1H, H-4a), 0.90 (dd, ^{2}J=13.51 Hz, ^{3}J=5.56 Hz, 1H, H-6′a), 1.04 (ddpt, ^{2}J=12.62 Hz, ^{3}J=6.16 Hz, ^{3}J=2.14 Hz, 1H, H-4′a), 1.33 (ddpt, ^{2}J=12.52 Hz, ^{3}J=9.94 Hz, ^{3}J=8.17 Hz, 1H, H-4′b), 1.57 (ddd, ^{2}J=12.47 Hz, ^{3}J=7.15 Hz, ^{3}J=4.22 Hz, 1H, H-4b), 2.92 (ddd, ^{2}J=13.51 Hz, ^{3}J=9.14 Hz, ^{4}J=2.09 Hz, 1H, H-6′b), 3.24–3.34 (m, 2H, H-3′a and H-5′), 3.60–3.72 (m, 3H, H-3a/b and H-3′b), 4.58 (dd, ^{3}J=6.26 Hz, ^{4}J=1.89 Hz, 1H, H-1′); ^{13}C NMR (133.3 MHz, CDCl$_3$): δ 29.20 (C-4), 31.78 (C-4′), 32.44 (C-6′), 36.29 (C-5′), 69.93 (C-3′), 74.82 (C-5), 89.92 (C-1′), 83.22 (C-3), 216.41(*cis*-CO), 222.78 (*trans*-CO), 346.70 (C-1); FT-IR (cm^{-1}): $\tilde{\nu}_{CO} = 2064$ (w), 1952 (vs), 1989 (w), 1950 (sh), 1931 (m); EI-MS (70 eV): *m*/*z* (%)=344 (37) [M^{+}], 316 (7) [M^{+}−CO], 288 (14) [M^{+}−2CO], 260 (21) [M^{+}−3CO], 232 (70) [M^{+}−4CO], 204 (100) [M^{+}−5CO], 174 (49), 1348) [M$_{204}$−C$_4$H$_6$O], 70.0 (27) [C$_4$H$_6$O^{+}], 52 (53) [Cr^{+}]; HR-MS calcd for M^{+}: 343.9988; found: 343.9989.

Pentacarbonyl[5-(3′-oxo-)but-1′-yl-2-oxacyclopentylidene]-chromium (13). 2.4 ml (24.4 mmol) 2-Methoxypropene were added by syringe to a dry THF solution (12.2 ml) of 168 mg (0.61 mmol) **2**. The color of the solution immediately changed from dark red to yellow. The solvent was removed in vacuo, and the crude product was purified by column chromatography (SiO$_2$, petroleum ether/dichloromethane: 1/1) at 10°C to give 188 mg (93%) of **13** as a yellow solid. *R*$_f$ (petroleum ether/dichloromethane: 1/1): 0.69; ^{1}H NMR (500 MHz, CDCl$_3$): δ=1.58–1.68 (m, 2H, H-4a and H-4′a), 2.02 (dpq, ^{2}J=12.69 Hz, ^{3}J=8.18 Hz, 1H, H-4b), 2.17 (s, 3H, CH$_3$), 2.52–2.60 (m, 3H, H-3′a/b and H-4′b), 3.51 (dddd, ^{3}J=10.90 Hz, ^{3}J=8.24 Hz, ^{3}J=5.43 Hz, ^{3}J=2.81 Hz, 1H, H-5), 4.81–4.89 (m, 2H, H-3a/b); ^{13}C NMR (125 MHz, CDCl$_3$): δ=25.23 (C-4′), 26.10 (C-4), 29.85 (CH$_3$), 41.42 (C-3′), 69.62 (C-5), 84.12 (C-3), 207.03 (C-2′), 216.29 (*cis*-CO), 223.11 (*trans*-CO), 347.08 (C-1); FT-IR (cm^{-1}): $\tilde{\nu}_{CO} = 2066$ (w), 1991 (w), 1954 (vs), 1935 (m); EI-MS (70 eV): *m*/*z* (%)=332 (12) [M^{+}], 276 (22) [M^{+}−2CO], 248 (5) [M^{+}−3CO], 220 (43), [M^{+}−4CO], 192 (83) [M^{+}−5CO], 162 (74), 136 (79), 110 (54), 80 (20), 52 (100) [Cr^{+}]; HR-MS calcd for M^{+}: 331.9988; found: 331.9993.

5*R**,2′*S**-Pentacarbonyl[5-(oxocyclopent-2′-yl)methylene-2-oxacyclopentylidene]chromium (14). 0.18 ml (1.20 mmol) 1-(4-Morpholino)cyclopentene were added by syringe to a dry THF solution (12.0 ml) of 164 mg (0.60 mmol) **2**. The color of the solution changed immediately from dark red to yellow. The solvent was removed in vacuo, and the crude product was purified by column chromatography (SiO$_2$, petroleum ether/dichloromethane: 1/3) at 10°C to give 214 mg (85%) of **14** as a yellow solid. Recrystallization from hexane afforded yellow crystals (mp 103–104°C).

R$_f$ (petroleum ether/dichloromethane: 1/3): 0.69; ^{1}H NMR (500 MHz, CDCl$_3$): δ=11.46 (ddd, ^{2}J=14.01 Hz, ^{3}J=11.47 Hz, ^{3}J=4.92 Hz, 1H, H$_a$-methylene bridge), 1.61 (ddpt, ^{2}J=12.57 Hz, ^{3}J=8.16 Hz, ^{3}J=6.93 Hz, 1H, H-4a), 1.69 (ddpt, ^{2}J=12.37 Hz, ^{3}J=9.47 Hz, ^{3}J=6.64 Hz, 1H, H-3′a), 1.85 (ddpq, ^{2}J=12.84 Hz, ^{3}J=9.11 Hz, ^{3}J=6.33 Hz, 1H, H-4′a), 2.04–2.35 (m, 6H, H-4b, H-2′, H-3′b, H-4′b and H-5′a/b), 2.72 (ddd, ^{2}J=13.96 Hz, ^{3}J=9.59 Hz, ^{3}J=3.28 Hz, 1H, H$_b$-methylene bridge), 3.82 (dddd, ^{3}J=11.47 Hz, ^{3}J=8.23 Hz, ^{3}J=6.63 Hz, ^{3}J=3.25 Hz, 1H, H-5), 4.80 (ddd, ^{2}J=9.86 Hz, ^{3}J=8.22 Hz, ^{3}J=7.23 Hz, 1H, H-3a), 4.91 (ddd, ^{2}J=9.86 Hz, ^{3}J=8.22 Hz, ^{3}J=6.29 Hz, 1H, H-3b); ^{13}C NMR (125 MHz, CDCl$_3$): δ=20.69 (C-4′), 26.78 (C-4), 30.32 (C-3′), 31.76 (CH$_2$, methylene bridge), 38.05 (C-5′), 46.42 (C-2′), 68.66 (C-5), 84.06 (C-3), 216.39 (*cis*-CO), 220.05 (C-1′), 223.14 (*trans*-CO), 347.24 (C-1); FT-IR (cm^{-1}): $\tilde{\nu}_{CO} = 2066$ (w), 1991 (w), 1955 (vs), 1934 (s); EI-MS (70 eV): *m*/*z* (%)=358 (11) [M^{+}], 302 (12) [M^{+}−2CO], 274 (4) [M^{+}−3CO], 246 (32), [M^{+}−4CO], 218 (100) [M^{+}−5CO], 190 (38), 162 (54), 136 (44), 52 (56) [Cr^{+}]; HR-MS calcd for M^{+}: 358.0145; found: 358.0137; Anal. calcd for C$_{15}$H$_{14}$O$_7$Cr: C 50.29; H 3.94; found: C 49.78; H 4.00.

Crystal data for [**14**]: C$_{15}$H$_{14}$CrO$_7$, M$_r$=358.26, monoclinic, space group *C*2/c (No. 15), crystal size 0.20×0.10×0.03 mm^3, *a*=24.6525(10) *b*=6.4757(2), *c*=23.0394(9) Å, β=120.786(2)°, *V*=3159.8(2) Å^3, ρ_{calcd}=1.506 Mg m^{-3}, *Z*=8, μ(MoKα)=0.757 mm^{-1}, *T*=123(2) K, *F*(000)=1472; 18301 measured reflections, 3718 symmetry-independent reflections (*R*$_{int}$=0.052), 208 refined parameters, *wR*2=0.095 [*R*$_1$=0.040 for *I*>2σ(*I*)].

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