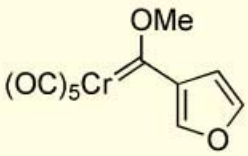
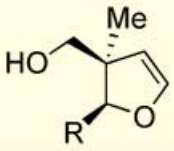
Regio- and Diastereoselective Dearomatization of Furan Rings

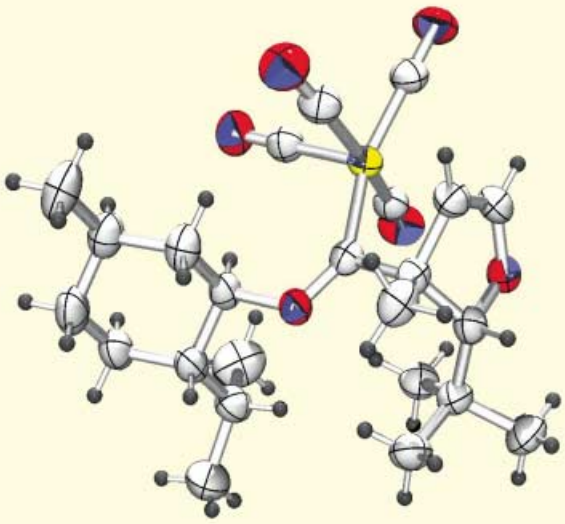
Asymmetric Synthesis





Nucleophilic Addition

Dihydrofurans



Chelate Carbene Complexes

For more details see the following pages.

 DOI: 10.1002/chem.200305241

Asymmetric Dearomatization of the Furan Ring Promoted by Conjugate Organolithium Addition to (Menthyloxy)(3-furyl)carbene Complexes of Chromium

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Abstract: The sequential low-temperature addition reaction of an organolithium compound and methyl triflate to (menthyloxy)(3-furyl)carbene complexes of chromium and tungsten proceeded with excellent regioselectivity (1,4-addition) and diastereoselectivity (2,3-*trans* disposition of the nucleophile and electrophile groups) to afford new 2,3-disubstituted (2,3-dihydro-3-furyl)-carbene complexes. In addition, a high degree of diastereofacial selectivity was achieved by employing alkenyllithium compounds. After detachment of both the metal fragment and the chiral auxiliary group, trisubstituted 2,3-dihydrofuran derivatives containing a quaternary stereogenic center at the C3 position were obtained. The characterization, including X-ray crystallography, of a novel type of stable four-membered chelate (η^2-alkene)tetracarbonylcarbene complex of chromium is also reported.

Keywords: asymmetric synthesis · carbene complexes · dearomatization · dihydrofurans · nucleophilic addition

Introduction

The transformation of readily available aromatic compounds into functionalized alicyclic derivatives is widely recognized as a useful strategy for the construction of valuable synthetic intermediates.[1] In the case of furans, the successful utilization of these heterocycles in organic synthesis often relies on the ability to dearomatize them with a high degree of regio- and stereochemical control. There are a number of different methods that, with unequal scope, allow the dearomatization of the furan ring.[2] Reduction of furans under Birch-type conditions leads to 2,5-dihydrofurans.[3] High levels of diastereoselectivity have been obtained in the Birch reductive alkylation of chiral amides of 3-methyl-2-furoic acid.[4] Furans have been widely used as dienes[5] and less frequently as dienophiles[6] in [4+2] cycloaddition reactions with alkenes, alkynes, or allenes[5] and with reactive dienes,[6] respectively. These aromatic heterocycles also behave as dienes in [4+3] cycloaddition reactions with in situ generated 2-oxyallyl cations[7] or vinylcarbenoids,[8] as dipolarophiles in [3+2] cycloadditions to nitrones[9] and nitrile oxides,[10] and as olefins in [2+2] photocycloadditions to carbonyl compounds[11] and in rhodium(II)-[12a] or copper(I)-catalyzed[12b] [2+1] cycloadditions to metal-stabilized α-ketocarbenoids. All these cycloaddition processes lead to different bicyclic or tricyclic skeletons in which the conjugated π system of the furan ring is broken up. Oxidation of the furan ring without ring opening represents another way by which this heteroaromatic nucleus has been modified with concomitant dearomatization.[13] Product formation is a function of both the substitution pattern on the ring and the oxidation reagent employed. For example, 2,5-dialkoxy-2,5-dihydrofurans are formed as a mixture of diastereoisomers by bromination or chlorination of furans in hydroxylic solvents[14] or by using electrochemical procedures,[15,16] while butenolides are obtained from 2-(trimethylsilyl)furans under the influence of peracetic acid.[17] Additionally, furan dearomatization has been achieved by preformation of the cationic pentaammine(η^2-furan)osmium(II) complex followed by successive reaction with an electrophile and then a moder-

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author: ORTEP plots of the X-ray crystal structures of minor-**4e** and **12** are provided.

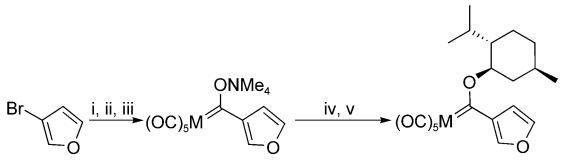
DOI: 10.1002/chem.200305241

ate nucleophile present in the reaction medium. After decomplexation of osmium, 2,2- or 2,3-disubstituted-2,3-dihydrofuran derivatives are formed with a high degree of diastereoselectivity.[18] More recently the acid-catalyzed methanol addition to dihapto-coordinated rhenium complexes of furan[19] leading to dihapto-coordinated 2-methoxy-2,3-dihydrofuran complexes has been reported.[20]

Our research into dearomatization chemistry promoted by nucleophilic addition to electron-deficient Fischer arylcarbene complexes followed by electrophilic trapping of the intermediate anionic complex[21] has led us to apply this methodology to aromatic heterocycles. We report here the regio- and diastereoselective dearomatization of the furan ring which has been achieved by a sequential nucleophile–electrophile addition reaction to the pentacarbonylchromium ((−)-menthyloxy)(3-furyl)carbene complex and which proceeds with high asymmetric induction when alkenyllithium compounds are employed as nucleophiles.

Results and Discussion

3-Furylcarbene complexes **1** were synthesized from 3-bromofuran by sequential treatment with butyllithium, the corresponding hexacarbonylmetal (chromium or tungsten), and tetramethylammonium bromide (Scheme 1).[22] Subsequent reaction of the appropriate tetramethylammonium complex thus formed with pivaloyl chloride and (−)- or (±)-menthol led to menthyloxycarbene complexes **1a,b**, which after silica gel column chromatography were isolated as a stable dark-red thick oil (−)-**1a** and an orange solid (−)-**1b**.



1	M	R*OH	yield
(-)-**1a**	Cr	(-)-menthol	50%
(±)-**1a**	Cr	(±)-menthol	47%
(-)-**1b**	W	(-)-menthol	49%

Scheme 1. Preparation of 3-furylcarbene complexes **1**. i) BuLi, THF, −80 °C; ii) $M(CO)_6$, 0 °C→RT; iii) Me_4NBr, H_2O, 0 °C→RT; iv) *t*BuCOCl, CH_2Cl_2, DMF, −45 °C; v) R*OH, −45 °C→RT.

Abstract in Spanish: *La reacción a baja temperatura de complejos (mentiloxi)(3-furil)carbeno de cromo o wolframio con un compuesto organolítico y posteriormente con triflato de metilo ocurrió con excelente regioselectividad (adición nucleófila 1,4) y diastereoselectividad (disposición relativa 2,3-trans de los sutituyentes procedentes del nucleófilo y electrófilo) dando lugar a nuevos complejos (2,3-dihidro-3-furil)carbeno 2,3-disustituídos. Además, en esta reacción se observó un alto grado de diastereoselectividad facial cuando se utilizó como nucleófilo un alquenillitio. La eliminación del fragmento metálico (oxidación al aire) y del auxiliar quiral (reducción con $LiAlH_4$) condujo a 2,3-dihidrofuranos trisustituidos que contienen un centro estereogénico cuaternario en la posición C3. Asimismo, se describe un nuevo tipo de complejos quelato de cuatro eslabones (η^2-alqueno)tetracarbonilcarbeno estables cuya caracterización incluye un análisis de difracción de rayos X.*

Conjugate addition of alkyllithiums and phenyllithium: When an alkyllithium or phenyllithium was added to a solution of carbene complex (−)-**1a**, (±)-**1a**, or (−)-**1b** in diethyl ether a very fast reaction took place at −80 °C, and we observed an immediate color change of the starting carbene complex. The reaction was quenched with methyl triflate at this low temperature and after purification by silica gel column chromatography gave pentacarbonylcarbene complex **2**, tetracarbonylcarbene complex **3**, or a mixture of these two carbene complexes depending on the nature of both the organolithium reagent and the starting carbene complex **1** (Scheme 2 and Table 1).

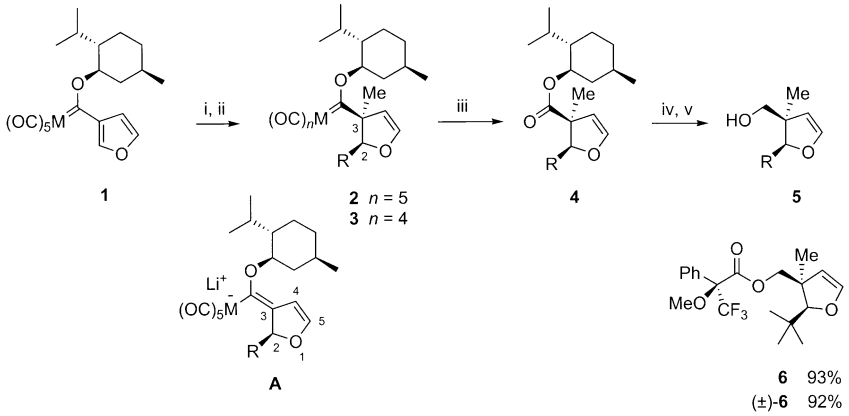
In the case of chromium–carbene complexes (−)-**1a** and (±)-**1a**, the reaction with *tert*-butyllithium provided exclusively the corresponding tetracarbonyl complexes **3a** and (±)-**3a** (Table 1, entries 1 and 2), while the experiments with cyclopentyllithium, neopentyllithium, butyllithium, and phenyllithium furnished a mixture of the corresponding penta- and tetracarbonyl complexes **2** and **3**. These products were isolated in practically equimolar ratios in the case of BuLi and PhLi (Table 1, entries 6–9) and as mixtures in which the tetracarbonyl derivative was favored ($(CH_2)_4CHLi$; Table 1, entry 4) or was clearly the major component (*t*$BuCH_2Li$; Table 1, entry 5). In addition, we observed that except for compounds **2e**:**3e** (R = Ph), these mixtures evolved to the corresponding tetracarbonyl complex on standing. In contrast, the reactions of tungsten carbene complex (−)-**1b** with *t*BuLi and PhLi gave only pentacarbonyl complexes **2ab** and **2eb**, respectively (Table 1, entries 3 and 10). Compounds **2** and **3** were each generated as a mixture of two diastereoisomers which have the same relative configuration at the newly created stereogenic centers, as will be shown below. The diastereoselectivity of the reaction seems to depend on the substitution pattern of the organolithium reagent. The highest value (84:16) was observed in the reaction with the tertiary alkyllithium (*t*BuLi). The diastereoselectivity was lower (79:21) with both the secondary derivative ($(CH_2)_4CHLi$) and the aryllithium (PhLi) and even lower with the primary alkyllithiums (BuLi 70:30; *t*$BuCH_2Li$ 60:40).

The tandem organolithium–methyl triflate addition reaction to tungsten carbene complex (−)-**1b** did not improve the results obtained with the corresponding chromium complex (−)-**1a**. As pointed out, the experiments carried out with (−)-**1b** and *t*BuLi or PhLi led to the corresponding pentacarbonylcarbene complex **2ab** or **2eb** with lower chemical yields but similar diastereomeric ratios (Table 1, entries 3 and 10 versus entries 1 and 8, respectively). The structures of products **2** and **3** were established on the basis of their spectroscopic data and in the case of tetracarbonylcarbene complexes **3**, a single-crystal X-ray diffraction of the minor isomer of **3a** (minor-**3a**)[23] revealed that the vacant coordination site at the chromium atom is capped by

Table 1. Furan dearomatized products **2**, **3**, **4**, and **5** prepared from 3-furylcarbene complexes **1** and organolithium compounds by sequential conjugate addition, oxidation, and reduction.

	1	R	2:3	Ratio[a]	Yield [%][b]	*dr*[c]	4	Yield [%][d]	*dr*[e]	5[f]	Yield [%][g]	*ee* [%]
1	(−)-**1a**	*t*Bu	**3a**[h]		66	84:16	**4a**	78	84:16	**5a**	90	78[i]
2	(±)-**1a**	*t*Bu	(±)-**3a**[h]		62	84:16	(±)-**4a**	80	84:16	(±)-**5a**	82	
3	(−)-**1b**	*t*Bu	**2ab**[j]		53	86:14	**4a**[k]	39	–[l]			
4	(−)-**1a**	$(CH_2)_4CH$[m]	**2b**:**3b**	35:65[n]	65	–[o]	**4b**	85	79:21	**5b**	92	–[p]
5	(−)-**1a**	$tBuCH_2$	**2c**:**3c**	10:90[q]	71	56:44[r]	**4c**	82	60:40	**5c**	85	–[p]
6	(−)-**1a**	Bu	**2d**:**3d**	50:50[n]	66	70:30	**4d**	80	70:30	**5d**	84	30[s]
7	(±)-**1a**	Bu	(±)-**2d**:(±)-**3d**	50:50[n]	60	70:30	(±)-**4d**	85	70:30	(±)-**5d**	92	
8	(−)-**1a**	Ph	**2e**:**3e**	47:53[t]	62	78:22	**4e**	83	79:21	**5e**	83	57[s]
9	(±)-**1a**	Ph	(±)-**2e**:(±)-**3e**,	47:53	64	78:22	(±)-**4e**	80	78:22	(±)-**5e**	82	
10	(−)-**1b**	Ph	**2eb**[j]		37	76:24						

[a] Ratio of the corresponding pentacarbonyl:tetracarbonyl (**2**:**3**) complexes determined by ^{1}H NMR spectroscopy. [b] Isolated yield after column chromatography based on the corresponding carbene complex **1**. [c] Diastereomeric ratio was determined by ^{1}H NMR spectroscopy; integration of signals corresponding to the tetracarbonyl complex. [d] Isolated yield after column chromatography based on the corresponding carbene complex **3/2** or mixture of carbene complexes **2**:**3**. [e] Diastereomeric ratio determined from the ^{1}H NMR spectrum. [f] Single diastereoisomer. [g] Isolated yield after column chromatography based on compound **4**. [h] Only the tetracarbonyl complex was observed in this experiment. [i] Enantiomeric excess determined by ^{1}H NMR analysis of the corresponding Mosher ester **6** in comparison with racemic mixture (±)-**6**. [j] Only the pentacarbonyl complex was observed in this experiment. [k] Oxidation of tungsten carbene complex **2ab** was carried out with $C_5H_5N^+$–O^- in THF at room temperature. [l] Poor resolution in the ^{1}H NMR spectrum: two diastereoisomers in an approximate ratio of 86:14. [m] Cyclopentyl. [n] After overnight in the refrigerator the pentacarbonyl complex completely converted to the tetracarbonyl complex. [o] Poor resolution in the ^{1}H NMR spectrum. [p] Not determined. [q] These two complexes were separated by silica gel column chromatography. [r] Determined by ^{13}C NMR spectroscopy (inverse gated decoupling experiment). [s] Enantiomeric excess determined by HPLC analysis on a chiral support (Chiralcel OD-H column) in comparison with the corresponding racemic mixture. [t] Pentacarbonyl complex **2e** did not convert to tetracarbonyl complex **3e** after several days in the refrigerator.

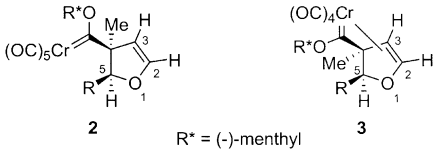


Scheme 2. Conjugate addition of organolithium compounds to 3-furylcarbene complexes **1**. Only the major diastereoisomer of compounds **2**, **3**, **4**, and **6** and the major enantiomer of products **5** are shown. i) R-Li, Et_2O, −80 °C; ii) MeOTf, −80 °C→RT; iii) air, *hν*, hexane, RT; iv) $LiAlH_4$, THF, 0 °C→RT; v) MeOH/H_2O, NaCl.

the carbon–carbon double bond to form a four-membered ring olefin-chelated complex with an almost perpendicular arrangement of the Cr=C and C=C bonds (Figure 1).[24,25] Presumably owing to the enol ether nature of the double bond in addition to geometrical constraints, the alkene ligand is not bonded symmetrically to Cr. The bond length of Cr to the more electron-rich carbon atom C3 (2.374(3) Å) is significantly shorter than that of Cr to C2 (2.663(3) Å). These distances are slightly or much longer, respectively, than the Cr–C(olefin) bond lengths reported for *cis*-(η^2-olefin)(tetracarbonyl)(carbene)chromium complexes (2.238–2.414 Å, mean 2.312 Å)[25a–c] but are in agreement with those found in a related (η^1-phosphine)(η^2-electron-rich alkene)(tricarbonyl)(carbene)chromium complex with a bicyclic chelate structure (η^2-(EtO–C=CH)Cr: Cr–CH 2.384(4) Å, Cr–C 2.619(4) Å).[26] The unsymmetrical coordination of the alkene moiety to chromium is readily observed in the ^{1}H NMR spectra of **3** (complexed double bond) in comparison with those of **2** (uncomplexed double bond) (Table 2). While the resonance of vinyl proton H3 of complexes **3** is shifted to higher field relative to that of the corresponding complex **2**, the signal of vinyl proton H2 of **3** is shifted downfield. The crystal chosen for the above X-ray structure determination was grown by cooling (−5 °C) a solution of a mixture of **3a** and minor-**3a** (approximately 84:16 ratio) in dry pentane. After crystallization, the solid product was separated from the solution by decantation. ^{1}H NMR spectra of the crystals and the residue obtained after solvent removal from the solution indicated that the crystals were enriched in the minor isomer (**3a**:minor-**3a** 1:1.9), whereas the solution was enriched in the major one (**3a**:minor-**3a**, 2.1:1). Based on these observations and according to following results we assume that the crystal selected for the X-ray analysis belongs to the minor isomer of **3a**. In addition, this analysis unequivocally determined the relative and absolute configuration of the newly formed stereogenic centers and revealed a *trans* disposition of the *t*Bu and Me groups.

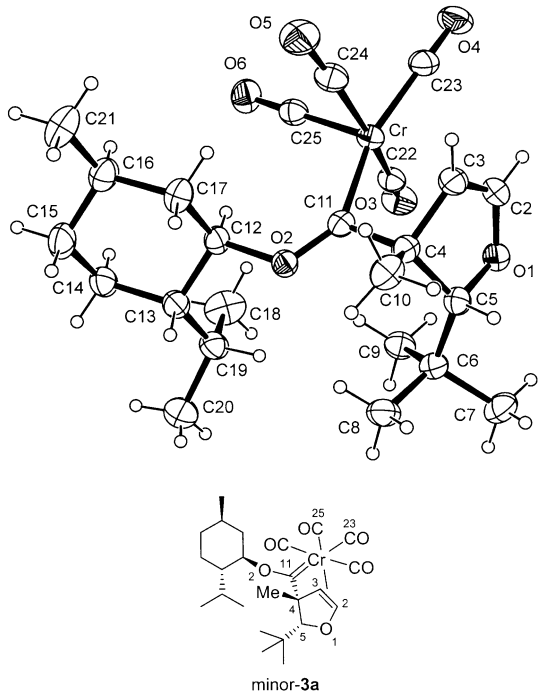
Due to the strong electron-withdrawing ability of the pentacarbonylmetal fragment, the furan ring directly bonded to the carbene carbon of complexes **1** becomes electron deficient enough to undergo regioselective nucleophilic attack with an organolithium (R–Li) at C2 to generate the

Table 2. ^{1}H NMR Chemical shifts of H2, H3, and H5 hydrogens corresponding to carbene complexes **2** and **3**.[a]



Compound	R	δ_{H2} [ppm]	δ_{H3} [ppm]	δ_{H5} [ppm]
2b	$(CH_2)_4CH$[b]	6.43	5.58	4.18
3b	$(CH_2)_4CH$[b]	7.26	4.36	3.77
2d	Bu	6.32	5.74	4.16
3d	Bu	7.26	4.42	3.96
2e	Ph	6.54	6.19	5.05
3e	Ph	7.52	4.70	5.13

[a] Spectra were recorded in $CDCl_3$. [b] Cyclopentyl.



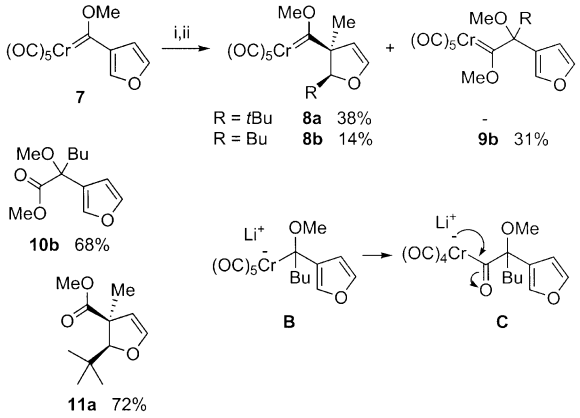
minor-**3a**

Figure 1. X-ray crystal structure of tetracarbonyl complex minor-**3a** (ORTEP, thermal ellipsoids with 30% probability). Selected bond lengths [Å], bond angles [°], and torsion angle [°]: C2–C3 1.336(4), Cr–C2 2.663(3), Cr–C3 2.374(3), Cr–C11 1.982(2), Cr–C23 1.895(3), Cr–C25 1.818(3), C11–C4 1.526(4), C11–O2 1.316(3); C11-Cr-C3 63.74(10), C23-Cr-C3 98.07(12), C25-Cr-C3 163.10(11), C2-C3-Cr 87.0(2), C4-C11-Cr 106.62(16), C11-C4-C3 98.6(2); C11-Cr-C3-C2 114.8(2).

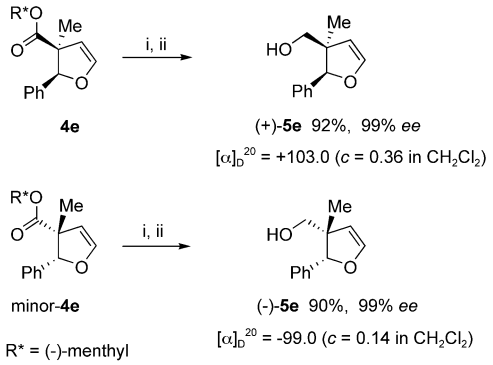
anionic enolate-type intermediate **A** (Scheme 2) which subsequently reacts with MeOTf in a regio- and diastereoselective electrophilic attack at C3 from the face opposite to the R group at C2.[27] The initially formed pentacarbonylcarbene complexes **2** of chromium undergo a spontaneous dissociation of a CO ligand to give tetracarbonylcarbene complexes **3** in which the alkene unit is attached to the metal. The driving force for this CO dissociation could be relaxation of the steric strain induced by the bulky carbene ligand, which has the larger groups at C2 and C3 placed on the same side of the ring and in addition contains a quaternary carbon center at the α position to the carbene carbon.[28] Indeed, the tendency of complexes **2** (M = Cr) to eliminate a CO ligand correlates with the steric bulk of the R group (tBu > tBuCH$_2$ > $(CH_2)_4CH$ > Ph > Bu; Table 1). In the case of compound **2e** (R = Ph), the planar geometry of the Ph group may allow it to adopt a more favorable conformation which could account for the lower bias to give product **3e**. Decarbonylation of pentacarbonylcarbene complexes **2** (M = W) was not observed under the reaction conditions. Presumably, in these complexes the steric crowdedness is smaller due to the greater size of the tungsten atom (atomic radii: Cr 1.35 Å, W 1.37 Å)[29a] and the consequently longer metal–carbene carbon bond.[29b,c] Additionally, dissociation of a W–CO bond ($\Delta G^{\neq} = 28.0$ kcal mol^{-1}) is more difficult than dissociation of a Cr–CO bond ($\Delta G^{\neq} = 24.0$ kcal mol^{-1}).[30]

The presence of a bulky alkoxy group bonded to the carbene carbon seems to be necessary to efficiently direct nucleophile attack to the heteroaromatic ring. Thus, when analogous reactions were carried out with (methoxy)(3-furyl)carbene complex **7** we observed either lower chemical yield of the conjugate addition product **8a** (reaction with a tertiary alkyllithium: RLi = tBuLi)[31] or a mixture of two products **8b** and **9b** (reaction with a primary alkyllithium: RLi = BuLi); the major product **9b** arises from an initial addition of the organolithium to the carbene carbon (Scheme 3). Carbene-complex **9b** is particularly unstable. It must be purified and stored rigorously under N_2 to avoid a very fast oxidative transformation to the corresponding carboxylic ester **10b**. Formation of **9b** could involve 1,2-nucleophilic addition of BuLi to carbene complex **7** to give tetrahedral intermediate **B**, which subsequently would undergo migratory insertion of carbon monoxide followed by O-methylation of lithium acylchromate intermediate **C**.[32] The relative configuration of products **8** was elucidated from a NOESY experiment carried out with carboxylic ester **11a**[33] generated by air–light oxidation of carbene complex **8a**.

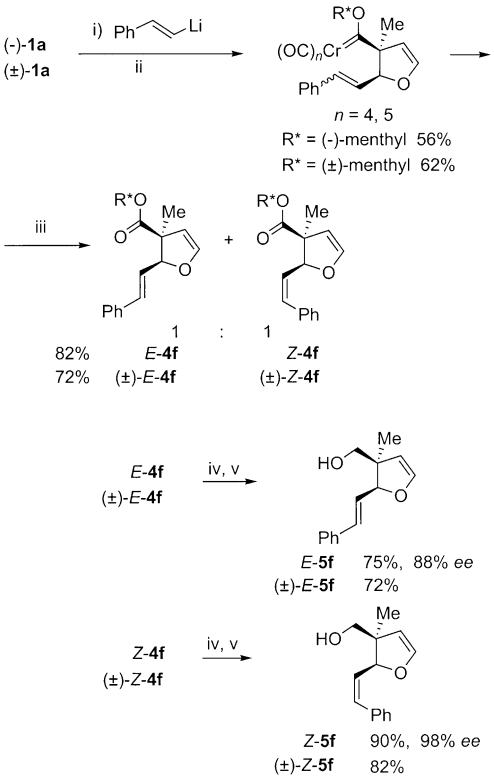
Removal of the metal fragment and chiral auxiliary group: The metal moiety of complexes **2** and **3** was eliminated by oxidation of the metal–carbene functional group which led to the corresponding carboxylic ester **4** (Scheme 2 and Table 1). In the case of the chromium derivatives, the oxidation was carried out by simply exposing a hexane solution of either the appropriate tetracarbonylcarbene complex **3** or a mixture of the corresponding penta- and tetracarbonylcarbene complexes **2** and **3** to the air in the presence of light. Oxidation of tungsten carbene complex **2ab**, which was a much slower reaction, was best performed with pyridine *N*-oxide in THF as solvent. Compounds **4** were each isolated as a mixture of two diastereoisomers in a ratio analogous to that observed at the level of the starting carbene complex **2** and **3** (Table 1, entries 1–9). The two diastereoisomers of



Scheme 3. Organolithium additions to methoxycarbene complex **7**. i) R-Li, Et_2O, −80 °C; ii) MeOTf, −80 °C→RT.



Scheme 4. Reduction of compounds **4e** and minor-**4e**. i) $LiAlH_4$, THF, 0 °C→RT; ii) MeOH/H_2O, NaCl.



Scheme 5. Reactions with (*E*)-2-phenylethenyllithium. i) reagent, Et_2O, −80 °C; ii) MeOTf, −80 °C→RT; iii) air, *hν*, hexane, RT; iv) $LiAlH_4$, THF, 0 °C→RT; v) MeOH/H_2O, NaCl.

carboxylic ester **4e** (R = Ph) were easily separated by silica gel column chromatography. An X-ray crystallographic study of a single crystal of the minor isomer (minor-**4e**) confirmed its structure and the absolute configuration previously assigned to the newly formed stereogenic carbons.[34]

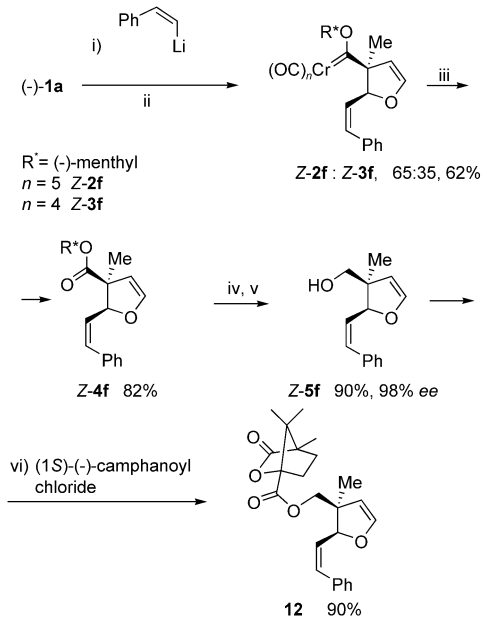
The chiral auxiliary group was successfully removed by lithium aluminum hydride reduction of esters **4** (the mixture of diastereoisomers summarized in Table 1 was used as starting material). After hydrolysis the corresponding primary alcohol **5** was isolated as a single diastereoisomer (Scheme 2 and Table 1). The structure and relative stereochemistry of products **5** was confirmed by one- and two-dimensional NMR experiments carried out with alcohols **5b** and **5e**.[33] The enantiomeric purity of trisubstituted dihydrofurans **5** was checked in the case of compounds **5d** (R = Bu, 30 % *ee*) and **5e** (R = Ph, 57 % *ee*) by HPLC analysis on a chiral support and in the case of compound **5a** (R = *t*Bu, 78 % *ee*), which could not be resolved in the chiral HPLC columns used, by ^{1}H NMR analyses of Mosher esters **6** and (±)-**6** prepared by reaction of **5a** with (*R*)-α-methoxy-α-trifluoromethylphenylacetyl chloride [(*R*)-MTPA-Cl] according to Mosher's protocol (Scheme 2).[35]

Parallel reductions of the previously separated diastereoisomeric esters **4e** and minor-**4e** afforded enantiomerically pure alcohols (+)-**5e** and (−)-**5e**, respectively, as shown in Scheme 4. The *ee* values of products (+)-**5e** and (−)-**5e** were similarly determined by chiral-phase HPLC analysis.

Reactions with alkenyllithium compounds: The sequential reaction of chromium–carbene complex (−)-**1a** with (*E*)-2-phenylethenyllithium[36] and methyl triflate under reaction conditions analogous to those mentioned above yielded a complex mixture of at least four major compounds that was directly submitted to air–light oxidation (Scheme 5). After purification a 1:1 mixture of carboxylic esters (*E*)-**4f** (with the expected *trans* exocyclic C=C double bond) and (*Z*)-**4f** (with the unexpected *cis* exocyclic C=C double bond) was obtained. These *E*/*Z* diastereoisomers, each one of which had a single set of signals in the ^{1}H and ^{13}C NMR spectra, were separated by column chromatography. Independent $LiAlH_4$ reduction of (*E*)-**4f** and (*Z*)-**4f** furnished alcohols (*E*)-**5f** and (*Z*)-**5f** with high and very high enantiomeric purity, respectively. The same sequence of reactions was carried out starting with racemic carbene complex (±)-**1a**. The enantiomeric ratio of products (*E*)-**5f** and (*Z*)-**5f** was likewise determined by chiral-phase HPLC analysis. The structure and relative configuration of diastereomeric alcohols (*E*)-**5f** and (*Z*)-**5f** were ascertained on the basis of the NMR data.[33] The absolute configuration assigned to these compounds has been assumed by analogy.

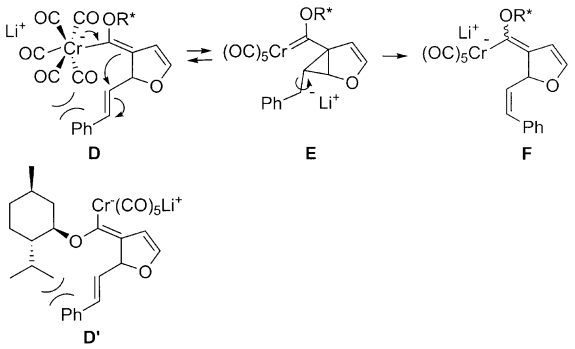
In contrast, the reaction of the carbene complex (−)-**1a** with (*Z*)-2-phenylethenyllithium[37] followed by quenching with methyl triflate afforded exclusively the *Z* diastereoisomer isolated as a 65:35 mixture of penta- and tetracarbonylcarbene complexes (*Z*)-**2f** and (*Z*)-**3f**, which after oxi-

dative cleavage of the metal moiety provided carboxylic ester (*Z*)-**4f** as a single diastereoisomer (Scheme 6). Reduction of (*Z*)-**4f**, as previously described, furnished alcohol



Scheme 6. Reaction with (*Z*)-2-phenylethenyllithium. i) reagent, Et_2O, −80 °C; ii) MeOTf, −80 °C→RT; iii) air, *hv*, hexane, RT; iv) $LiAlH_4$, THF, 0 °C→RT; v) $MeOH/H_2O$, NaCl; vi) reagent, Et_3N, DMAP, CH_2Cl_2, 0 °C→RT.

(*Z*)-**5f** practically as a single enantiomer. In order to ascertain the absolute configuration of the stereogenic centers formed in these alkenyllithium addition reactions, primary alcohol (*Z*)-**5f** was transformed into the camphanate derivative **12** by reaction with (1*S*)-(−)-camphanoyl chloride. A single-crystal X-ray analysis of **12** confirmed the relative and absolute configuration as outlined in Schemes 5 and 6.[38] The unexpected *trans*→*cis* C=C double bond isomerization found in the experiments with (*E*)-2-phenylethenyllithium but not in the reactions with the corresponding *Z* isomer could be promoted by a release of the steric congestion, which will be higher in intermediate **D**/**D**′ than in intermediate **F** as a result of the Ph group orientation towards either the "wall" of CO moieties (**D**) or the bulky alkoxy group (**D**′) (Scheme 7).[39,40] Conversion of *E* anionic intermediate



Scheme 7. Proposed mechanism for the C=C bond isomerization.

D/**D**′ to *Z* anionic derivative **F** could take place through the benzylic cyclopropylmethyl anion intermediate **E**. However, so far, we do not have any evidence to support this hypothesis.

Conclusion

This tandem organolithium addition–methyl triflate alkylation represents an efficient new strategy to successfully dearomatize the furan ring of Fischer (menthyloxy)(3-furyl)carbene complexes with complete regio- and stereocontrol. This methodology provides tetracarbonyl- and/or pentacarbonylcarbene complexes in which two carbon-based substituents have been added across the heteroarene 2-positioned C=C double bond. Furthermore, the reactions with alkenyllithium derivatives proceed with very high asymmetric induction. After successive elimination of the metal unit (air–light oxidation) and chiral auxiliary group ($LiAlH_4$ reduction), this methodology allows access to functionalized 2,3,3-trisubstituted 2,3-dihydrofurans as enantiomerically pure compounds.[41]

Chromium–carbene complexes are effective starting materials for this synthetic procedure. Lower chemical yields and a more sluggish oxidation process was observed in the experiments with the corresponding tungsten derivative. Presumably as a result of steric hindrance, the initially formed pentacarbonylcarbene complexes of chromium underwent a spontaneous intramolecular displacement of a *cis*-CO ligand by the electron-rich C=C double bond to give (η^2-alkene)tetracarbonylcarbene complexes containing an unprecedented chelated four-membered ring structure that was unambiguously characterized by X-ray analysis, and which revealed that the olefin function is bonded unsymmetrically to the metal. The unpredicted isomerization of an *E* carbon–carbon double bond to the corresponding *Z* isomer observed in this work may also be explained on the basis of unfavorable steric interactions.

Experimental Section

General: All reactions involving organometallic species were carried out under an atmosphere of dry N_2 using oven-dried glassware and syringes. All common reagents and solvents were obtained from commercial suppliers and used without further purification unless otherwise indicated. THF and Et_2O were distilled from sodium/benzophenone under N_2 immediately prior to use, MeOH and DMF from CaH_2, and CH_2Cl_2 from phosphorus pentoxide (P_4O_{10}). The solvents used in column chromatography (hexane and AcOEt) were used as received. TLC was performed on aluminum-backed plates coated with silica gel 60 with F_{254} indicator (Scharlau). Flash column chromatography was carried out on silica gel 60, 230–240 mesh. ^1H NMR (200, 300, 400 MHz) and ^{13}C NMR (75.5, 100 MHz) spectra were measured at room temperature on a Bruker AC-200, AC-300, and AMX-400 instruments, respectively, with tetramethylsilane ($\delta = 0.0$, ^1H NMR) or $CDCl_3$ ($\delta = 77.00$, ^{13}C NMR) as internal standard. Carbon multiplicities were assigned by DEPT techniques. Low-resolution electron impact (EI, 70 eV) or FAB+ mass spectra (LRMS) were obtained on an HP 5987A instrument, and the intensities are reported as a percentage relative to the base peak after the corresponding *m*/*z* value. High-resolution mass spectra (HRMS) were determined on a Finnigan MAT 95 spectrometer. Optical rotations were measured at

room temperature with a Perkin–Elmer 241 polarimeter using a Na lamp; sample concentrations are reported in g per 100 mL of solvent. Enantiomer compositions were determined by HPLC analysis with a chiral column in comparison with the corresponding racemic mixtures, and were carried out on a Waters LC-1 instrument with a UV/Vis photodiode array detector at a flow rate of 1.0 mL min^{-1} and employing a Chiralcel OD-H column for **5d** (hexane/EtOH 1000:1), **5e**, (+)-**5e**, (−)-**5e** (hexane/EtOH 2000:1), (*E*)-**5f** (hexane/EtOH 1500:1); and a Chiralcel OJ column for (*Z*)-**5f** (hexane/EtOH 750:1).

Materials: Commercially available solutions of BuLi (1 M in hexane), *t*BuLi (1.5 M in pentane), and $LiAlH_4$ (1 M in THF) were used as received. Phenyllithium,[42] neopentyllithium,[43] cyclopentyllithium,[44] (*Z*)-β-bromostyrene,[37] and pentacarbonyl-[1-(3-furyl)-1-methoxymethylidene]-chromium (**7**)[45] were prepared according to literature procedures. (*Z*)- or (*E*)-2-Phenylethenyllithium were preformed by addition at −80 °C of 2 equiv *t*BuLi to (*Z*)- or (*E*)-β-bromostyrene dissolved in Et_2O and the mixture was stirred for 2 h at −80 °C and then for 30 min at room temperature.

General procedure for the preparation of 3-furylcarbene complexes 1: BuLi (1.6 M in hexane, 15.9 mL, 25 mmol) was added dropwise to a solution of 3-bromofuran (2.30 mL, 25.5 mmol) in dry THF (33 mL) cooled to −80 °C. The mixture was stirred for 1 h at this temperature. The resulting solution was transferred by using a cannula to a suspension of the corresponding $M(CO)_6$ (24 mmol) in THF (75 mL) at 0 °C. The mixture was stirred for 20 min at 0 °C and then for 2 h at room temperature. The solvents were removed by using a rotary evaporator. The residue obtained was dissolved in deoxygenated H_2O (60 mL) and cooled in an ice bath. Me_4NBr (4.16 g, 27 mmol) was then added and the mixture was stirred for 20 min. The aqueous layer was extracted with CH_2Cl_2 (100 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to give pentacarbonyl-[1-(3-furyl)-1-[(tetramethylammonio)oxy]methylidene]chromium as a red solid (6.01 g, 67 %) or pentacarbonyl-[1-(3-furyl)-1-[(tetramethylammonio)oxy]methylidene]tungsten as a yellow solid (7.16 g, 59 %). Pivaloyl chloride (3.07 mL, 25 mmol) and DMF (2 drops) were added to a solution of the corresponding ammonium salt (16 mmol) in dry CH_2Cl_2 (100 mL) at −45 °C. After the mixture had been stirred at −45 °C for 1 h, a solution of the appropriate alcohol (+)- or (±)-menthol (3.90 g, 25 mmol) in dry CH_2Cl_2 (20 mL) was added dropwise at −45 °C. The resulting mixture was stirred overnight allowing it to warm slowly to room temperature without removing the cold bath. The reaction was quenched with silica gel, the solvents were removed under reduced pressure, and the residue was purified by column chromatography (silica gel, hexane) to give the corresponding carbene complex **1**. Yields are listed in Scheme 1.

Pentacarbonyl-[1-(3-furyl)-1-[(1*R*,2*S*,5*R*)-menthyloxy]methylidene]chromium [(−)-1a]: Red oil; R_f = 0.37 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (d, *J* = 7.0 Hz, 3H), 1.01 (d, *J* = 6.5 Hz, 3H), 1.02 (d, *J* = 6.1 Hz, 3H), 0.97–1.18 (m, 2H), 1.25–1.43 (m, 2H), 1.61–1.97 (m, 4H), 2.21–2.25 (m, 1H), 5.18 (m, 1H), 6.68 (s, 1H), 7.44 (s, 1H), 8.23 ppm (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 17.5, 21.9, 22.0, 24.4, 26.8, 31.0, 34.0, 42.7, 48.7, 91.9, 107.1, 142.4, 143.3, 149.6, 216.9 (4C), 222.9, 323.6 ppm; IR (neat): $\tilde{\nu}$ = 2960, 2872, 2058, 1930, 1552, 1510 cm^{-1}; LRMS (70 eV, EI): *m*/*z* (%): 426 (16) [*M*$^+$], 398 (42), 315 (26), 314 (100), 286 (48); HRMS (70 eV, EI): *m*/*z*: calcd for $C_{20}H_{23}CrO_7$ [*M*$^+$+H]: 427.0849; found: 427.0830.

Pentacarbonyl-[1-(3-furyl)-1-[(1*R*,2*S*,5*R*)-menthyloxy]methylidene]tungsten [(−)-1b]: Orange solid; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.89 (d, *J* = 6.8 Hz, 3H), 0.91–1.15 (m, 6H), 1.19–1.41 (m, 3H), 1.60–2.00 (m, 5H), 2.15–2.31 (m, 1H), 5.07 (td, *J* = 10.0, 4.4 Hz, 1H), 7.21 (dd, *J* = 1.9, 0.8 Hz, 1H), 7.45 (dd, *J* = 1.9, 1.3 Hz, 1H), 8.27 ppm (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 17.7, 21.8, 24.5, 27.0, 31.1, 34.1, 42.5, 48.5, 94.0, 107.8, 143.5, 144.3, 152.3, 197.7 (4C), 201.9, 296.1 ppm.

General procedure for the preparation of carbene complexes 2 and 3: A solution of the corresponding organolithium compound (1.80 mmol) was added dropwise to a solution of the appropriate 3-furylcarbene complex **1** (1.50 mmol) in Et_2O (20 mL) at −80 °C. The mixture was stirred at this temperature for 20 min. The initial red color turned dark red. Methyl triflate (1.95 mmol) was then added at −80 °C and the stirring was continued for 30 min at this temperature and 1 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, hexane) to give compounds **2** and **3**. Yields and ratios are listed in Table 1 and Schemes 5 and 6.

***cis*-[1-[η^2-(2*S*,3*S*)-2-*tert*-Butyl-3-methyl-2,3-dihydro-3-furyl]-1-[(1*R*,2*S*,5*R*)-menthyloxy]methylidene]tetracarbonylchromium (3a)**: Data on the 84:16 mixture of diastereoisomers: red oil; R_f = 0.30 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (s, 9H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.97 (d, *J* = 6.5 Hz, 3H), 0.98 (d, *J* = 7.0 Hz, 3H), 0.98–1.10 (m, 1H), 1.50 (s, 3H), 1.12–1.26 (m, 2H), 1.52–1.71 (m, 1H), 1.72–1.80 (m, 3H), 2.00–2.10 (m, 1H), 2.27–2.31 (m, 1H), 3.83 (s, 1H), 4.33 (d, *J* = 2.2 Hz, 1H), 4.90 (td, *J* = 10.7, 4.8 Hz, 1H), 7.42 ppm (d, *J* = 2.2 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 15.6, 18.8, 21.2, 22.1, 22.8, 25.5, 27.2, 31.3, 33.4, 33.9, 40.6, 47.8, 65.2, 68.1, 90.1, 101.4, 146.0, 220.4, 221.2, 228.8, 233.7, 352.1 ppm; LRMS (70 eV, EI): *m*/*z* (%): 470 (2) [*M*$^+$], 219 (24), 138 (40), 95 (68), 83 (59), 57 (100); HRMS (70 eV, EI): *m*/*z*: calcd for $C_{24}H_{34}CrO_6$ [*M*$^+$]: 470.1736; found: 470.1761. Resolvable resonances of minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.77 (d, *J* = 6.5 Hz, 3H), 3.88 (s, 1H), 4.26 (d, *J* = 2.2 Hz, 1H), 4.96–5.11 (m, 1H), 7.39 ppm (d, *J* = 2.2 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 15.3, 20.7, 31.6, 41.3, 47.3, 91.6, 101.7 ppm.

[1-[(2*S*,3*S*)-2-*tert*-Butyl-3-methyl-2,3-dihydro-3-furyl]-1-[(1*R*,2*S*,5*R*)-menthyloxy]methylidene]pentacarbonyltungsten (2ab): Data on the 86:14 mixture of diastereoisomers: orange oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83 (d, *J* = 6.9 Hz, 3H), 0.89–1.03 (m, 9H), 1.06 (s, 9H), 1.07–1.54 (m with s at 1.28, 5H), 1.65–2.46 (m, 4H), 3.96 (s, 1H), 5.30–5.37 (m, 1H), 5.41 (d, *J* = 3.1 Hz, 1H), 6.70 ppm (d, *J* = 3.1 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 16.1, 21.3, 21.7, 22.0, 23.2, 25.3, 27.4, 27.8 (3C), 31.7, 34.0, 40.8, 43.4, 48.5, 73.5, 98.5, 104.6, 115.6, 198.3 (4C), 202.3, 347.9 ppm.

Pentacarbonyl-[1-[(2*S*,3*S*)-3-methyl-2-phenyl-2,3-dihydro-3-furyl]-1-[(1*R*,2*S*,5*R*)-menthyloxy]methylidene]tungsten (2eb): Data on the 76:24 mixture of diastereoisomers: orange oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.69 (d, *J* = 7.0 Hz, 3H), 0.81 (d, *J* = 7.1 Hz, 3H), 0.83–1.25 (m, 6H), 1.27–1.48 (m, 2H), 1.51 (s, 3H), 1.55–1.79 (m, 4H), 4.62 (td, *J* = 10.9, 4.0 Hz, 1H), 5.15 (s, 1H), 6.15 (d, *J* = 2.6 Hz, 1H), 7.21–7.40 ppm (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 29.9, 30.3, 30.6, 33.5, 33.6, 39.2, 41.2, 76.3, 92.0, 95.6, 110.6, 111.7, 126.4 (2C), 127.7 (2C), 128.6, 139.0, 145.8, 197.6 (4C), 201.8, 337.3 ppm. Resolvable resonances of minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.61 (d, *J* = 7.1 Hz, 3H), 1.82 (s, 3H), 4.85 (td, *J* = 10.8, 4.0 Hz, 1H), 5.29 (s, 1H), 5.59 (d, *J* = 2.6 Hz, 1H), 6.51 ppm (d, *J* = 2.6 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 30.6, 47.7, 93.7, 96.2, 128.4, 146.1 ppm.

***cis*-Tetracarbonyl-[1-[η^2-(2*S*,3*S*)-2-cyclopentyl-3-methyl-2,3-dihydro-3-furyl]-1-[(1*R*,2*S*,5*R*)-menthyloxy]methylidene]chromium (3b)**: Data on a 65:35 mixture of **3b** and **2b**, respectively, each one as a likely 79:21 mixture of diastereoisomers: red oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84–1.10 (m, 13H), 1.17–1.29 (m, 3H), 1.43–1.79 (m, 11H), 1.96 (m, 2H), 2.18–2.41 (m, 1H), 3.77 (d, *J* = 10.8 Hz, 1H), 4.36 (d, *J* = 2.0 Hz, 1H), 4.97 (td, *J* = 10.7, 4.5 Hz, 1H), 7.26 ppm (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 18.4, 17.9, 21.4, 22.6, 23.4, 24.5, 25.9, 26.3, 28.8, 31.9, 32.1, 34.4, 41.0, 41.6, 47.9, 66.3, 66.8, 90.2, 98.2, 147.6, 220.2, 220.9, 229.7, 234.5, 351.4 ppm. Resolvable signals of the corresponding pentacarbonyl complex **2b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.18 (d, *J* = 5.4 Hz, 1H), 5.48 (d, *J* = 2.9 Hz, 1H), 6.43 ppm (d, *J* = 2.9 Hz, 1H). Resolvable signal of minor diastereoisomer of **2b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.48 ppm (apparent d, 1H).

***cis*-Tetracarbonyl-[1-[η^2-(2*S*,3*S*)-3-methyl-2-neopentyl-2,3-dihydro-3-furyl]-1-[(1*R*,2*S*,5*R*)-menthyloxy]methylidene]chromium (3c)**: Data on the 56:44 mixture of diastereoisomers: red oil; R_f = 0.29 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84 (d, *J* = 10.8 Hz, 6H), 0.90 (s, 18H), 0.93–1.17 (m, 12H), 1.18–1.35 (m, 8H), 1.68–1.84 (m, 16H), 1.90–2.19 (m, 4H), 4.06–4.11 (m, 2H), 4.41–4.43 (m, 2H), 4.92–5.03 (m, 2H), 7.30 ppm (br s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 15.0, 15.9, 16.3, 20.7, 22.1, 22.9, 23.4, 25.4, 25.8 (3C), 29.4, 29.8, 30.0, 31.4, 31.5, 33.9, 41.6, 42.0, 42.5, 46.6, 47.4, 64.5, 64.7, 66.6, 67.1, 80.1, 90.2, 90.4, 91.5, 91.6, 219.8, 220.6, 229.2, 233.9, 234.1, 350.8, 352.7 ppm; LRMS (70 eV, EI): *m*/*z* (%): 484 (3) [*M*$^+$], 233 (72), 206 (56), 153 (100), 83 (66); HRMS (70 eV, EI): *m*/*z*: calcd for $C_{25}H_{36}CrO_6$ [*M*$^+$]: 484.1938; found: 484.1917.

***cis*-[1-[η^2-(2*S*,3*S*)-2-Butyl-3-methyl-2,3-dihydro-3-furyl]-1-[(1*R*,2*S*,5*R*)-menthyloxy]methylidene]tetracarbonylchromium (3d)**: Data on the 70:30 mixture of diastereoisomers: red oil; R_f = 0.56 (hexane/AcOEt 9:1);

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85–1.03 (m, 16H), 1.40 (s, 3H), 1.21–1.66 (m, 6H), 1.55–2.05 (m, 3H), 2.15–2.48 (m, 2H), 3.96 (m, 1H), 4.42 (d, J = 2.0 Hz, 1H), 4.91–4.98 (m, 1H), 7.26 ppm (brs, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.8, 15.8, 16.6, 20.9, 22.3, 22.5, 22.9, 25.8, 26.7, 29.4, 31.5, 33.9, 41.4, 47.4, 65.2, 66.1, 89.9, 92.9, 147.4, 219.8, 220.6, 229.8, 234.08, 351.0 ppm; LRMS (70 eV, EI): m/z (%): 470 (4) [M^+], 414 (3), 219 (60), 192 (57), 83 (100), 52 (91). Resolvable resonances of minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.39 ppm (d, J = 2.0, Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.7, 15.0, 16.5, 20.8, 22.1, 22.4, 22.5, 25.5, 28.6, 29.2, 31.4, 33.9, 41.2, 46.9, 65.0, 66.5, 91.5, 93.4, 146.7, 219.7, 220.6, 229.3, 233.9, 352.8 ppm. Resolvable signals of the corresponding pentacarbonyl complex **2d**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.08–4.17 (m, 1H), 5.20–5.26 (m, 1H), 5.74 (d, J = 2.9 Hz, 1H), 6.31–6.32 ppm (m, 1H). Resolvable resonance of minor diastereoisomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.71 ppm (d, J = 2.8 Hz, 1H).

Pentacarbonyl-[1-[(2*S*,3*S*)-3-methyl-2-phenyl-2,3-dihydro-3-furyl]-1-[(1*R*,2*S*,5*R*)-menthyloxy]methylidene]chromium and *cis*-tetracarbonyl-[1-[η^2-(2*S*,3*S*)-3-methyl-2-phenyl-2,3-dihydro-3-furyl]-1-[(1*R*,2*S*,5*R*)-menthyloxy]methylidene]chromium (2e:3e 47:53): Data on a 78:22 mixture of diastereoisomers: red oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.62 (d, J = 6.8 Hz, 6H), 0.66 (d, J = 11.7 Hz, 6H), 0.70–1.30 (m, 36H), 1.49–1.73 (m with 3s at 1.28, 1.30, and 1.49, 30H), 1.75–1.91 (m with s at 1.90, 6H), 4.59–4.71 (m, 2H), 4.70 (d, J = 2.3 Hz, 2H), 4.78–4.92 (m, 2H), 5.05 (s; 1H of **2e**), 5.12 (s; 1H of **3e**), 5.17 (s; 1H of **3e**), 5.27 (s; 1H of **2e**), 5.61 (d, J = 2.9 Hz, 2H), 6.20 (d, J = 3.1 Hz; 2H of **3e**), 6.54 (d, J = 2.8 Hz, 2H), 7.18–7.24 (m, 20H), 7.52 ppm (d, J = 2.8 Hz; 1H of **3e**); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 18.3, 18.4, 18.8, 19.1, 23.3, 24.0, 24.2, 24.3, 24.4, 24.5, 24.6, 25.1, 25.3, 25.6, 28.1, 28.2, 32.8, 33.1, 33.5, 36.0, 36.1, 41.8, 42.6, 49.2, 50.3, 68.3, 70.8, 79.0, 79.4, 79.8, 92.0, 94.7, 95.1, 95.2, 96.5, 97.0, 112.6, 113.0, 128.0, 128.4, 130.0, 130.4, 130.6, 130.7, 130.9, 131.1, 131.2, 136.5, 142.6, 147.9, 148.2, 149.2, 219.1, 219.2, 222.7, 224.8, 225.0, 230.8, 236.5, 350.7, 363.1 ppm. Resolvable resonances of minor diastereoisomers: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.18 (s; 1H of **3e**), 5.27 (s; 1H of **2e**), 5.60 ppm (d, J = 2.9 Hz; 1H of **2e**).

Pentacarbonyl-[1-[(2*S*,3*S*)-3-methyl-2-[(*Z*)-2-phenylethenyl]-2,3-dihydro-3-furyl]-1-[(1*R*,2*S*,5*R*)-menthyloxy]methylidene]chromium [(*Z*)-2f) and *cis*-tetracarbonyl-[1-[η^2-(2*S*,3*S*)-3-methyl-2-[(*Z*)-2-phenylethenyl]-2,3-dihydro-3-furyl]-1-[(1*R*,2*S*,5*R*)-menthyloxy]methylidene]chromium [(*Z*)-3f)]: A 65:35 mixture, respectively: red oil. Data for (*Z*)-**2f**: ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 16.8, 22.5, 26.0, 26.7, 28.7, 31.4, 34.5, 42.7, 48.6, 66.0, 67.7, 86.2, 95.0, 110.6, 126.8, 127.6 (2C), 123.1 (2C), 134.0, 136.2, 145.5, 217.0 (4C), 221.3, 361.6 ppm. Data for (*Z*)-**3f**: ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 16.3, 16.5, 21.4, 22.3, 23.4, 26.3, 32.0, 41.9, 47.7, 88.0, 90.6, 129.0, 133.3, 135.7, 146.7, 220.5, 223.2, 229.5, 234.5, 350.4 ppm. The ^{1}H NMR spectrum had poor resolution.

General procedure for the preparation of esters 4: Either the corresponding tetracarbonylcarbene complex **3** or a mixture of both penta- and tetracarbonylcarbene complexes **2** and **3** (1.0 mmol) was dissolved in hexane (150 mL) and the resulting solution was exposed to air and sunlight (in its absence a 100-W tungsten lamp was used) until the initial red color of the starting carbene complex disappeared. The resulting colorless solution was filtered through a plug of Celite. Evaporation of the solvent and column chromatography (silica gel, hexane/ethyl acetate 97:3) afforded pure compounds **4**. Yields and ratios of isomers are given in Table 1 and Schemes 5 and 6.

(1*R*,2*S*,5*R*)-Menthyl (2*S*,3*S*)-2-*tert*-butyl-3-methyl-2,3-dihydrofuran-3-carboxylate (4a): Data on the 84:16 mixture of diastereoisomers: colorless oil; R_f = 0.55 (hexane/AcOEt 9:1); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.71 (d, J = 6.9 Hz, 3H), 0.90 (d, J = 7.0 Hz, 3H), 0.91 (d, J = 7.4 Hz, 3H), 0.95–0.98 (m, 2H), 1.05 (s, 3H), 1.16–1.45 (m, 3H), 1.46 (s, 3H), 1.63–1.71 (m, 2H), 1.89–1.97 (m, 1H), 2.10–2.16 (m, 1H), 3.87 (s, 1H), 4.61 (td, J = 10.8, 4.4 Hz, 1H), 4.87 (d, J = 2.8 Hz, 1H), 6.48 ppm (d, J = 2,8 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.7, 21.0, 22.0, 22.8, 25.5, 26.4 (3C), 27.0, 31.3, 34.1, 34.2, 40.4, 47.2, 54.3, 75.4, 99.2, 109.0, 145.7, 174.4 ppm; LRMS (70 eV, EI): m/z (%): 322 (5) [M^+], 169 (14), 139 (100), 83 (90), 57 (95).

(1*R*,2*S*,5*R*)-Menthyl (2*S*,3*S*)-2-cyclopentyl-3-methyl-2,3-dihydrofuran-3-carboxylate (4b): Data on the 79:21 mixture of diastereoisomers: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.72 (d, J = 7.1 Hz, 3H), 0.79–1.09 (m, 9H), 1.25–1.58 (m, 8H), 1.59–2.03 (m, 9H), 2.21–2.27 (m, 1H), 3.98 (d, J = 8.8 Hz, 1H), 4.65 (td, J = 10.8, 4.3 Hz, 1H), 4.90 (d, J = 2.9 Hz, 1H), 6.42 ppm (d, J = 2.9 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 16.2, 21.4, 22.5, 23.4, 25.3, 25.7, 26.2, 29.6, 30.5, 31.8, 34.6, 41.0, 41.7, 47.3, 56.0, 75.5, 95.8, 108.2, 147.0, 174.2 ppm; LRMS (70 eV, EI): m/z (%): 334 (2) [M^+], 197 (100), 151 (46), 116 (45), 83 (69), 69 (41); HRMS (70 eV, EI): m/z: calcd for $C_{21}H_{34}O_3$ [M^+]: 334.2508; found: 334.2500. Resolvable resonances of minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.00 (d, J = 8.8 Hz, 1H), 4.87 ppm (d, J = 2.9 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 16.3, 29.2, 30.8, 41.6, 108.0 ppm.

(1*R*,2*S*,5*R*)-Menthyl (2*S*,3*S*)-3-methyl-2-neopentyl-2,3-dihydrofuran-3-carboxylate (4c): Data on the 60:40 mixture of diastereoisomers: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.73 (d, J = 6.8 Hz, 3H), 0.88–1.10 (m, 7H), 0.91 (s, 8H), 1.38 (s, 3H), 1.43–1.69 (m, 9H), 1.85–2.01 (m, 2H), 4.15–4.19 (m, 1H), 4.59–4.68 (m, 1H), 4.92 (d, J = 2.9 Hz, 1H), 6.38–6.41 ppm (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 15.8, 20.8, 21.9, 22.9, 23.9, 25.7, 29.7 (3C), 30.1, 31.3, 34.1, 40.7, 43.5, 46.7, 56.3, 74.9, 88.3, 106.6, 146.9, 173.6 ppm; LRMS (70 eV, EI): m/z (%): 336 (2) [M^+], 153 (100), 97 (42), 57 (20); HRMS (70 eV, EI): m/z: calcd for $C_{21}H_{36}O_3$ [M^+]: 336.2668; found: 336.2664. Resolvable resonances of minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.31 (s, 3H), 4.89 ppm (d, J = 2.9 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 15.9, 20.8, 23.0, 25.9, 29.9, 31.3, 40.7, 43.8, 46.8, 56.4, 88.4, 106.7, 147.1, 173.6 ppm.

(1*R*,2*S*,5*R*)-Menthyl (2*S*,3*S*)-2-butyl-3-methyl-2,3-dihydrofuran-3-carboxylate (4d): Data on the 70:30 mixture of diastereoisomers: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.73 (d, J = 6.8 Hz, 3H), 0.84–0.99 (m, 9H), 1.38 (s, 3H), 1.30–1.58 (m, 1H), 1.64–1.89 (m, 2H), 1.91–2.03 (m, 2H), 4.09–4.14 (m, 1H), 4.61 (td, J = 11.0, 4.3 Hz, 1H), 4.97 (d, J = 2.9 Hz, 1H), 6.36 ppm (d, J = 2.6 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.2, 16.1, 21.1, 22.3, 22.9, 23.2, 25.3, 26.1, 29.0, 30.9, 31.7, 34.5, 41.1, 47.1, 56.3, 75.2, 90.9, 107.2, 146.2, 173.2, 173.8 ppm; LRMS (70 eV, EI): m/z (%): 322 (1) [M^+], 139 (100), 95 (12), 83 (13), 55 (13). Resolvable resonances of minor isomer: ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 16.3, 31.2, 32.9, 47.2, 56.0, 75.3, 91.2, 146.6 ppm.

(1*R*,2*S*,5*R*)-Menthyl (2*S*,3*S*)-3-methyl-2-phenyl-2,3-dihydrofuran-3-carboxylate (4e): White solid; R_f = 0.48 (hexane/AcOEt 9:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.60 (d, J = 6.8 Hz, 3H), 0.70 (d, J = 6.6 Hz, 3H), 0.81 (d, J = 6.8 Hz, 3H), 0.80–0.94 (m, 3H), 1.10–1.21 (m, 2H), 1.52–1.66 (m, 4H), 1.59 (s, 3H), 4.27 (td, J = 10.8, 4.3 Hz, 1H), 5.14 (d, J = 2.8 Hz, 1H), 5.18 (s, 1H), 6.60 (d, J = 2,8 Hz, 1H), 7.34–7.24 ppm (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 16.3, 21.4, 22.2, 23.3, 26.2, 26.9, 31.4, 34.4, 39.6, 47.1, 59.2, 74.9, 92.4, 107.4, 127.1 (2C), 128.6 (2C), 128.7, 138.4, 147.0, 172.8 ppm.

(1*R*,2*S*,5*R*)-Menthyl (2*R*,3*R*)-3-methyl-2-phenyl-2,3-dihydrofuran-3-carboxylate (minor-4e): White solid; R_f = 0.49 (hexane/AcOEt 9:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.54 (d, J = 6.8 Hz, 3H), 0.73 (d, J = 6.6 Hz, 3H), 0.77 (d, J = 7.1 Hz, 3H), 0.78–0.89 (m, 3H), 1.05–1.35 (m, 3H), 1.22–1.61 (m, 3H), 1.62 (s, 3H), 4.27 (td, J = 10.8, 4.3 Hz, 1H), 5.07 (d, J = 2.8 Hz, 1H), 5.28 (s, 1H), 6.62 (d, J = 2,8 Hz, 1H), 7.26–7.35 ppm (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 16.4, 21.3, 22.3, 23.5, 26.2, 27.6, 31.5, 34.5, 39.5, 46.9, 58.8, 75.2, 92.2, 107.4, 126.6 (2C), 128.4 (2C), 128.5, 138.4, 147.0, 172.9 ppm. Suitable single crystals for X-ray structure analysis were obtained by cooling (in a freezer) a solution of minor-**4e** in dry pentane.

(1*R*,2*S*,5*R*)-Menthyl (2*S*,3*S*)-3-methyl-2-[(*E*)-2-phenylethenyl]-2,3-dihydrofuran-3-carboxylate [(*E*)-4f]: Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.57 (d, J = 6.6 Hz, 3H), 0.66 (d, J = 6.9 Hz, 3H), 0.84 (d, J = 7.1 Hz, 3H), 0.61–0.98 (m, 5H), 1.28–1.49 (m, 3H), 1.55 (s, 3H), 1.50–1.72 (m, 2H), 1.74–1.86 (m, 1H), 4.59 (td, J = 11.0, 4.3 Hz, 1H), 4.77 (d, J = 8.0 Hz, 1H), 6.63 (d, J = 15.9 Hz, 1H), 7.21–7.28 ppm (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 16.2, 21.2, 22.0, 23.3, 25.4, 26.3, 31.5, 34.4, 41.3, 47.1, 57.8, 75.2, 91.1, 107.3, 124.4, 127.1 (2C), 128.3, 128.8 (2C), 133.7, 136.4, 146.3, 173.1 ppm.

(1*R*,2*S*,5*R*)-Menthyl (2*S*,3*S*)-3-methyl-2-[(*Z*)-2-phenylethenyl]-2,3-dihydrofuran-3-carboxylate [(*Z*)-4f]: Colorless oil; R_f = 0.37 (hexane/AcOEt 9:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.79 (d, J = 6.8 Hz, 3H), 0.86–1.02 (m, 9H), 1.43–1.45 (m, 2H), 1.47 (s, 3H), 1.68 (m, 2H), 2.03 (m, 2H), 4.69 (td, J = 10.8, 4.3 Hz, 1H), 5.10 (d, J = 10.3 Hz, 1H), 5.13 (d, J = 2,9 Hz, 1H), 5.75 (dd, J = 11.1, 10.5 Hz, 1H), 6.37 (d, J = 2.6 Hz, 1H), 6.71 (d, J = 11.7 Hz, 1H), 7.28–7.39 ppm (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 15.7, 20.8, 21.9, 22.9, 25.2, 25.9, 31.2, 34.0, 40.4, 46.8, 57.0,

75.2, 84.9, 106.7, 126.5, 127.3, 128.1 (2C), 128.8 (2C), 133.6, 138.9, 145.2, 172.9 ppm.

Formation of 4a by oxidation of tungsten carbene complex 2ab: Pyridine *N*-oxide (0.40 g, 4.167 mmol) was added to a solution of carbene complex **2ab** (0.30 g, 0.476 mmol) in THF (30 mL) and the mixture was stirred at room temperature for 8 d. THF was then removed under reduced pressure, and the residue was taken up in hexane and filtered through Celite. Solvent removal under vacuum gave the crude product which was purified by column chromatography (silica gel deactivated with 10% Et_3N in hexane and using a mixture of hexane/AcOEt 95:5 as eluant) to yield **4a** (0.06 g, 0.181 mmol, 39%) as a colorless oil.

General procedure for the preparation of alcohols 5: The corresponding carboxylic ester **4** (0.6 mmol) was dissolved in THF (6 mL) and $LiAlH_4$ (1M in THF, 0.66 mmol, 0.66 mL) was added dropwise at 0°C. After 30 min the ice bath was removed and the stirring was continued for 6 h at room temperature. The resulting mixture was successively quenched at 0°C with MeOH (dropwise until the vigorous gas evolution stopped) and a saturated aqueous NaCl solution (5 mL). The aqueous layer was extracted with AcOEt. The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/ethyl acetate 9:1) to give compounds **5**. Yields are listed in Table 1 and Schemes 5 and 6.

(2*S*,3*R*)-(2-*tert*-Butyl-3-methyl-2,3-dihydro-3-furyl)methanol (5a): Colorless oil; $R_f=0.14$ (hexane/AcOEt 9:1); $[\alpha]_D^{20}=+29.4$ ($c=0.27$ in CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=1.10$ (s, 9H), 1.27 (s, 3H), 1.46–1.51 (m, 1H), 3.46–3.53 (m, 1H), 3.64–3.73 (m, 1H), 3.77 (s, 1H), 4.81 (d, $J=2.8$ Hz, 1H), 6.49 ppm (d, $J=2.8$ Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=24.5$, 27.9 (3C), 34.4, 50.8, 66.3, 98.5, 109.6, 146.3 ppm; LRMS (70 eV, EI): *m*/*z* (%): 170 (5) [M^+], 140 (8), 139 (82), 95 (14), 83 (100); HRMS (70 eV, EI): *m*/*z*: calcd for $C_{10}H_{18}O_2$ [M^+]: 170.1307; found: 170.1307.

(2*S*,3*R*)-(2-Cyclopentyl-3-methyl-2,3-dihydro-3-furyl)methanol (5b): Colorless oil; $R_f=0.13$ (hexane/AcOEt 9:1); $[\alpha]_D^{20}=+22.2$ ($c=0.30$ in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.13$ (s, 3H), 1.16–1.26 (m, 1H), 1.33–1.54 (m, 1H), 1.56–1.72 (m, 5H), 1.76–1.83 (m, 1H), 1.90–1.96 (m, 1H), 2.41 (m, 1H), 3.30 (d, $J=11.0$ Hz, 1H), 3.61 (m, 1H), 3.80 (d, $J=10.4$ Hz, 1H), 4.73 (d, $J=2.9$ Hz, 1H), 6.46 ppm (d, $J=2.9$ Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=23.4$, 25.1, 26.0, 29.4, 32.2, 39.8, 49.6, 66.6, 95.9, 107.9, 146.9 ppm; LRMS (70 eV, EI): *m*/*z* (%): 182 (19) [M^+], 151 (80), 83 (100), 69 (56); HRMS (70 eV, EI): *m*/*z*: calcd for $C_{11}H_{18}O_2$ [M^+]: 182.1307; found: 182.1310.

(2*S*,3*R*)-(3-Methyl-2-neopentyl-2,3-dihydro-3-furyl)methanol (5c): Colorless oil; $R_f=0.17$ (hexane/AcOEt 9:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.97$ (s, 9H), 1.03 (s, 3H), 1.46 (d, $J=14.8$ Hz, 1H), 1.57 (brs, 1H), 1.84 (dd, $J=14.6$, 10.5 Hz, 1H), 3.23 (d, $J=11.1$ Hz, 1H), 3.43–3.49 (m, 1H), 4.07 (d, $J=10.5$ Hz, 1H), 4.76 (d, $J=2.8$ Hz, 1H), 6.51 ppm (d, $J=2.8$ Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=22.0$, 30.2 (3C), 30.5, 41.6, 50.0, 66.3, 88.1, 106.6, 147.5 ppm; LRMS (70 eV, EI): *m*/*z* (%): 185 (35) [M^++H], 153 (100), 97 (89), 85 (29); HRMS (70 eV, EI): *m*/*z*: calcd for $C_{11}H_{20}O_2$ [M^+]: 184.1463; found: 184.1461.

(2*S*,3*R*)-(2-Butyl-3-methyl-2,3-dihydro-3-furyl)methanol (5d): Colorless oil; $R_f=0.16$ (hexane/AcOEt 9:1); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=0.94$ (t, $J=7.4$ Hz, 3H), 1.26–1.49 (m, 4H), 1.10 (s, 3H), 1.52–186 (m, 3H), 3.32 (dd, $J=11.0$, 2.8 Hz, 1H), 3.51 (dd, $J=11.0$, 8.5 Hz, 1H), 4.00 (dd, $J=10.2$, 2.6 Hz, 1H), 6.50 ppm (d, $J=2.6$ Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=14.3$, 22.8, 23.0, 28.5, 29.8, 49.3, 66.2, 91.1, 107.3, 146.8 ppm; LRMS (70 eV, EI): *m*/*z* (%): 171 (100) [M^++H], 153 (15), 139 (20), 65 (20); HRMS (70 eV, EI): *m*/*z*: calcd for $C_{10}H_{18}O_2$ [M^+]: 170.1307; found: 170.1301.

(2*S*,3*R*)-(3-Methyl-2-phenyl-2,3-dihydro-3-furyl)methanol [(+)-5e]: Colorless oil; $R_f=0.13$ (hexane/AcOEt 9:1); $[\alpha]_D^{20}=+103.0$ ($c=0.36$ in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.83$ (dd, $J=8.6$, 4.8 Hz, 1H), 1.34 (s, 3H), 3.05 (dd, $J=11.5$, 8.5 Hz, 1H), 3.16 (dd, $J=11.5$, 4.8 Hz, 1H), 4.87 (d, $J=2.8$ Hz, 1H), 5.14 (s, 1H), 6.59 (d, $J=2.8$ Hz, 1H), 7.25–7.42 ppm (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=23.5$, 51.7, 66.8, 91.6, 108.0, 126.3 (2C), 128.4, 128.8 (2C), 137.5, 146.5 ppm; LRMS (70 eV, EI): *m*/*z* (%): 190 (23) [M^+], 159 (100), 144 (41), 131 (75), 91 (62); HRMS (70 eV, EI): *m*/*z*: calcd for $C_{12}H_{14}O_2$ [M^+]: 190.0991; found: 190.0993.

(2*S*,3*R*)-[3-Methyl-2-[(*E*)-2-phenylethenyl]-2,3-dihydro-3-furyl]methanol [(*E*)-5f]: Colorless oil; $[\alpha]_D^{20}=-31.5$ ($c=0.12$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.63$ (s, 3H), 1.71 (brs, 1H), 3.33–3.48 (m, 2H), 4.64 (d, $J=8.0$ Hz, 1H), 4.85 (d, $J=2.9$ Hz, 1H), 6.53 (dd, $J=15.9$, 8.0 Hz, 1H), 6.54 (d, $J=2.3$ Hz, 1H), 6.70 (d, $J=15.9$ Hz, 1H), 7.25–7.45 ppm (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=22.7$, 51.5, 66.8, 91.8, 107.1, 124.8, 127.1 (2C), 128.4, 129.0 (2C), 134.3, 136.6, 147.0 ppm; LRMS (70 eV, EI): *m*/*z* (%): 216 (23) [M^+], 187 (33), 157 (64), 133 (100), 115 (71), 91 (93), 83 (43); HRMS (70 eV, EI): *m*/*z*: calcd for $C_{14}H_{16}O_2$ [M^+]: 216.1152; found: 216.1152.

(2*S*,3*R*)-[3-Methyl-2-[(*Z*)-2-phenylethenyl]-2,3-dihydro-3-furyl]methanol [(*Z*)-5f]: Colorless oil; $[\alpha]_D^{20}=-32.1$ ($c=0.70$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.07$ (s, 3H), 1.70 (brs, 1H), 3.41–3.58 (m, 2H), 4.77 (d, $J=2.9$ Hz, 1H), 4.99 (d, $J=10.3$ Hz, 1H), 6.08 (dd, $J=11.7$, 10.3 Hz, 1H), 6.48 (d, $J=2.6$ Hz, 1H), 6.88 (d, $J=11.7$ Hz, 1H), 7.26–7.35 ppm (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=23.0$, 51.3, 66.8, 85.6, 107.0, 126.6, 127.8, 128.6 (2C), 129.0 (2C), 135.8, 136.4, 146.8 ppm; LRMS (70 eV, EI): *m*/*z* (%): 216 (38) [M^+], 187 (50), 169 (53), 157 (98), 129 (100), 115 (92), 91(93), 83 (79); HRMS (70 eV, EI): *m*/*z*: calcd for $C_{14}H_{16}O_2$ [M^+]: 216.1152; found: 216.1150.

(2*S*,3*R*)-[2-*tert*-Butyl-3-methyl-2,3-dihydro-3-furyl]methyl (*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropionate (6): (*R*)-α-Methoxy-α-(trifluoromethyl)phenylacetyl chloride (*R*-MTPA-Cl, 106 mg, 0.42 mmol), Et_3N (0.072 mL, 0.52 mmol), and 4-dimethylaminopyridine (DMAP, 122 mg, 1 mmol) were added to a solution of **5a** (60.0 mg, 0.35 mmol) in CH_2Cl_2 (3 mL). The mixture was stirred for 12 h at room temperature. Water was then added (5 mL) and the reaction mixture was extracted with Et_2O (3×10 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude compound was purified by column chromatography (silica gel, hexane/AcOEt 9:1) to give compound **6** (133.2 mg, 93%) as a 86:14 mixture of diastereoisomers. Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.01$ (s, 9H), 1.25 (s, 3H), 3.59 (s, 3H), 3.75 (s, 1H), 4.21 (d, $J=11.5$ Hz, 1H), 4.38 (d, $J=10.5$ Hz, 1H), 4.79 (d, $J=2.6$ Hz, 1H), 6.38 (d, $J=2.6$ Hz, 1H), 7.38–7.45 (m, 3H), 7.56–7.51 ppm (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=24.3$, 27.7 (3C), 31.9, 48.8, 55.9, 70.4, 98.2, 109.7, 121.9, 125.7, 127.7 (2C), 128.8 (2C), 130.0, 132.6, 146.1, 167.1 ppm; LRMS (70 eV, EI): *m*/*z* (%): 386 (5) [M^+], 189 (54), 140 (11), 139 (100), 105 (15), 95 (35); HRMS (70 eV, EI): *m*/*z*: calcd for $C_{20}H_{25}F_3O_4$ [M^+]: 386.1705; found: 386.1696. Resolvable resonances of minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.06$ (s, 9H), 3.60 (s, 3H), 4.74 ppm (d, $J=2.8$ Hz, 1H).

The reactions of carbine-complex **7** with *t*BuLi, BuLi, or (*E*)-2-phenylethenyllithium and MeOTf to give compounds **8a**, **8b** and **9b**, and **13**, respectively, were carried out according to the general procedure described for the preparation of carbene complexes **2** and **3**. Yields are reported in Scheme 3 and ref. [39].

(2*S,3*S**)-[1-(2-*tert*-Butyl-3-methyl-2,3-dihydro-3-furyl)-1-(methoxy)methylidene]pentacarbonylchromium (8a)**: Red oil; $R_f=0.50$ (hexane/AcOEt 9:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.95$ (s, 9H), 1.28 (s, 3H), 3.90 (s, 1H), 4.91 (s, 3H), 5.59 (d, $J=2.9$ Hz, 1H), 6.61 ppm (d, $J=2.9$ Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=26.8$, 27.6 (3C), 34.7, 67.2, 73.4, 103.2, 113.1, 147.3, 216.5 (4C), 223.2, 374.5 ppm.

(2*S,3*S**)-[1-(2-Butyl-3-methyl-2,3-dihydro-3-furyl)-1-(methoxy)methylidene]pentacarbonylchromium (8b)**: Red oil; $R_f=0.48$ (hexane/AcOEt 9:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.87$ (brsignal, 3H), 1.05–1.56 (m, 9H), 4.17 (d, $J=10.0$ Hz, 1H), 4.89 (s, 3H), 5.75 (d, $J=2.9$ Hz, 1H), 6.37 ppm (d, $J=2.9$ Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=13.5$, 22.4, 27.4, 28.7, 30.6, 67.3, 75.6, 91.6, 110.7, 145.5, 216.3 (4C), 223.1, 371.7 ppm; LRMS (70 eV, EI): *m*/*z* (%): 374 (4) [M^+], 358 (28), 262 (26), 241 (64), 223 (48), 167 (100); HRMS (70 eV, EI): *m*/*z*: calcd for $C_{16}H_{19}CrO_7$ [M^++H]: 375.0536; found: 375.0534.

Pentacarbonyl-[2-(3-furyl)-1,2-dimethoxyhexylidene]chromium (9b): Red oil; $R_f=0.53$ (hexane/AcOEt 9:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.89$–1.10 (m, 3H), 1.21–1.39 (m, 2H), 1.41–1.54 (m, 2H), 1.92 (td, $J=14.0$, 4.0 Hz, 1H), 2.13 (td, $J=14.0$, 5.1 Hz, 1H), 3.31 (s, 3H), 4.80 (s, 3H), 6.25 (s, 1H), 7.31 (s, 1H), 7.34 ppm (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=13.7$, 23.2, 24.1, 34.6, 49.8, 67.6, 92.0, 109.4, 125.1, 141.1, 143.1, 216.9 (4C), 224.9, 365.8 ppm.

Methyl 2-(3-furyl)-2-methoxyhexanoate (10b): Colorless oil; $R_f=0.32$ (hexane/AcOEt 9:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.89$ (t, $J=6.9$ Hz, 3H), 1.08–1.34 (m, 4H), 2.00–2.08 (m, 2H), 3.19 (s, 3H), 3.79 (s, 3H), 6.39 (dd, $J=1.8$, 0.8 Hz, 1H), 7.40 (dd, $J=1.8$, 1.7 Hz, 1H), 7.54 ppm (dd,

$J=1.3$, 1.0 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=13.9$, 22.6, 25.4, 36.6, 52.1, 52.3, 80.8, 109.1, 124.5, 141.1, 143.0, 172.7 ppm; LRMS (FAB+): *m*/*z* (%): 227 (10) [M^++H], 207 (41), 193 (24), 183 (23), 167 (100), 154 (14); HRMS (FAB+): *m*/*z*: calcd for $C_{12}H_{19}O_4$ [M^++H]: 227.1283; found: 227.1287.

Methoxy (2*S,3*S**)-2-*tert*-butyl-3-methyl-2,3-dihydrofuran-3-carboxylate (11a)**: This product was prepared in 72% yield by following the above general procedure for the preparation of esters **4**. Colorless oil; $R_f=0.37$ (hexane/AcOEt 9:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.01$ (s, 9H), 1.49 (s, 3H), 3.69 (s, 3H), 3.91 (s, 1H), 4.90 (d, $J=2.8$ Hz, 1H), 6.51 ppm (d, $J=2.8$ Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=26.2$ (3C), 26.4, 33.9, 52.0, 53.5, 99.5, 108.5, 146.4, 175.2 ppm; LRMS (FAB+): *m*/*z* (%): 199 (62) [M^++H], 194 (67), 167 (68), 165 (100); HRMS (FAB+) *m*/*z*: calcd for $C_{11}H_{19}O_3$ [M^++H]: 199.1334; found: 199.1343.

(2*S*,3*R*)-3-Methyl-2-[(*Z*)-2-phenylethenyl]-2,3-dihydro-3-furylmethyl (1*S*)-camphanoate (12): Et_3N (0.09 mL, 0.65 mmol), 4-dimethylaminopyridine (DMAP, 100 mg, 0.82 mmol), and then (1*S*)-(−)-camphanoyl chloride (107 mg, 0.50 mmol) were added to a solution of (*Z*)-**5f** (90.0 mg, 0.416 mmol) in CH_2Cl_2 (2 mL) at 0°C. The mixture was stirred at room temperature for 3 h. Water was then added (5 mL), and the mixture was extracted with Et_2O (3×10 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude compound was purified by column chromatography (silica gel, hexane/AcOEt 9:1) to give compound **12** (148.3 mg, 90%) as a white solid. $R_f=0.52$ (hexane/AcOEt 9:1); $[\alpha]_D^{20}=+13.2$ ($c=0.95$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.95$ (s, 3H), 1.06 (s, 3H), 1.11 (s, 3H), 1.15 (s, 3H), 1.61–1.72 (m, 1H), 1.86–1.72 (m, 1H), 2.42 (ddd, $J=14.1$, 9.8, 4.3 Hz, 1H), 4.03 (d, $J=11.1$ Hz, 1H), 4.32 (d, $J=11.1$ Hz, 1H), 4.84 (d, $J=2.9$ Hz, 1H), 5.00 (d, $J=10.2$ Hz, 1H), 5.85 (dd, $J=11.5$, 10.3 Hz, 1H), 6.37 (d, $J=2.9$ Hz, 1H), 6.84 (d, $J=11.7$ Hz, 1H), 7.26–7.38 ppm (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=9.6$, 16.6, 16.7, 22.9, 28.8, 30.5, 48.9, 53.9, 54.7, 68.1, 84.7, 91.1, 106.9, 125.4, 127.5, 128.2 (2C), 128.5 (2C), 135.5, 135.6, 145.9, 167.2, 177.9 ppm; LRMS (70 eV, EI): *m*/*z* (%): 396 (10) [M^+], 367 (18), 170 (89), 169 (100), 155 (80), 91 (31); HRMS (70 eV, EI): *m*/*z*: calcd for $C_{24}H_{28}O_5$ [M^+]: 396.1937; found: 396.1936. Crystals of **12** suitable for X-ray diffraction studies were grown by cooling (in a refrigerator) a solution of the compound in dry pentane containing a few drops of CH_2Cl_2.

Pentacarbonyl-[1-methoxy-1-[(2*S,3*S**)-3-methyl-2-[(*E*)-2-phenylethenyl]-2,3-dihydro-3-furyl]methylidene]chromium (13)**: Data taken from the 7:1 mixture of *E*:*Z* isomers: red oil; $R_f=0.35$ (hexane/AcOEt 9:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.35$ (s, 3H), 4.75–4.80 (m with s at 4.79, 4H), 5.89 (d, $J=2.9$ Hz, 1H), 6.00 (dd, $J=15.7$, 8.4 Hz, 1H), 6.48 (d, $J=2.9$ Hz, 1H), 6.51 (d, $J=15.7$ Hz, 1H), 7.22–7.43 ppm (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=27.3$, 67.2, 76.9, 91.2, 110.4, 124.9, 126.2 (2C), 127.9, 128.4 (2C), 132.8, 135.8, 145.7, 216.1 (4C), 223.1, 369.6 ppm; LRMS (FAB+): *m*/*z* (%): 420 (6) [M^+], 336 (32), 309 (32), 308 (100), 248 (57), 237 (36); HRMS (FAB+): *m*/*z*: calcd for $C_{20}H_{17}CrO_7$ [M^++H]: 421.0379; found: 421.0395. Resolvable resonances of minor *Z* isomer: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.30$ (s, 3H), 4.69 (s, 3H), 5.23 (d, $J=10.5$ Hz, 1H), 5.56 ppm (apparent t, $J=11.2$ Hz, 1H).

X-ray crystal structure determinations: Data for the X-ray structure analysis of compounds minor-**3a**, minor-**4e**, and **12** were collected on a Nonius Kappa CCD single-crystal diffractometer by using ϕ and ω scans ($\theta_{max}=70°$) with $Cu_{K\alpha}$ radiation (graphite crystal monochromator, $\lambda=1.54184$ Å). Crystal–detector distance was fixed at 29 mm with 2° oscillation and 40 s exposure time per image. Data collection strategy was calculated with the program Collect (Collect, Nonius BV, 1997–2000). Data reduction and cell refinement were performed with the programs DENZO and SCALEPACK.[46] Lorentz, polarization, and empirical XABS2[47] absorption corrections were performed. The crystal structure was solved with direct methods by using the program SHELXS-97.[48] Anisotropic least-squares refinement was carried out with SHELXL-97.[49] Atomic scattering factors were taken from the *International Tables for Crystallography (Vol. C)*. Geometrical calculations were made with PARST.[50] The crystallographic plots were made with ORTEP3.[51]

CCDC-210973 (minor-**3a**), -210974 (minor-**4e**), and -210975 (**12**) contain the supplementary crystallographic data for the structures reported in this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgement

This work was financially supported by the DGICYT (grants PB97-1271 and PB00-0219). S.K.N. and Y.R.S.L. thank the Ministerio de Educación, Cultura y Deporte of Spain for a postdoctoral fellowship.

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[23] Crystal data for minor-**3a**: $C_{24}H_{34}CrO_6$, $M_r = 470.51$, crystal size $0.17 \times 0.15 \times 0.10$ mm, orthorhombic, space group $P2_12_12_1$, $a = 10.9770(8)$, $b = 14.9881(9)$, $c = 15.3515(16)$ Å, $V = 2525.7(4)$ Å^3, $\rho_{calcd} = 1.237$ Mg m^{-3}, $T = 200(2)$ K. 11974 reflections were measured, 4722 independent and 4167 ($I > 2\sigma(I)$), with $\mu = 4.007$ mm^{-1}, $T_{min} = 0.466$ and $T_{max} = 0.670$. All hydrogen atoms were treated by a mixture of independent and constrained refinement. Final conventional $R = 0.0417$, $wR2 = 0.1019$ for 280 parameters refined on F^2. Final residual electron density 0.196 and -0.298 e Å^{-3}. Absolute configuration Flack parameter, 0.009(5).

[24] The size of the chelate ring has been defined by taking the center of the coordinated double bond as one ring member.

[25] For related η^2-alkene(tetracarbonyl)carbene complexes of Group 6 metals with either a three-, five-, or six-membered chelate structure and which have been characterized by X-ray crystallography, see: Cr derivatives: a) K. H. Dötz, W. Kuhn, G. Müller, B. Huber, H. G. Alt, *Angew. Chem.* **1986**, *98*, 826; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 812; b) C. Alvarez, A. Parlier, H. Rudler, R. Yefsah, J. C. Daran, C. Knobler, *Organometallics* **1989**, *8*, 2253; c) J. Barluenga, F. Aznar, A. Martín, S. García-Granda, E. Pérez-Carreño, *J. Am. Chem. Soc.* **1994**, *116*, 11191; Mo derivative: d) K. H. Dötz, M. Popall, G. Müller, *J. Organomet. Chem.* **1987**, *334*, 57; W derivatives: e) C. A. Toledano, J. Levisalles, M. Rudler, H. Rudler, J. C. Daran, Y. Jeannin, *J. Organomet. Chem.* **1982** *228*, C7; f) C. P. Casey, A. J. Shusterman, N. W. Vollendorf, K. J. Haller, *J. Am. Chem. Soc.* **1982**, *104*, 2417; g) C. P. Casey, N. W. Vollendorf, K. J. Haller, *J. Am. Chem. Soc.* **1984**, *106*, 3754; h) C. A. Toledano, H. Rudler, J. C. Daran, Y. Jeannin, *J. Chem. Soc. Chem. Commun.* **1984**, 574; i) C. A. Toledano, A. Parlier, H. Rudler, J. C. Daran, Y. Jeannin, *J. Chem. Soc. Chem. Commun.* **1984**, 576; j) C. Alvarez, A. Pacreau, A. Parlier, H. Rudler, *Organometallics* **1987**, *6*, 1057; k) C. Alvarez-Toledano, A. Parlier, H. Rudler, M. Rudler, J. C. Daran, C. Knobler, Y. Jeannin, *J. Organomet. Chem.* **1987**, *328*, 357. See also: l) U. Schick, L. Jordi, S. Ricart, J. Veciana, K. H. Dötz, J. M. Moretó, *J. Am. Chem. Soc.* **1998**, *120*, 2283; m) J. Barluenga, F. Aznar, I. Gutiérrez, A. Martín, S. García-Granda, M. A. Llorca-Baragaño, *J. Am. Chem. Soc.* **2000**, *122*, 1314.

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[27] Intermediate **A** reacts also with other electrophilic reagents; for example with benzaldehyde a different regioisomer was obtained corresponding to electrophile addition to C5. Further work on this subject is underway.

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[31] In this experiment we also observed a mixture of unidentified products.

[32] The scope and limitations of this latter reaction are currently being studied in our laboratory. These results will be reported separately.

[33] The NMR spectra measured included ^{1}H, ^{13}C, DEPT, gHMQC, gHMBC, gCOSY, and NOESY.

[34] Crystal data for minor-**4e**: $C_{22}H_{30}O_3$, $M_r = 342.48$, crystal size $0.32 \times 0.25 \times 0.25$ mm, orthorhombic, space group $P2_12_12_1$, $a = 9.3736(1)$, $b = 11.0456(2)$, $c = 18.6432(3)$ Å, $V = 1930.26(5)$ Å^3, $\rho_{calcd} = 1.178$ Mg m^{-3}, $T = 200(2)$ K. 3615 independent and 3339 ($I > 2\sigma(I)$), $\mu = 0.603$ mm^{-1}, $T_{min} = 0.817$ and $T_{max} = 0.865$. All hydrogen atoms were treated by a mixture of independent and constrained refinement. Final conventional $R = 0.0468$, $wR2 = 0.1093$ for 307 parameters refined on F^2. Final residual electron density 0.262 and -0.340 e Å^{-3}. Absolute configuration Flack parameter, 0.00(3).

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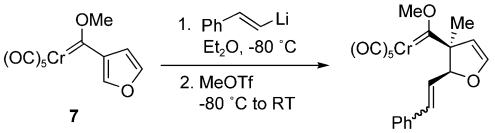
[36] Prepared from commercially available β-bromostyrene (*E*:*Z* 90:10) by bromine–lithium exchange reaction with *t*BuLi.

[37] Prepared from diastereomerically pure (*Z*)-β-bromostyrene which was synthesized according to: C. Kuang, H. Senboku, M. Tokuda, *Tetrahedron Lett.* **2001**, *42*, 3893.

[38] Crystal data for **12**: $C_{24}H_{28}O_5$, $M_r = 396.49$, crystal size $0.40 \times 0.20 \times 0.08$ mm, monoclinic, space group $P2_1$, $a = 16.4134(3)$, $b = 6.1783(1)$, $c = 21.1099(4)$ Å, $V = 2054.25(6)$ Å^3, $\rho_{calcd} = 1.282$ Mg m^{-3}, $T = 120(2)$ K. 23416 reflections were measured, 7564 independent and 7071 ($I > 2\sigma(I)$). $\mu = 0.720$ mm^{-1}, $T_{min} = 0.764$ and $T_{max} = 0.954$. All hydrogen atoms were treated by a mixture of independent and constrained refinement. Final conventional $R = 0.0576$, $wR2 = 0.1960$ for 520 parameters refined on F^2. Final residual electron density 0.417 and -0.401 e Å^{-3}. Absolute configuration Flack parameter, $-0.2(2)$.

[39] Indeed the analogous reaction of methoxycarbene complex **7** with (*E*)-2-phenylethenyllithium afforded only pentacarbonylcarbene complex **13** with mainly a *trans* configuration of the exocyclic C=C bond. The observed 7:1 mixture of *E*:*Z* isomers of **13** is close to the *E*:*Z* mixture of the starting β-bromostyrene.



13 66% *E*:*Z* 7:1

[40] A competing intramolecular displacement by one of the π systems of a CO ligand at the level of intermediate **D**, which will certainly reduce the steric strain, could account for the finally observed 1:1 ratio of *E*:*Z* isomers.

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Received: June 17, 2003 [F5241]