Chiral 2-Oxacyclopentylidene Complexes via Metal-Assisted Cycloisomerization of Carbohydrate-Derived Butynols[1]

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Reaction of 2,3-di-*O*-isopropylidene-D-glyceraldehyde with allenylmagnesium bromide affords a mixture of diastereomeric butynols which undergo cycloisomerization upon reaction with pentacarbonyl(tetrahydrofuran)chromium(0) and -tungsten(0) to yield the corresponding 2-oxacyclopentylidene complexes. These chiral 2-oxacyclopentylidene complexes are modified into their α-*exo*-methylene and -benzylidene derivatives, respectively. The absolute configurations of the diastereomeric pentacarbonyl{2′,2′-dimethyl-3(*S*/*R*)-(4′(*R*)-1′,3′-dioxacyclopentyl)-2-oxacyclopentylidene}chromium(0) and -tungsten(0) complexes have been determined by single-crystal X-ray analysis of one of the two diastereomers in each case. First studies on the chromium α-*exo*-alkylidene 2-oxacyclopentylidene complexes show good to very good diastereoselectivities in the Diels−Alder reaction with 2,3-dimethylbutadiene.

Introduction

Fischer-type ylidene complexes are valuable reagents in stereoselective organic synthesis, and a dramatic increase in the interest in these reagents can be noted.[2] The synthetic potential of group 6 metal ylidene complexes is based both on the pronounced α-CH acidity[3] within the alkyl ylidene side chain and on either metal-centered or ylidene ligand-centered cycloaddition reactions.[2,4] To perform these reactions in a stereoselective manner much interest has been paid to the preparation of metal ylidene complexes bearing chiral substituents at the ylidene carbon atom, such as amino acids,[5] amines,[6] and terpene alcohols.[7] However, there are only a few examples reported of the chiral modification of the ylidene ligand using carbohydrates.[8] Recently, we focused on the synthesis of carbohydrate functionalized 2-oxacyclopentylidene complexes[9] in order to investigate the influence of the chiral information provided by the carbohydrate moiety on stereoselective reactions and to evaluate their potential in the synthesis of natural products.

Results and Discussion

2′,2′-Dimethyl-1-(4′(*R*)-1′,3′-dioxacyclopentyl)-but-3-yn-1(*S*/*R*)-ol (1a/b). As the cycloisomerization of butynols at coordinatively unsaturated group 6 metal templates[9,10] is the most common approach to 2-oxacyclopentylidene complexes, we focused our interest on the preparation of carbohydrate-derived butynols for the synthesis of the desired carbohydrate-functionalized 2-oxacyclopentylidene complexes. In general, butynols are easily accessible via addition of propargylic organometallics to carbonyl compounds.[11] In our case,

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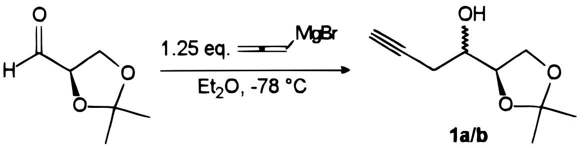
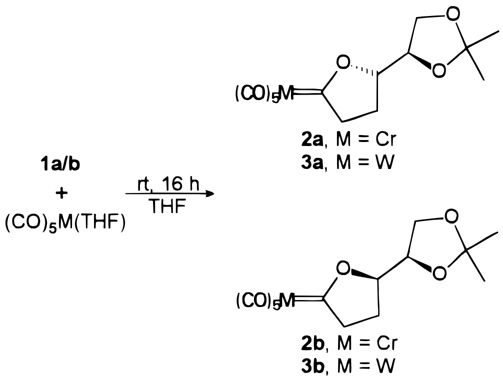
Scheme 1. Synthesis of Carbohydrate-Derived Butynols



Scheme 2. Synthesis of Chiral 2-Oxacyclopentylidene Complexes



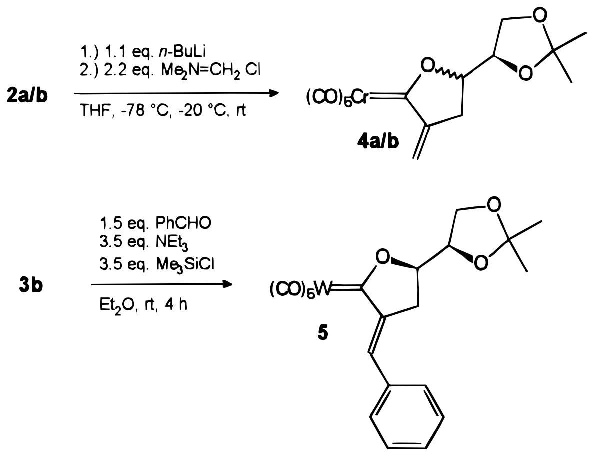
however, the reagent of choice turned out to be allenylmagnesium bromide,[12] which undergoes clean γ-addition to the carbonyl functionality of 2,3-di-*O*-isopropylidene-D-glyceraldehyde to give the butynols **1a/b** in a total yield of 78% as a mixture of diastereomers in a ratio of 1.7:1 (Scheme 1).

Pentacarbonyl{2′,2′-dimethyl-3(*S*/*R*)-(4′(*R*)-1′,3′-dioxacyclopentyl)-2-oxacyclopentylidene}chromium(0) (2a/b) and -tungsten(0) (3a/b). As the diastereomeric butynols **1a/b** cannot be separated using chromatographic techniques, they are reacted as a mixture of diastereomers with pentacarbonyl(tetrahydrofuran)chromium(0) and -tungsten(0) generated by UV-irradiation of the corresponding metal hexacarbonyl in tetrahydrofuran at −10 °C. The cyclization of the diastereomeric butynols **1a/b** at the pentacarbonylmetal template in tetrahydrofuran at room temperature affords the 2-oxacyclopentylidene complexes **2a/b** and **3a/b** in about 60% yield (the yields refer to the amount of metal hexacarbonyl applied in the synthesis of the pentacarbonyl(tetrahydrofuran)metal complexes). The separation of the diastereomeric ylidene complexes is achieved by column chromatography on silica gel using a 1:2 mixture of petroleum ether/diethyl ether as eluent (Scheme 2).

The products exhibit characteristic downfield ^{13}C NMR signals for the metal coordinated ylidene carbon atoms (342.75 and 343.25 ppm for **2a/b** and 314.48 and 315.31 ppm for **3a/b**, respectively). The absolute configuration of the major diastereomers **2a** and **3a** has been determined by single-crystal X-ray analysis to be 3(*S*),4′(*R*).

α-*exo*-Alkylidene Functionalization of Pentacarbonyl{2′,2′-dimethyl-3(*S*/*R*)-(4′(*R*)-1′,3′-dioxacyclopentyl)-2-oxacyclopentylidene}chromium(0) (2a/b) and of Pentacarbonyl{2′,2′-dimethyl-3(*R*)-(4′(*R*)-1′,3′-dioxacyclopentyl)-2-oxacyclopentylidene}tungsten(0) (3b). The α-CH acidity of 2-oxacyclopentylidene complexes allows the synthesis of the *exo*-alkylidene derivatives. Following the procedure reported by Maiorana et al.,[13] **2a/b** are deprotonated with *n*-butyllithium in tetrahydrofuran at −78 °C and subsequently treated with *N*,*N*-dimethylmethyleneiminium chloride to give pentacarbonyl{2′,2′-dimethyl-3(*S*)-(4′(*R*)-1′,3′-dioxacyclopentyl)-5-methylene-2-oxacyclopentylidene}chromium(0) (**4a)** in 42% yield and pentacarbonyl{2′,2′-dimethyl-3(*R*)-(4′(*R*)-1′,3′-dioxacyclopentyl)-5-methylene-2-oxacyclopentylidene}chromium(0) (**4b)** in 39% yield. Further, complex **3b** is reacted with benzaldehyde in the presence of trimethylamine and trimethylsilyl chloride[14] at room temperature to afford pentacarbonyl{5-benzylidene-2′,2′-dimethyl-3(*R*)-(4′(*R*)-1′,3′-dioxacyclopentyl)-2-oxacyclopentylidene}tungsten(0) (**5**) in 75% yield. Although there is no proof, it is assumed that the α-*exo*-benzylidene structure of **5** is *E*-configurated since it is reported by Aumann et al.[14] that the method using benzaldehyde in the presence of trimethylamine and trimethylsilyl chloride always leads to the *E*-configurated α,β-unsaturated ylidene complex (Scheme 3).

Scheme 3. α-*exo*-Alkylidene Functionalization of 2-Oxacyclopentylidene Complexes 2a and 3b



Diels–Alder Reaction of Pentacarbonyl{2′,2′-dimethyl-3(*S*/*R*)-(4′(*R*)-1′,3′-dioxacyclopentyl)-5-methylene-2-oxacyclopentylidene}chromium(0) (4a/b) with 2,3-Dimethylbutadiene. α,β-Unsaturated ylidene complexes are expected to reveal promising diastereoselectivities in cycloaddition reactions such as Diels–Alder[15] or benzannulation[16] reactions due to the chiral information provided by the vicinal stereocenters connecting the two five-membered rings. Thus, we turned our attention to the Diels–Alder reaction of complexes **4a/b** with 2,3-dimethylbutadiene in order to investigate the extent of diastereoselectivity in this reaction. A solution of **4a/b** in 2,3-dimethylbutadiene was stirred for 12 h at room temperature. Then the diene was removed, and the yellow residue was purified

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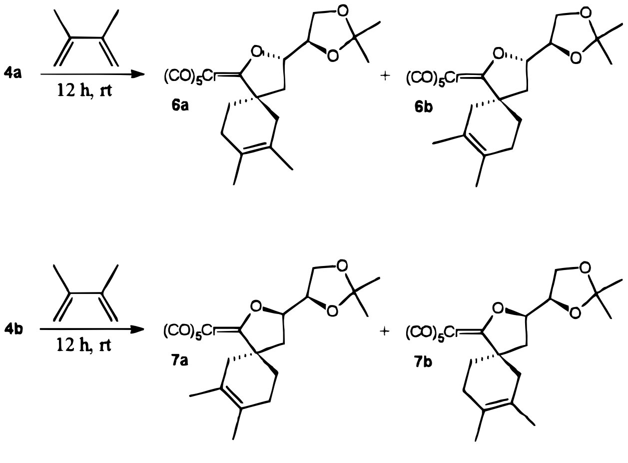
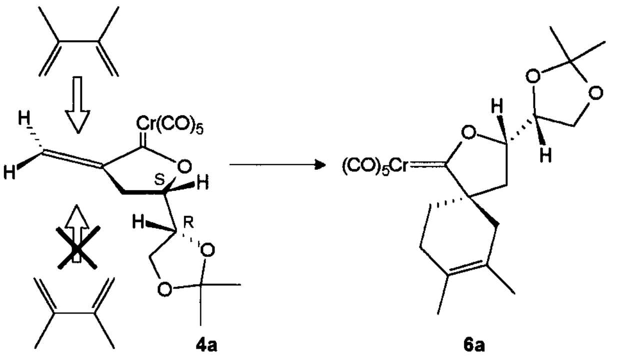
Scheme 4. Diels–Alder Reaction of 4a/b with 2,3-Dimethylbutadiene



Scheme 5. Stereopreference for the Addition of the Diene to the *exo*-Methylene Double Bond of 4a



by column chromatography on silica gel using 3:1 petroleum ether/diethyl ether as eluent to give spiro complexes **6a/b** and **7a/b** in total yields of about 40% as mixtures of diastereomers. On the basis of the ^1H NMR signals for the H-2″b (**6a/b**) and H-6″b (**7a/b**) protons the diastereomeric ratios were determined as 9.5:1 for **6a/b** and 18:1 for **7a/b**, respectively (Scheme 4).

If we take into consideration the absolute stereochemistry at C-3 of complex **4a**, the diene is expected to add to the α-*exo*-methylene double bond from the top face (*re*-side) due to the sterical hindrance of the bottom face (*si*-side) caused by the dioxacyclopentyl substituent to afford **6a** as the major diastereomer. On the basis of the same argument, addition of the diene to the α-*exo*-methylene double bond in **4b** should preferably occur from the bottom face to give **7a** as the major diastereomer (Scheme 5).

Conclusions

The cycloisomerization of carbohydrate-derived butynols at group 6 metal templates provides an approach to novel metal ylidene modified 2,3-deoxy sugar skeletons.[17] The multifunctionality of these compounds and their inherent chiral information may be exploited in subsequent addition reactions of nucleophiles as well as in metal- or ligand-centered cycloaddition reactions aiming at targets both in organometallic and carbohydrate chemistry. First studies on complexes **4a**/**b** show good to very good diastereoselectivities in the Diels–Alder reaction with 2,3-dimethylbutadiene.

Experimental Section

General Information. All reactions, manipulations, and purifications involving organometallics were performed under dry argon atmosphere using Schlenk techniques. Solvents were dried by distillation from sodium hydride (diethyl ether), calcium hydride (petroleum ether, bp 40–60 °C), or potassium/sodium alloy (tetrahydrofuran) and saturated with argon. Silica gel (Merck, type 60, 0.063–0.200 mm) was degassed at high vacuum and stored under argon. 2,3-Di-*O*-isopropylidene-D-glyceraldehyde[18] and allenylmagnesium bromide[12] were prepared according to methods reported previously. NMR spectra were recorded in $CDCl_3$ if not stated otherwise.

2′,2′-Dimethyl-1-(4′(*R*)-1′,3′-dioxacyclopentyl)-but-3-yn-1(*S*/*R*)-ol (1a/b). A 14.6 mL volume of a 2.5 M solution of allenylmagnesium bromide in diethyl ether was added at −78 °C dropwise to a solution of 3.8 g (29.2 mmol) of 2,3-di-*O*-isopropylidene-D-glyceraldehyde in 250 mL of diethyl ether. After the solution was stirred for 1 h at −78 °C, the cooling bath was removed and stirring was continued for an additional 1 h. Then a saturated aqueous solution of ammonium chloride was added until the reaction mixture was neutralized. The organic layer was separated, and the aqueous layer was extracted three times with 50 mL portions of diethyl ether. The combined organic extracts were washed twice with 50 mL portions of water and dried over magnesium sulfate, and the solvent was removed. Column chromatography on silica gel using 1:1 petroleum ether/diethyl ether as eluent gave 3.9 g (22.7 mmol, 78%) of **1a/b** as a light yellow oil containing both diastereomers in a ratio of 1.7:1. R_f = 0.32 (1:1 petroleum ether/diethyl ether). ^1H NMR (200 MHz): δ = 1.34 (s, 3H, CH_3, **1a**), 1.36 (s, 3H, CH_3, **1b**), 1.40 (s, 3H, CH_3, **1a**), 1.43 (s, 3H, CH_3, **1b**), 2.04 (t, $^4J_{HH}$ = 2.68 Hz, 1H, H-4, **1b**), 2.07 (t, $^4J_{HH}$ = 2.68 Hz, 1H, H-4, **1a**), 2.38–2.54 (m, 4H, H-2), 3.01 (s, 2H, OH), 3.70 (pqui, $^3J_{HH}$ = 2.39 Hz, 1H, H-1), 3.76 (pqui, $^3J_{HH}$ = 2.26 Hz, 1H, H-1), 3.84 (dd, $^2J_{HH}$ = 8.39 Hz, $^3J_{HH}$ = 6.46 Hz, 1H), 3.95–3.99 (m, 1H), 4.05–4.10 (m, 3H), 4.20 (dt, $^3J_{HH}$ = 4.97 Hz, $^3J_{HH}$ = 6.46 Hz, 1H). ^{13}C NMR (125 MHz) (major and minor diastereomers): δ = 23.55, 23.81 (C-2), 25.10 (2C, CH_3), 26.62, 26.46 (CH_3), 65.84, 65.93 (C-5′), 70.04, 70.22 (C-1), 71.24, 70.73 (C-4), 77.22, 77.32 (C-4′), 79.82, 79.92 (C-3), 109.35, 109.49 (C-2′). FT-IR (cm^{-1}, film): 3457 (s, OH), 3297 (vs, C≡CH), 2123 (w, C≡C). MS (EI): *m*/*z* (%) = 155 ($M^+ - CH_3$, 75), 101 ($M^+ - CH(OH)CH_2C_2H$, 100). HRMS calcd for $M^+ - CH_3$: 155.0708. Found: 155.0708. Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.27; H, 8.27.

General Procedure for the Synthesis of the 2-Oxacyclopentylidene Complexes 2a/b and 3a/b. A solution of 10 mmol of metal carbonyl [$Cr(CO)_6$ or $W(CO)_6$] in 400 mL of tetrahydrofuran was irradiated for 5 h at −10 °C using a mercury vapor lamp (Phillips 125 HPK) and special quartz glassware. A color change to orange occurred. After addition of 15 mmol of 2′,2′-dimethyl-1-(4′(*R*)-1′,3′-dioxacyclopentyl)-but-3-yn-1(*R*/*S*)-ol **(1a/b)** the cooling bath was removed and the solution was concentrated to one-third volume before the reaction mixture was stirred at room temperature for 16 h. Then the solvent was stripped off and the dark brown residue was purified by column chromatography at 10 °C using 1:1 petroleum ether/diethyl ether as eluent.

Pentacarbonyl{2′,2′-dimethyl-3(*S*/*R*)-(4′(*R*)-1′,3′-dioxacyclopentyl)-2-oxacyclopentylidene}chromium(0) (2a/b). Chromatography yielded 1.95 g (5.4 mmol, 54%) of a diastereomeric mixture of **2a/b** (ratio 1.7:1) as a yellow oil. The

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separation of the diastereomers was achieved by a second column chromatography using 1:2 petroleum ether/diethyl ether as eluent. The major diastereomer **2a** was obtained as a yellow solid, while the minor diastereomer **2b** was isolated as a yellow viscous oil. Crystallization of **2a** from hexane at −30 °C gave yellow crystals. **2a**: Yellow crystals; mp 68−69 °C. R_f = 0.40 (1:2 petroleum ether/diethyl ether). ^{1}H NMR (500 MHz): δ = 1.36 (s, 3H, CH$_3$), 1.45 (s, 3H, CH$_3$), 1.82−1.89 (m, 1H, H-4a), 1.97−2.05 (m, 1H, H-4b), 3.63 (ddd, $^2J_{HH}$ = 20.66 Hz, $^3J_{HH}$ = 9.86 Hz, $^3J_{HH}$ = 6.08 Hz, 1H, H-5a), 3.76 (ddd, $^2J_{HH}$ = 20.76 Hz, $^3J_{HH}$ = 9.52 Hz, $^3J_{HH}$ = 6.44 Hz, 1H, H-5b), 3.93 (dd, $^2J_{HH}$ = 8.44 Hz, $^3J_{HH}$ = 5.36 Hz, 1H, H-5′a), 4.19 (dd, $^2J_{HH}$ = 8.65 Hz, $^3J_{HH}$ = 6.85 Hz, 1H, H-5′b), 4.30 (dpt, $^3J_{HH}$ = 6.65 Hz, $^3J_{HH}$ = 5.32 Hz, 1H, H-4′), 5.14 (dpt, $^3J_{HH}$ = 8.44 Hz, $^3J_{HH}$ = 5.6 Hz, 1H, H-3). ^{13}C NMR (125 MHz): δ = 22.35 (C-4), 24.79 (CH$_3$), 26.31 (CH$_3$), 60.62 (C-5), 66.07 (C-5′), 75.76 (C-4′), 98.19 (C-3), 110.34 (C-2′), 216.23 (*cis*-CO), 223.41 (*trans*-CO), 342.75 (*ylidene*-C). FT-IR (cm^{-1}, hexane): ν_{CO} = 2068 (m, A$_1^1$), 1989 (w, B), 1965 (sh, A$_1^2$), 1952 (vs, E). MS (EI): *m/z* (%) = 362 (M$^+$, 22), 347 (M$^+$ − CH$_3$, 15), 334 (M$^+$ − CO, 9), 306 (M$^+$ − 2CO, 5), 278 (M$^+$ − 3CO, 5), 250 (M$^+$ − 4CO, 31), 222 (M$^+$ − 5CO, 100), 207 (M$^+$ − 5CO, −CH$_3$, 17), 140 (M$^+$ − Cr(CO)$_5$, −2CH$_3$, 25), 101 (2′,2′-dimethyl-4′-(*R*)-1′,3′-dioxacyclopentyl, 19). HRMS calcd for M$^+$: 362.0094. Found: 362.0094. Anal. Calcd for C$_{14}$H$_{14}$O$_8$Cr: C, 46.42; H, 3.90. Found: C, 46.46; H, 3.87. **2b**: Yellow viscous oil. R_f = 0.36 (1:2 petroleum ether/diethyl ether). ^{1}H NMR (500 MHz): δ = 1.36 (s, 3H, CH$_3$), 1.39 (s, 3H, CH$_3$), 1.91−2.05 (m, 2H, H-4a/b), 3.64 (ddd, $^2J_{HH}$ = 20.52 Hz, $^3J_{HH}$ = 9.61 Hz, $^3J_{HH}$ = 6.19 Hz, 1H, H-5a), 3.77 (ddd, $^2J_{HH}$ = 20.37 Hz, $^3J_{HH}$ = 9.34 Hz, $^3J_{HH}$ = 6.86 Hz, 1H, H-5b), 4.16 (pqui, J_{HH} = 8.17 Hz, 2H, H-5′a/b), 4.29 (pt, $^3J_{HH}$ = 5.81 Hz, $^3J_{HH}$ = 5.32 Hz, 1H, H-4′) 5.21 (pt, $^3J_{HH}$ = 6.11 Hz, 1H, H-3). ^{13}C NMR (125 MHz): δ = 23.26 (C-4), 25.35 (CH$_3$), 26.10 (CH$_3$), 60.67 (C-5), 65.21 (C-5′), 76.58 (C-4′), 95.90 (C-3), 110.0 (C-2′), 216.33 (*cis*-CO), 223.34 (*trans*-CO), 343.24 (*ylidene*-C). FT-IR (cm^{-1}, hexane): ν_{CO} = 2068 (*m*, A$_1^1$), 1989 (*w*, B), 1965 (*sh*, A$_1^2$), 1952 (vs, E). MS (EI): *m/z* (%) = 362 (M$^+$, 15), 347 (M$^+$ − CH$_3$, 29), 334 (M$^+$ − CO, 13), 306 (M$^+$ − 2CO, 7), 278 (M$^+$ − 3CO, 8), 250 (M$^+$ − 4CO, 37), 222 (M$^+$ − 5CO, 100), 207 (M$^+$ − 5CO, −CH$_3$, 22), 140 (M$^+$ − Cr(CO)$_5$, −2CH$_3$, 20), 101 (2′,2′-dimethyl-4′-(*R*)-1′,3′-dioxacyclopentyl, 10). HRMS calcd for M$^+$: 362.0094. Found: 362.0103.

Pentacarbonyl{2′,2′-dimethyl-3(*S*/*R*)-(4′(*R*)-1′,3′-dioxacyclopentyl)-2-oxacyclopentylidene}tungsten(0) (3a/b). Chromatography of the residue gave 3.31 g (6.7 mmol, 67%) of **3a/b** as a yellow oil as a mixture of diastereomers (ratio 1.7:1) which were separated by column chromatography on silica gel using 1:2 petroleum ether/diethyl ether as eluent. The major diastereomer **3a** was obtained as a yellow solid, while the minor diastereomer **3b** remained as a yellow viscous syrup. Yellow crystals of **3a** were grown from hexane by crystallization at −30 °C. **3a**: Yellow crystals; mp 64 °C. R_f = 0.65 (1:2 petroleum ether/diethyl ether). ^{1}H NMR (500 MHz): δ = 1.36 (s, 3H, CH$_3$), 1.45 (s, 3H, CH$_3$), 1.86 (dddd, $^2J_{HH}$ = 12.82 Hz, $^3J_{HH}$ = 9.66 Hz, $^3J_{HH}$ = 6.06 Hz, $^3J_{HH}$ = 6.06 Hz, 1H, H-4a), 2.02 (dddd, $^2J_{HH}$ = 18.18 Hz, $^3J_{HH}$ = 9.84 Hz, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 6.21 Hz, 1H, H-4b), 3.35 (ddd, $^2J_{HH}$ = 20.67 Hz, $^3J_{HH}$ = 9.86 Hz, $^3J_{HH}$ = 6.14 Hz, 1H, H-5a), 3.51 (ddd, $^2J_{HH}$ = 20.71 Hz, $^3J_{HH}$ = 9.71 Hz, $^3J_{HH}$ = 6.13 Hz, 1H, H-5b), 3.91 (dd, $^2J_{HH}$ = 8.84 Hz, $^3J_{HH}$ = 5.37 Hz, 1H, H-5′a), 4.19 (dd, $^2J_{HH}$ = 8.85 Hz, $^3J_{HH}$ = 6.76 Hz, 1H, H-5′b), 4.32 (dpt, $^3J_{HH}$ = 6.65 Hz, $^3J_{HH}$ = 5.32 Hz, 1H, H-4′), 5.10 (dpt, $^3J_{HH}$ = 8.24 Hz, $^3J_{HH}$ = 5.59 Hz, 1H, H-3). ^{13}C NMR (125 MHz): δ = 22.82 (C-4), 24.81 (CH$_3$), 26.32 (CH$_3$), 63.33 (C-5), 66.11 (C-5′), 75.67 (C-4′), 98.51 (C-3), 110.38 (C-2′), 196.98 (J_{CW} = 63.2 Hz, *cis*-CO), 204.32 (*trans*-CO), 314.48 (*ylidene*-C). FT-IR (cm^{-1}, hexane): ν_{CO} = 2074 (m, A$_1^1$), 1985 (*w*, B), 1954 (vs, A$_1^2$), 1942 (s, E). MS (EI): *m/z* (%) = 492 (M$^+$, 12), 477 (M$^+$ − CH$_3$, 7), 464 (M$^+$ − CO, 1), 436 (M$^+$ − 2CO, 1), 408 (M$^+$ − 3CO, 1), 380 (M$^+$ − 4CO, 3), 352 (M$^+$ − 5CO, 2), 337 (M$^+$ − 5CO, −CH$_3$, 3), 322 (M$^+$ − 5CO, −2CH$_3$, 7), 294 (W(CO)$_4$, 100), 266 (W(CO)$_3$, 9), 101 (2′,2′-dimethyl-4′(*R*)-1′,3′-dioxacyclopentyl, 3). HRMS calcd for M$^+$: 492.0171. Found: 492.0151. Anal. Calcd for C$_{14}$H$_{14}$O$_8$W: C, 34.03; H, 2.85. Found: C, 34.03; H, 2.83. **3b**: Yellow syrup. R_f = 0.62 (1:2 petroleum ether/diethyl ether). ^{1}H NMR (400 MHz): δ = 1.35 (s, 3H, CH$_3$), 1.38 (s, 3H, CH$_3$), 1.90−2.07 (m, 2H, H-4a/b), 3.39 (ddd, $^2J_{HH}$ = 20.54 Hz, $^3J_{HH}$ = 9.34 Hz, $^3J_{HH}$ = 6.11 Hz, 1H, H-5a), 3.47 (ddd, $^2J_{HH}$ = 20.59 Hz, $^3J_{HH}$ = 8.76 Hz, $^3J_{HH}$ = 6.90 Hz, 1H, H-5b), 4.12 (dd, $^2J_{HH}$ = 8.41 Hz, $^3J_{HH}$ = 7.43 Hz, 1H, H-5′a), 4.16 (dd, $^2J_{HH}$ = 8.41 Hz, $^3J_{HH}$ = 6.65 Hz, 1H, H-5′b), 4.29 (ddd, $^3J_{HH}$ = 7.44 Hz, $^3J_{HH}$ = 6.65 Hz, $^3J_{HH}$ = 2.35 Hz, 1H, H-4′), 5.17 (ddd, $^3J_{HH}$ = 8.51 Hz, $^3J_{HH}$ = 6.02 Hz, $^3J_{HH}$ = 2.50 Hz, 1H, H-3). ^{13}C NMR (100 MHz): δ = 23.74 (C-4), 25.32 (CH$_3$), 26.19 (CH$_3$), 63.31 (C-5), 65.22 (C-5′), 76.53 (C-4′), 96.47 (C-3), 109.99 (C-2′), 197.05 (J_{CW} = 63.32 Hz, *cis*-CO), 204.21 (J_{CW} = 60.27 Hz, *trans*-CO), 314.75 (J_{CW} = 50.36 Hz, *ylidene*-C). FT-IR (cm^{-1}, hexane): ν_{CO} = 2074 (m, A$_1^1$), 1985 (w, B), 1954 (vs, A$_1^2$), 1942 (*s*, E). MS (EI): *m/z* (%) = 492 (M$^+$, 7), 477 (M$^+$ − CH$_3$, 4), 380 (M$^+$ − 4CO, 2), 352 (M$^+$ − 5CO, 8), 294 (W(CO)$_4$, 11), 266 (W(CO)$_3$, 13), 101 (2′,2′-dimethyl-4′(*R*)-1′,3′-dioxacyclopentyl, 100). HRMS calcd for M$^+$: 492.0171. Found: 492.0157.

General Procedure for the α-*exo*-Methylene Functionalization of the 2-Oxacyclopentylidene Complexes 2a/b. A 0.69 mL volume of *n*-butyllithium (1.1 mmol, 1.6 M solution in hexane) was slowly added at −78 °C to a solution of 362 mg (1 mmol) of **2a/b** in 25 mL of tetrahydrofuran. After 30 min 206 mg (2.2 mmol) of *N*,*N*-dimethylmethyleneiminium chloride was added, and the reaction mixture was warmed to −20 °C. The color changed from yellow to red. After 30 min at −20 °C the reaction mixture was warmed to room temperature, and stirring was continued for an additional 2 h before the solvent was removed. The red residue was purified by column chromatography at 10 °C using 1:1 petroleum ether/diethyl ether as eluent.

Pentacarbonyl{2′,2′-dimethyl-3(*S*)-(4′(*R*)-1′,3′-dioxacyclopentyl)-5-methylene-2-oxacyclopentylidene}chromium(0) (4a). Chromatography gave 156 mg (0.42 mmol, 42%) of **4a** as a red syrup. R_f = 0.5 (1:1 petroleum ether/diethyl ether). ^{1}H NMR (500 MHz): δ = 1.34 (s, 3H, CH$_3$), 1.43 (s, 3H, CH$_3$), 2.67 (ddpt, $^2J_{HH}$ = 16.59 Hz, $^3J_{HH}$ = 4.92 Hz, $^4J_{HH}$ = 2.42 Hz, 1H, H-4a), 2.89 (ddpt, $^2J_{HH}$ = 16.64 Hz, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 2.65 Hz, 1H, H-4b), 4.02 (dd, $^2J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 4.82 Hz, 1H, H-5′a), 4.10 (dpt, $^3J_{HH}$ = 6.46 Hz, $^3J_{HH}$ = 4.87 Hz, 1H, H-4′), 4.18 (dd, $^2J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 6.41 Hz, 1H, H-5′b), 5.03 (ddd, $^3J_{HH}$ = 8.54 Hz, $^3J_{HH}$ = 6.46 Hz, $^3J_{HH}$ = 4.87 Hz, 1H, H-3), 6.25 (pt, J_{HH} = 2.38 Hz, 1H, H-vinyl), 6.58 (pt, J_{HH} = 2.64 Hz, 1H, H-vinyl). ^{13}C NMR (125 MHz): δ = 24.91 (C-4), 26.40 (CH$_3$), 29.35 (CH$_3$), 66.20 (C-5′), 76.09 (C-4′), 94.54 (C-3), 110.29 (C-2′), 132.22 (C-vinyl), 156.94 (C-vinyl), 216.95 (*cis*-CO), 224.41 (*trans*-CO), 324.56 (*ylidene*-C). FT-IR (cm^{-1}, hexane): ν_{CO} = 2063 (m, A$_1^1$), 1989 (w, B), 1961 (s, A$_1$2), 1951 (vs, E). MS (EI): *m/z* (%) = 374 (M$^+$, 19), 359 (M$^+$ − CH$_3$, 7), 346 (M$^+$ − CO, 4), 318 (M$^+$ − 2CO, 5), 290 (M$^+$ − 3CO, 7), 262 (M$^+$ − 4CO, 36), 234 (M$^+$ − 5CO, 100), 101 (2′,2′-dimethyl-4′(*R*)-1′,3′-dioxacyclopentyl, 23). HRMS calcd for M$^+$: 374.0094. Found: 374.0098.

Pentacarbonyl{2′,2′-dimethyl-3(*R*)-(4′(*R*)-1′,3′-dioxacyclopentyl)-5-methylene-2-oxacyclopentylidene}chromium(0) (4b). Chromatography yielded 146 mg (0.39 mmol, 39%) of **4b** as a red syrup. R_f = 0.45 (1:1 petroleum ether/diethyl ether). ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ = 1.10 (s, 3H, CH$_3$), 1.31 (s, 3H, CH$_3$), 1.63 (ddpt, $^2J_{HH}$ = 16.26 Hz, $^3J_{HH}$ = 8.99 Hz, $^4J_{HH}$ = 2.60 Hz, 1H, H-4a), 1.91 (ddpt, $^2J_{HH}$ = 16.26 Hz, $^3J_{HH}$ = 5.72 Hz, $^4J_{HH}$ = 2.52 Hz, 1H, H-4b), 3.37 (dpt, $^2J_{HH}$ = 6.83 Hz, $^3J_{HH}$ = 3.08 Hz, 1H, H-4′b), 3.50 (dd, $^2J_{HH}$ = 8.34 Hz, $^3J_{HH}$ = 6.86 Hz, 1H, H-5′a), 3.68 (dd, $^3J_{HH}$ = 8.34 Hz, $^3J_{HH}$ = 7.05 Hz, 1H, H-5′b), 3.95 (ddd, $^3J_{HH}$ = 8.94 Hz, $^3J_{HH}$ = 5.40 Hz, $^3J_{HH}$ = 3.30 Hz, 1H, H-3), 5.41 (pt, J_{HH} = 2.25 Hz, 1H, H-vinyl), 6.35 (pt, J_{HH} = 2.70 Hz, 1H, H-vinyl). ^{13}C NMR

(C_6D_6, 125 MHz): $\delta = 25.84$ (CH_3), 26.98 (CH_3), 29.51 (C-4), 65.46 (C-5′), 76.88 (C-4′), 93.76 (C-3), 110.61 (C-2′), 132.42 (C-vinyl), 158.23 (C-vinyl), 218.34 (*cis*-CO), 225.20 (*trans*-CO), 325.23 (*ylidene*-C). FT-IR (cm^{-1}, hexane): $\nu_{CO} = 2063$ (m, A_1^1), 1989 (w, B), 1961 (s, A_1^2), 1951 (vs, E). MS (EI): *m/z* (%) = 374 (M^+, 24), 359 ($M^+ - CH_3$, 10), 346 ($M^+ - CO$, 7), 318 ($M^+ - 2CO$, 7), 303 ($M^+ - CH_3$, $-2CO$, 5), 290 ($M^+ - 3CO$, 58), 262 ($M^+ - 4CO$, 64), 234 ($M^+ - 5CO$, 100), 101 (2′,2′-dimethyl-4′(*R*)-1′,3′-dioxacyclopentyl, 23). HRMS calcd for M^+: 374.0094. Found: 374.0097.

Pentacarbonyl{2′,2′-dimethyl-3(*R*)-(4′(*R*)-1′,3′-dioxacyclopentyl)-5-benzylidene-2-oxacyclopentylidene}tungsten(0) (5). To a solution of 250 mg (0.5 mmol) of complex **3b** in 5 mL of diethyl ether were added 1.5 equiv (80.5 mg, 77 μL, 0.75 mmol) of benzaldehyde, 3.5 equiv (192 mg, 225 μL, 1.8 mmol) of trimethylsilyl chloride, and 3.5 equiv (179 mg, 245 μL, 1.8 mmol) of triethylamine. The reaction mixture was stirred for 4 h at room temperature while the color changed from yellow to purple. After evaporation of the solvent the residue was chromatographed on silica gel using petroleum 1:1 ether/diethyl ether as eluent and 220 mg (0.38 mmol, 75%) of complex **5** was obtained as a purple oil. $R_f = 0.38$ (1:1 petroleum ether/diethyl ether). ^1H NMR (500 MHz): $\delta = 1.34$ (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 3.05 (ddd, $^2J_{HH} = 16.54$ Hz, $^3J_{HH} = 5.76$ Hz, $^4J_{HH} = 2.64$ Hz, 1H, H-4a), 3.11 (ddpt, $^2J_{HH} = 16.54$ Hz, $^3J_{HH} = 8.62$ Hz, $^4J_{HH} = 2.66$ Hz, 1H, H-4b), 4.12 (dd, $^2J_{HH} = 8.49$ Hz, $^3J_{HH} = 6.73$ Hz, 1H, H-5′a), 4.16 (dd, $^3J_{HH} = 8.45$ Hz, $^3J_{HH} = 6.76$ Hz, 1H, H-5′b), 4.40 (dpt, $^2J_{HH} = 6.71$ Hz, $^3J_{HH} = 2.98$ Hz, 1H, H-4′), 5.23 (ddd, $^3J_{HH} = 8.69$ Hz, $^3J_{HH} = 5.73$ Hz, $^3J_{HH} = 2.96$ Hz, 1H, H-3), 7.49 (d, $^3J_{HH} = 1.29$ Hz, 1H, *para*-Ar-H), 7.51 (d, $^3J_{HH} = 2.18$ Hz, 2H, *ortho*-Ar-H), 7.64 (m, 2H, *meta*-Ar-H), 8.12 (pt, $^4J_{HH} = 2.63$ Hz, 1H, H-vinyl). ^{13}C NMR (125 MHz): $\delta = 25.10$ (C-4), 26.28 (CH_3), 28.58 (CH_3), 64.99 (C-5′), 75.99 (C-4′), 93.85 (C-3), 110.13 (C-2′), 129.25 (2C, *meta*-Ar-C), 130.97 (2C, *ortho*-Ar-C), 131.12 (*para*-Ar-C), 135.28 (*ipso*-Ar-C), 152.24 (1C, CH-vinyl), 152.40 (1C, C-vinyl), 197.70 ($J_{CW} = 63.58$ Hz, *cis*-CO), 203.82 ($J_{CW} = 61.66$ Hz, *trans*-CO), 295.52 ($J_{CW} = 50.63$ Hz, *ylidene*-C). FT-IR (cm^{-1}, hexane): $\nu_{CO} = 2073$ (m, A_1^1), 1983 (w, B), 1952 (vs, A_1^2), 1939 (vs, E). MS (EI): *m/z* (%) = 580 (M^+, 4), 565 ($M^+ - CH_3$, 1), 496 ($M^+ - 3CO$, 8), 350 ($M^+ - 5CO$, $-CHPh$, 15), 294 ($W(CO)_4$, 16), 266 ($W(CO)_3$, 100), 238 ($W(CO)_2$, 21), 210 (W(CO), 23), 182 (W, 13), 101 (2′,2′-dimethyl-4′(*R*)-1′,3′-dioxacyclopentyl, 6). HRMS calcd for M^+: 580.0484. Found: 580.0477.

General Procedure for the Diels−Alder Reactions of 4a/b with 2,3-Dimethylbutadiene. A 200 mg (0.53 mmol) amount of **4a/b** was dissolved in 5 mL of dimethylbutadiene. After the solution was stirred for 12 h at room temperature, the diene was removed and the yellow residue chromatographed on silica gel using 3:1 petroleum ether/diethyl ether as eluent.

Table 1. Crystallographic Data for 2a and 3a and Summary of Data Collection and Refinement

	2a	**3a**
formula	$C_{14}H_{14}O_8Cr$	$C_{14}H_{14}O_8W$
dimens, mm	0.10 × 0.15 × 0.23	0.25 × 0.25 × 0.25
cryst syst	orthorhombic	orthorhombic
space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)
a, Å	9.3918(1)	9.3701(1)
b, Å	12.2805(3)	12.4892(3)
c, Å	14.1932(3)	14.4234(4)
V, Å^3	1636.99(6)	1687.90(6)
Z	4	4
ρ_{calcd}, g cm^{-3}	1.47	1.94
μ	0.735	6.879
F(000)	744	944
diffractometer	Enraf-Nonius Kappa-CCD	
radiation	Mo Kα	
λ, Å	0.710 73	
T, K	123(2)	123(2)
max 2θ, deg	52.7	54.0
no. of data	11 544	22 537
no. of unique data	3244	3352
no. of unique data [$I > 2\sigma(I)$]	3132	3255
no. of variables	208	209
Flack param	−0.003(13)	0.004(10)
R(*F*)[a]	0.023	0.019
wR2(F^2) for all data	0.061	0.042

[a] For $I > 2\sigma(I)$.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 2a

Cr(1)−C(1)	2.0155(14)	C(1A)−O(1A)	1.138(2)
Cr(1)−C(1A)	1.9086(17)	C(1B)−O(1B)	1.136(2)
Cr(1)−C(1B)	1.8998(17)	C(1C)−O(1C)	1.153(2)
Cr(1)−C(1C)	1.8951(18)	C(1D)−O(1D)	1.142(2)
Cr(1)−C(1D)	1.8952(17)	C(1E)−O(1E)	1.146(2)
Cr(1)−C(1E)	1.8908(16)	C(1)−O(2)	1.3003(19)
O(2)−C(1)−Cr(1)	122.39(10)	O(1B)−C(1B)−Cr(1)	177.98(16)
C(5)−C(1)−Cr(1)	128.91(11)	O(1C)−C(1C)−Cr(1)	177.14(16)
O(2)−C(1)−C(5)	108.68(12)	O(1D)−C(1D)−Cr(1)	178.28(16)
O(1A)−C(1A)−Cr(1)	178.47(15)	O(1E)−C(1E)−Cr(1)	178.88(15)

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 3a

W(1)−C(1)	2.161(3)	C(1A)−O(1A)	1.138(6)
W(1)−C(1A)	2.041(5)	C(1B)−O(1B)	1.130(6)
W(1)−C(1B)	2.045(5)	C(1C)−O(1C)	1.137(6)
W(1)−C(1C)	2.048(5)	C(1D)−O(1D)	1.142(5)
W(1)−C(1D)	2.033(4)	C(1E)−O(1E)	1.139(6)
W(1)−C(1E)	2.042(5)	C(1)−O(2)	1.289(4)
O(2)−C(1)−W(1)	122.8(3)	O(1B)−C(1B)−W(1)	177.9(5)
C(5)−C(1)−W(1)	128.3(3)	O(1C)−C(1C)−W(1)	177.4(4)
O(2)−C(1)−C(5)	108.9(3)	O(1D)−C(1D)−W(1)	178.8(4)
O(1A)−C(1A)−W(1)	179.1(4)	O(1E)−C(1E)−W(1)	178.6(4)

Pentacarbonyl{2′,2′,3″,4″-tetramethyl-3(*S*)-(4′(*R*)-1′,3′-dioxacyclopentyl)spiro[cyclohex-3″-ene-1″,5(*R*/*S*)-2-oxacyclopent]ylidene}chromium(0) (6a/b). Chromatography gave 87 mg (0.19 mmol, 35%) of **6a/b** as a yellow oil containing both diastereoisomers in a ratio of 9.5:1. $R_f = 0.42$ (3:1 petroleum ether/diethyl ether). **6a** (major diastereomer): ^1H NMR (C_6D_6, 500 MHz): $\delta = 1.05-1.10$ (m, 2H, H-4a, H-2″a), 1.17 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.31−1.37 (m, 1H, H-5″a), 1.38 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.49 (dd, $^2J_{HH} = 12.67$ Hz, $^3J_{HH} = 6.81$ Hz, 1H, H-4b), 1.55 (dd, $^2J_{HH} = 9.0$ Hz, $^3J_{HH} = 1.94$ Hz, 1H, H-6″a), 1.73 (dd, $^2J_{HH} = 16.40$ Hz, $^3J_{HH} = 6.46$ Hz, 1H, H-5″b), 2.58 (d, $^2J_{HH} = 16.69$ Hz, 1H, H-2″b), 2.67 (m, 1H, H-6″b), 3.53 (m, 1H, H-4′), 3.72 (m, 2H, H-5′a, H-5′b), 4.20 (m, 1H, H-3). ^{13}C NMR (C_6D_6, 125 MHz): $\delta = 19.45$ (CH_3), 19.79 (CH_3), 25.59 (CH_3), 27.12 (CH_3), 29.30 (C-4), 32.85 (C-6″), 33.57 (C-5″), 37.60 (C-2″), 67.01 (C-5′), 72.91 (C-5), 76.98 (C-4′), 96.92 (C-3), 110.85 (C-2′), 122.34 (C-3″), 126.33 (C-4″), 217.93 (*cis*-CO), 224.02 (*trans*-CO), 353.47 (*ylidene*-C). FT-IR (cm^{-1}, hexane): $\nu_{CO} = 2064$ (m, A_1^1), 1987 (vw, B), 1962 (s, sh), 1955 (vs, A_1^2), 1936 (s, E). MS (EI): *m/z* (%) = 456 (M^+, 4), 441 ($M^+ - CH_3$, 3), 400 ($M^+ - 2CO$, 1), 372 ($M^+ - 3CO$, 18), 344 ($M^+ - 4CO$, 31), 316 ($M^+ - 5CO$, 100). HRMS calcd for M^+: 456.0891. Found: 456.0884. **6b** (minor diastereomer): ^{13}C NMR (C_6D_6, 125 MHz): $\delta = 19.36$ (CH_3), 19.97 (CH_3), 25.80 (CH_3), 27.42 (CH_3), 29.03 (C-4), 32.64 (C-6″), 33.57 (C-5″), 37.60 (C-2″), 66.57 (C-5′), 73.04 (C-5), 76.80 (C-4′), 97.60 (C-3), 110.89 (C-2′), 123.85 (C-3″), 125.28 (C-4″), 217.93 (*cis*-CO), 224.10 (*trans*-CO), 353.28 (*ylidene*-C). FT-IR (cm^{-1}, hexane): $\nu_{CO} = 2064$ (m, A_1^1), 1987 (vw, B), 1962 (s, sh), 1955 (vs, A_1^2), 1936 (s, E). MS (EI): *m/z* (%) = 456 (M^+, 4), 441 ($M^+ - CH_3$, 3), 400 ($M^+ - 2CO$, 1), 372 ($M^+ - 3CO$, 18), 344 ($M^+ - 4CO$, 31), 316 ($M^+ - 5CO$, 100). HRMS calcd for M^+: 456.0891. Found: 456.0884.

Pentacarbonyl{2′,2′,3″,4″-tetramethyl-3(*R*)-(4′(*R*)-1′,3′-dioxacyclopentyl)spiro[cyclohex-3″-ene-1″,5(*R*/*S*)-2-oxacyclopent]ylidene}chromium(0) (7a/b). Chromatography gave 97 mg (0.21 mmol, 40%) of **7a/b** as a yellow oil containing both diastereoisomers in a ratio of 16.7:1. $R_f = 0.41$

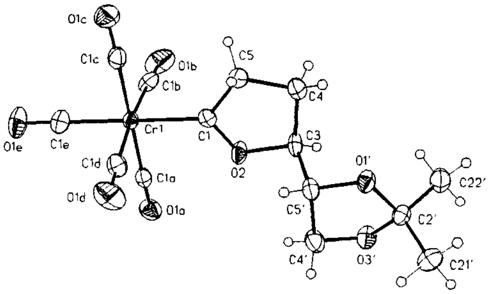

Figure 1. Molecular structure of (2-oxacyclopentylidene)-chromium complex **2a**. (Non-H atoms are shown with 50% probability ellipsoids.)

(3:1 petroleum ether/diethyl ether). **7a** (major diastereomer): ^{1}H NMR (C_6D_6, 500 MHz): δ = 1.09 (d, 1H, H-2″a), 1.22−1.25 (m, 2H, H-4a, H-4b), 1.26 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.43 (s, 6H, CH_3), 1.50−1.61 (m, 2H, H-5″a, H-6″a), 1.71 (dd, $^2J_{HH}$ = 17.43 Hz, $^3J_{HH}$ = 5.32 Hz, 1H, H-5″b), 2.59 (d, $^2J_{HH}$ = 16.59 Hz, 1H, H-2″b), 2.69 (dt, $^2J_{HH}$ = 11.94 Hz, $^3J_{HH}$ = 5.86 Hz, 1H, H-6″b), 3.57 (dpt, $^3J_{HH}$ = 6.91 Hz, $^3J_{HH}$ = 2.98 Hz, 1H, H-4′), 3.69 (dd, $^2J_{HH}$ = 8.15 Hz, $^3J_{HH}$ = 6.86 Hz, 1H, H-5′a), 3.85 (pt, J_{HH} = 7.80 Hz, 1H, H-5′b), 3.98 (dpt, $^3J_{HH}$ = 8.72 Hz, $^3J_{HH}$ = 2.98 Hz, 1H, H-3). ^{13}C NMR (C_6D_6, 125 MHz): δ = 19.49 (CH_3), 19.83 (CH_3), 26.29 (CH_3), 27.12 (CH_3), 29.25 (C-4), 32.64 (C-6″), 33.01 (C-5″), 37.53 (C-2″), 66.25 (C-5′), 72.71 (C-5), 76.24 (C-4′), 95.22 (C-3), 110.82 (C-2′), 122.24 (C-3″), 126.53 (C-4″), 217.97 (*cis*-CO), 224.01 (*trans*-CO), 353.02 (*ylidene*-C). FT-IR (cm^{-1}, hexane): ν_{CO} = 2064 (m, $A_1{}^1$), 1987 (vw, B), 1962 (s, sh), 1955 (vs, $A_1{}^2$), 1936 (s, E). MS (EI): *m*/*z* (%) = 456 (M^+, 7), 441 ($M^+ - CH_3$, 5), 400 ($M^+ - 2CO$, 3), 372 ($M^+ - 3CO$, 18), 344 ($M^+ - 4CO$, 33), 316 ($M^+ - 5CO$, 100). HRMS calcd for M^+: 456.0891. Found: 456.0885. **7b** (minor diastereomer): ^{13}C NMR (C_6D_6, 125 MHz): δ = 19.49 (CH_3), 19.83 (CH_3), 26.29 (CH_3), 27.12 (CH_3), 29.10 (C-4), 32.64 (C-6″), 33.01 (C-5″), 37.53 (C-2″), 66.25 (C-5′), 72.78 (C-5), 76.44 (C-4′), 95.62 (C-3), 110.82 (C-2′), 124.25 (C-3″), 124.87 (C-4″), 217.97 (*cis*-CO), 224.08 (*trans*-CO), 353.02 (*ylidene*-C). FT-IR (cm^{-1}, hexane): ν_{CO} = 2064 (m, $A_1{}^1$), 1987 (vw, B), 1962 (s, sh), 1955 (vs, $A_1{}^2$), 1936 (s, E). MS (EI): *m*/*z* (%) = 456 (M^+, 7), 441 ($M^+ - CH_3$, 5), 400 ($M^+ - 2CO$, 3), 372 ($M^+ - 3CO$, 18), 344 ($M^+ - 4CO$, 33), 316 ($M^+ - 5CO$, 100). HRMS calcd for M^+: 456.0891. Found: 456.0885.

X-ray Crystallographic Studies of 2a and 3a.[19] Crystallization of **2a** and **3a** from hexane at −30 °C provided yellow crystals which were subjected to single-crystal X-ray analysis. The structures were solved by direct methods (SHELXS-97).[20] The non-hydrogen atoms were refined anisotropically on F^2 (SHELXL-97).[21] Hydrogen atoms were refined using a riding model. An empirical absorption correction and an extinction correction were applied for **3a**. The absolute structure were determined by refinement of Flack's *x* parameter.[22] Further details are given in Table 1. See also Table 2 and 3 and Figures 1 and 2.

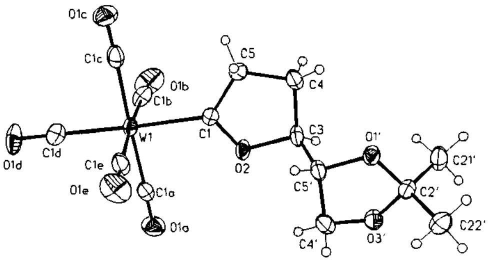

Figure 2. Molecular structure of (2-oxacyclopentylidene)-chromium complex **3a**. (Non-H atoms are shown with 50% probability ellipsoids.)

Acknowledgment. Support by the Volkswagenstiftung, the Graduiertenkolleg "Spektroskopie isolierter und kondensierter Moleküle", and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra for **1a/b**−**7a/b** and crystal structure data for **2a** and **3a**, including tables of crystal data and refinement details, atomic parameters, and bond distances and bond angles (36 pages). Ordering information is given on any current masthead page.

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(19) The numbering of the atoms of complexes **2a** and **3a** used in the text is not in accordance with that used in the ORTEP plot. Atoms C/H-4′ (text) correspond to C/H-5′ (ORTEP), and atoms C/H-5′ (text) correspond to C/H-4′ (ORTEP).

(20) Sheldrick, G. M. SHELXS. *Acta Crystallogr.* **1990**, *A46*, 467.

(21) Sheldrick, G. M. SHELXL-97, Universität Göttingen, FRG, 1997.

(22) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.