Stereospecific *exo*-Selective Diels−Alder Reactions with Carbohydrate-Functionalized α-*exo*-Methylene-2-oxacyclopentylidene Chromium Complexes[1]

Bernd Weyershausen,[†] Martin Nieger,[‡] and Karl Heinz Dötz*,[†]

Kekulé-Institut für Organische Chemie und Biochemie and Institut für Anorganische Chemie, Rheinische Friedrich-Wilhelms-Universität, Gerhard-Domagk-Strasse 1, 53121 Bonn, Germany

Received December 11, 1998

Introduction

Although the primary significance of carbohydrates rests on their major importance in biology, they represent a unique family of polyfunctional compounds that can be chemically manipulated in a multitude of ways. They play important roles in intracellular enzyme transport,[2] as recognition compounds, for example between cells,[3] as antigens,[4] and as blood group substances.[5] Whereas organometallic chemistry is widely used in stereoselective organic synthesis, its impact on carbohydrate chemistry is still underdeveloped. Carbohydrates are used as valuable auxiliaries in stereoselective synthesis.[6] As ligands bound through oxygen to titanium, they allow enantioselective Lewis acid catalyzed Diels−Alder[7] and aldol reactions.[8] In enantioselective catalytic hydroformylation[9] and hydrocyanation,[10] carbohydrates have been used as backbones of bisphosphinite ligands. Apart from the general interest in novel metal−ylidene complexes, we became interested in the combination of carbohydrates and Fischer-type ylidene complexes[11] to investigate the influence of the chiral information provided by the carbohydrate moiety on the stereoselectivity of cycloaddition reactions and to evaluate the potential of these organometallic sugars in the synthesis of natural products. Up to now, there have been only a few examples reported for the chiral modification of the ylidene ligand using carbohydrates.[12] Herein, we report on the synthesis of carbohydrate-functionalized α-*exo*-methylene-2-oxacyclopentylidene chromium complexes and their application to stereospecific *exo*-selective Diels−Alder reactions. This approach is expected to allow the stereoselective formation of spirocenters in bi- and tricyclic compounds bearing a metal ylidene moiety that may be exploited in either subsequent addition reactions to the electrophilic ylidene carbon atom or in template reactions occurring at the chromium carbonyl fragment.

Results and Discussion

An elegant methodology for the synthesis of 2-oxacyclopentylidene complexes is based on the cycloisomerization of ω-alkynols at a coordinatively unsaturated metal template.[13] Thus, we focused our efforts on the preparation of carbohydrate-derived 3-butyn-1-ols.[14] In general, butynols are easily accessible by addition of propargylic organometallics to carbonyl compounds.[15] In our case, however, the reagent of choice turned out to be allenylmagnesium bromide,[16] which undergoes clean γ-addition to the carbonyl functionality of 6-aldehydo-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **1** to give the butynols **2*R*/*S*** in a total yield of 74% as a 3.4:1 mixture of diastereomers (Scheme 1).

As the diastereomeric butynols **2*R*/*S*** could not be separated using chromatographic techniques, they were reacted as a mixture of diastereomers with pentacarbonyl(tetrahydrofuran)chromium(0) generated by UV irradiation of chromium hexacarbonyl in tetrahydrofuran at −10 °C. The cycloisomerization of butynols **2*R*/*S*** at the pentacarbonylchromium template at room temperature gave the 2-oxacyclopentylidene complexes **3*R*/*S*** in a total yield of 60%. The separation of the diastereomeric ylidene complexes was readily achieved by column chro-

* Fax: +49(0)228/735813.
† Kekulé-Institut für Organische Chemie und Biochemie.
‡ Institut für Anorganische Chemie.

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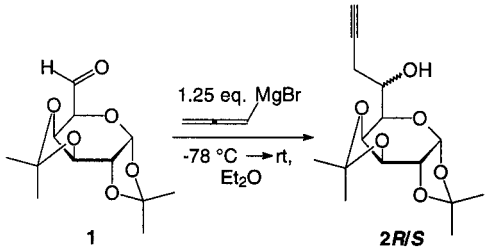
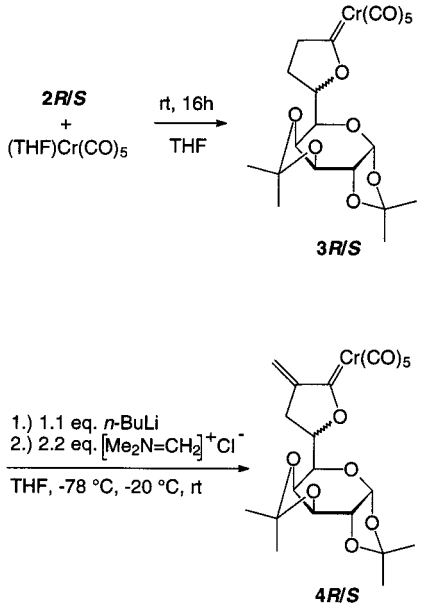
10.1021/jo982427i CCC: $18.00
Published on Web 05/13/1999

Scheme 1. Synthesis of Galactopyranose-Derived Butynols 2*R*/*S*



Scheme 2. Synthesis and α-*exo*-Methylene Functionalization of Carbohydrate-Derived 2-Oxacyclopentylidene Complexes 3*R*/*S*

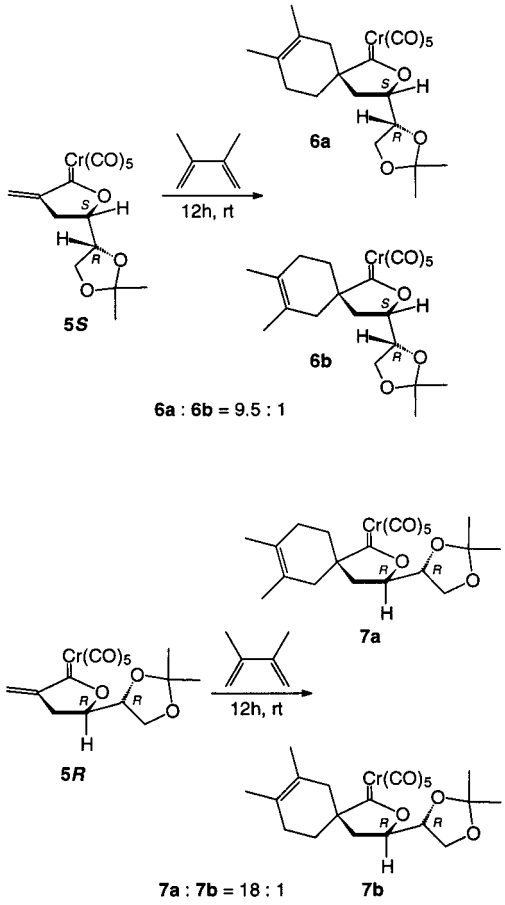


matography using a 2:1 mixture of petroleum ether/diethyl ether (Scheme 2).

The pronounced α-CH acidity[17] of complexes **3*R*/*S*** allows further functionalization into their α-*exo*-methylene derivatives following the procedure reported by Maiorana et al.[18] Deprotonation of **3*R*/*S*** with *n*-butyllithium in tetrahydrofuran at −78 °C and subsequent treatment with *N*,*N*-dimethylmethylene iminium chloride afforded after chromatographic workup complexes 3*R*-pentacarbonyl{3-[1′,2′:3′,4′-di-*O*-isopropylidene-α-L-5′-arabinopyranosyl]-5-methylene-2-oxacyclopentylidene}-chromium(0) (**4*R***) in 50% yield and 3*S*-pentacarbonyl{3-[1′,2′:3′,4′-di-*O*-isopropylidene-α-L-5′-arabinopyranosyl]-5-methylene-2-oxacyclopentylidene}chromium(0) (**4*S***) in 45% yield (Scheme 2).

The synthetic potential of α,*β*-unsaturated ylidene complexes is based on either metal-centered or ylidene ligand-centered cycloaddition reactions[19] such as benzannulation[20,21] or Diels−Alder[22] reactions. Recently, we

Scheme 3. Diels−Alder Reaction of 1′,3′-Dioxacyclopentyl-Substituted Complexes 5*R*/*S* with 2,3-Dimethylbutadiene



have reported first studies on carbohydrate-derived complexes **5*R*/*S***, which were modified into the spirocyclic complexes **6a**,**b** and **7a**,**b** as mixtures of diastereomers upon reaction with 2,3-dimethylbutadiene (Scheme 3).[23] We anticipated that the addition of the 2,3-dimethylbutadiene to the *exo*-methylene double bond should preferentially take place from the sterically less hindered side of the 2-oxacyclopentylidene ring, affording complexes **6a** and **7a** as the major diastereomers.

So far, we were unable to provide experimental evidence for the proposed stereopreference of the addition of 2,3-dimethylbutadiene to the *exo*-methylene double bond of carbohydrate-substituted 2-oxacyclopentylidene complexes. To elucidate the selectivity of the diene addition, we prepared complexes **4*R*/*S*** bearing the — in comparison to complexes **5*R*/*S*** — bulkier arabinopyranosyl substituent at C-3. Furthermore, the exchange of 2,3-dimethylbutadiene for cyclopentadiene as diene reagent was expected to reveal whether the addition to the *exo*-methylene double bond is *exo*-[24] or *endo*-selective. Generally, the [4 + 2] cycloaddition reaction gives the

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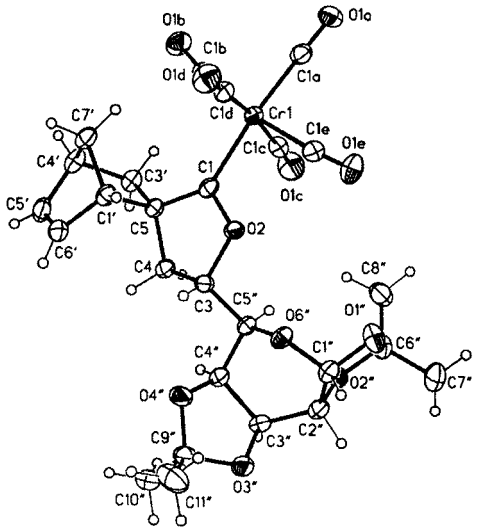
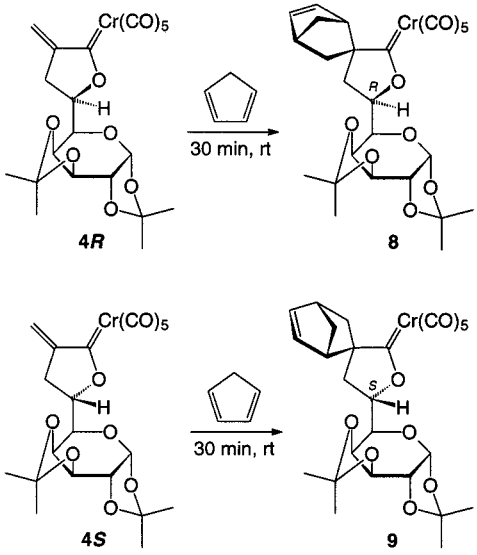


Figure 1. Molecular structure of **9**. Displacement ellipsoids are at the 50% probability level.

Scheme 4. Diels–Alder Reaction of 4*R*/*S* with Cyclopentadiene

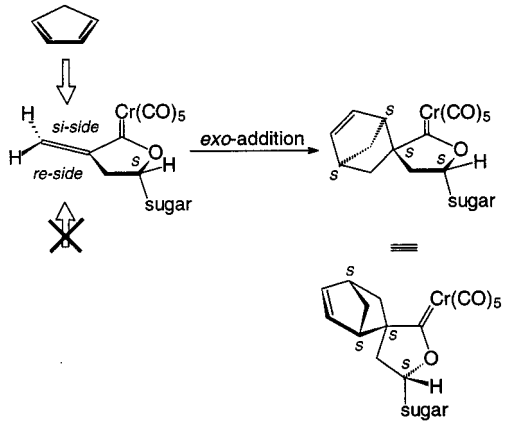


endo products, and there is no general method by which *exo*-products can be obtained,[25] although in some cases *exo*-selectivity has been observed.[26]

When complexes **4*R*/*S*** were reacted with cyclopentadiene at room temperature for 30 min, the spirocyclic cycloaddition products **8** and **9** were obtained as single stereoisomers as determined by ^{1}H NMR spectroscopy of the crude reaction mixtures (Scheme 4).

The absolute configurations of all new stereocenters of compound **9**, including the formerly unknown absolute configuration at C-3, have been determined by single-crystal X-ray analysis to be 3(*S*),5(*S*),1′(*S*),4′(*S*), and the ORTEP plot (Figure 1) shows that the ylidene carbon atom adopts the equatorial position at the spirocyclic center. This result demonstrates an *exo*-selective addition of the diene to the sterically less hindered face (*si* side) of the C=C bond and reflects the steric requirements of the bulky pentacarbonylchromium fragment resulting from the fixed *s-cis* configuration at the metal vinyl ylidene dienophile. It provides experimental evidence for the model developed to explain the stereopreference of the addition of dienes to the *exo*-methylene double bond of complexes **4*R*/*S*** and **5*R*/*S*** (Scheme 5). On the basis of these findings and similar arguments we assume a complementary 3(*R*),5(*R*),1′(*R*),4′(*R*) configuration for the other cycloaddition product **8**.

Scheme 5. *exo*-Stereopreference for the Addition of Dienes to the *exo*-Methylene Double Bond of Sugar-Modified 2-Oxacyclopentylidene Complexes



Conclusions

The [4 + 2] cycloaddition reaction of carbohydrate-functionalized α-*exo*-methylene-2-oxacyclopentylidene complexes with dienes proceeds via unusual *exo* addition of the diene to the dienophile and demonstrates the synthetic potential of sugar-modified organometallics. Through the carbohydrate moiety, a high asymmetric induction is achieved, and the pentacarbonylmetal fragment allows very mild reaction conditions, thus representing an interesting extension of known Diels–Alder reactions regarding the aspects of selectivity and reaction conditions. We are currently investigating the scope of this reaction toward the synthesis of natural product related spirocycles and *C*-glycoside analogues.

Experimental Section

General Information. All reactions, manipulations, and purifications involving organometallics were performed under a dry argon atmosphere using Schlenk techniques. Solvents were dried by distillation from sodium hydride (Et_2O), calcium hydride (petroleum ether, bp 40–60 °C) or potassium/sodium alloy (THF) and saturated with argon. Silica gel (Merck, type 60, 0.063–0.200 mm) was degassed at high vacuum and stored under argon. 1,2:3,4-Di-*O*-isopropylidene-α-D-galactopyranose,[27] 6-aldehydo-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **1**,[28] and allenylmagnesium bromide[16] were prepared according to methods reported previously. All NMR spectra were recorded in C_6D_6.

6*R*/*S*-1,2:3,4-Di-*O*-isopropylidene-6-*C*-(1′-propyn-3′-yl)-α-D-galacto-1,5-pyranose (2*R*/*S*). A 8.5 mL portion of a 2.5 M solution of allenylmagnesium bromide in Et_2O was added at −78 °C dropwise to a solution of 3.5 g (13.6 mmol) of 6-aldehydo-1,2:3,4-di-*O*-isopropylidene-α-D-galacto-pyranose **1** in 250 mL of Et_2O. After 1 h of stirring at −78 °C, the cooling bath was removed, and stirring was continued for another hour. A

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(28) Butterworth: R. F.; Hanessian, S. *Synthesis* **1971**, 70.

saturated aqueous solution of ammonium chloride was added to neutralize the reaction mixture. The organic layer was separated, and the aqueous layer was extracted three times with 50 mL portions of Et_2O. 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 petroleum ether/ethyl acetate 2:1 as eluent gave 3.02 g (10.1 mmol, 74%) of **2*R*/*S*** as a colorless oil containing both diastereomers in a ratio of 3.4:1 as determined by integration of the ^{1}H NMR signals of the alkynyl protons. R_f = 0.38 (petroleum ether/ethyl acetate 1:1). **2*R***: ^{1}H NMR (400 MHz) δ 1.05 (s, 3H), 1.14 (s, 3H), 1.42 (s, 3H), 1.47 (s, 3H), 1.72 (t, ^4J = 2.64 Hz, 1H), 2.60 (dd, ^3J = 4.99 Hz, ^4J = 2.64 Hz, 2H), 3.90−3.96 (m, 1H), 4.05−4.13 (m, 1H), 4.16 (dd, ^3J = 5.09 Hz, ^3J = 2.35 Hz, 1H), 4.41 (dd, ^3J = 8.02 Hz, ^3J = 1.96 Hz, 1H), 4.51 (dd, ^3J = 8.02 Hz, ^3J = 2.35 Hz, 1H), 5.44 (d, ^3J = 4.89 Hz, 1H); ^{13}C NMR (100.6 MHz) δ 24.95, 25.03, 25.63, 26.85, 26.88, 69.00, 69.93, 71.68, 71.82, 71.88, 71.84, 81.75, 97.39, 109.33, 109.83. **2*S***: ^{1}H NMR (400 MHz) δ 1.03 (s, 3H), 1.06 (s, 3H), 1.32 (s, 3H), 1.52 (s, 3H), 1.76 (t, ^4J = 2.64 Hz, 1H), 2.60 (dd, ^3J = 4.99 Hz, ^4J = 2.64 Hz, 2H), 3.90−3.96 (m, 1H), 4.05−4.13 (m, 1H), 4.15 (dd, ^3J = 5.28 Hz, ^3J = 2.35 Hz, 1H), 4.40 (dd, ^3J = 8.02 Hz, ^3J = 2.54 Hz, 1H), 4.51 (dd, ^3J = 8.02 Hz, ^3J = 2.35 Hz, 1H), 5.49 (d, ^3J = 5.09 Hz, 1H); ^{13}C NMR (100.6 MHz) δ 23.45, 24.77, 25.66, 26.58, 26.84, 69.25, 70.73, 71.31, 71.68, 72.09, 71.84, 81.93, 97.54, 109.38, 110.17. **2*R*/*S***: FT-IR (cm^{-1}, film) ν 3487 (s, OH), 3287 (s, C≡CH), 2986 (*vs*, CH), 2937 (*vs*, CH), 2867 (*m*, CH), 2124 (*w*, C≡C); MS (EI, 70 eV) *m*/*z* (%) 283 ($M^+ - CH_3$, 100); HRMS calcd for $M^+ - CH_3$ 283.1182, found 283.1180. Anal. Calcd for $C_{15}H_{22}O_6$: C, 60.39; H, 7.43. Found: C, 60.32; H, 7.62.

3*R*/*S*-Pentacarbonyl{3-[1′,2′:3′,4′-di-*O*-isopropylidene-α-L-5′-arabinopyranosyl]-2-oxacyclopentylidene}chromium-(0) (3*R*/*S*). A solution of 10 mmol of hexacarbonyl chromium in 400 mL of THF was irradiated for 5 h at −10 °C using a mercury vapor lamp (Phillips 125 HPK) and quartz glassware. A color change to orange occurred. After addition of 15 mmol of **2*R*/*S***, 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 petroleum ether/diethyl ether 1:1 as eluent. Chromatography yielded 2.94 g (6 mmol, 60%) of a diastereomeric mixture of **3*R*/*S*** (ratio 3.4:1) as a yellow oil. The separation of the diastereomers was achieved by a second column chromatography using petroleum ether/diethyl ether 2:1 as eluent, affording the separated diastereomers as yellow foams. The NMR assignments were made by 2D-NMR spectroscopy. **3*R***: R_f = 0.51 (petroleum ether/diethyl ether 2:1); $[\alpha]^{20}_D$ −28° (*c* 0.23, $CHCl_3$); ^{1}H NMR (500 MHz) δ 0.99 (s, 3H, CH_3), 1.07 (s, 3H, CH_3), 1.19 (dddd, ^2J = 12.89 Hz, ^3J = 9.38 Hz, ^3J = 9.38 Hz,^3J = 6.41 Hz, 1H, H-4a), 1.33 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.85 (dddd, ^2J = 12.93 Hz, ^3J = 10.03 Hz, ^3J = 5.15 Hz,^3J = 5.15 Hz, 1H, H-4b), 2.96 (ddd, ^2J = 20.68 Hz, ^3J = 9.99 Hz, ^3J = 5.42 Hz, 1H, H-5a), 3.31 (ddd, ^2J = 20.60 Hz, ^3J = 9.77 Hz, ^3J = 6.56 Hz, 1H, H-5b), 3.84 (dd, ^3J = 7.93 Hz, ^3J = 1.22 Hz, 1H, H-4′), 3.96 (dd, ^3J = 3.05 Hz, ^3J = 1.53 Hz, 1H, H-5′), 4.02 (dd, ^3J = 4.73 Hz, ^3J = 2.29 Hz, 1H, H-2′), 4.35 (dd, ^3J = 8.09 Hz, ^3J = 2.29 Hz, 1H, H-3′), 4.75 (ddd, ^3J = 8.62 Hz, ^3J = 4.96 Hz, ^3J = 3.89 Hz, 1H, H-3), 5.23 (d, ^3J = 4.88 Hz, 1H, H-1′); ^{13}C NMR (125.7 MHz) δ 22.50 (C-4), 24.58, 25.39, 26.50, 26.73 (4 × CH_3), 62.29 (C-5), 68.93 (C-5′), 71.51 (C-2′), 71.79 (C-3′), 71.81 (C-4′), 97.13 (C-1′), 98.88 (C-3), 109.66, 110.27 (2 × C_q), 217.64 (*cis*-CO), 224.65 (*trans*-CO), 342.54 (ylidene-C); FT-IR (cm^{-1}, petroleum ether) ν (ν_{CO}) 2066 (*m*, A_1^1), 1987 (*w*, B), 1951 (*vs*, E), 1944 (*sh*, A_1^2); MS (EI, 70 eV) *m*/*z* (%) 490 (4) [M^+], 475 ($M^+ - CH_3$, 6), 462 ($M^+ - CO$, 1), 447 ($M^+ - CO, - CH_3$, 2), 434 ($M^+ - 2CO$, 1), 406 ($M^+ - 3CO$, 1), 391 ($M^+ - 3CO, - CH_3$, 2), 378 ($M^+ - 4CO$, 9), 363 ($M^+ - 4CO, - CH_3$, 3), 350 ($M^+ - 5CO$, 7), 335 ($M^+ - 5CO, - CH_3$, 2), 84 (100); HRMS calcd for M^+ 490.0567, found 490.0579. **3*S***: R_f = 0.34 (petroleum ether/diethyl ether 2:1); $[\alpha]^{20}_D$ −107° (*c* 0.17, $CHCl_3$); ^{1}H NMR (250 MHz) δ 0.81−1.00 (m, 1H, H-4a), 1.01 (s, 3H, CH_3), 1.02−1.25 (m, 1H, H-4b), 1.12 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 2.58 (ddd, ^2J = 20.23 Hz, ^3J = 9.67 Hz, ^3J = 8.51 Hz, 1H, H-5a), 3.30 (ddd, ^2J = 20.29 Hz, ^3J = 9.49 Hz, ^3J = 4.00 Hz, 1H, H-5b), 3.69 (dd, ^3J = 7.39 Hz, ^3J = 1.53 Hz, 1H, H-5′), 3.75 (dd, ^3J = 7.81 Hz, ^3J = 1.59 Hz, 1H, H-4′), 4.07 (dd, ^3J = 4.82 Hz, ^3J = 2.38 Hz, 1H, H-2′), 4.38 (dd, ^3J = 7.93 Hz, ^3J = 2.32 Hz, 1H, H-3′), 4.75 (pq, ^3J = 7.77 Hz, 1H, H-3), 5.38 (d, ^3J = 4.88 Hz, 1H, H-1′); ^{13}C NMR (62.8 MHz) δ 23.41 (C-4), 24.79, 25.38, 26.66, 26.75 (4 × CH_3), 61.18 (C-5), 70.01 (C-5′), 71.31 (C-2′), 71.81 (C-3′, C-4′), 97.14 (C-1′), 98.66 (C-3), 109.47, 110.47 (2 × C_q), 217.64 (*cis*-CO), 224.65 (*trans*-CO), 342.38 (ylidene-C); FT-IR (cm^{-1}, petroleum ether): ν (ν_{CO}) 2066 (*m*, A_1^1), 1987 (*w*, B), 1951 (*vs*, E), 1944 (*sh*, A_1^2); MS (EI, 70 eV) *m*/*z* (%) 490 (M^+, 2), 475 ($M^+ - CH_3$, 5), 462 ($M^+ - CO$, 3), 447 ($M^+ - CO, - CH_3$, 2), 434 ($M^+ - 2CO$, 1), 406 ($M^+ - 3CO$, 1), 378 ($M^+ - 4CO$, 7), 363 ($M^+ - 4CO, - CH_3$, 3), 350 ($M^+ - 5CO$, 10), 335 ($M^+ - 5CO, - CH_3$, 2), 84 (100); HRMS calcd for M^+ 490.0567, found 490.0577.

General Procedure for the α-*exo*-Methylene Functionalization of Complexes 3*R*/*S*. A 0.69 mL portion of *n*-butyllithium (1.1 mmol, 1.6 M solution in hexane) was slowly added at −78 °C to a solution of 490 mg (1 mmol) of **3*R*** and **3*S***, respectively, in 25 mL of THF. After 30 min, 206 mg (2.2 mmol) of *N*,*N*-dimethylmethylene iminium chloride were 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 petroleum ether/diethyl ether 1:1 as eluent.

3*R*-Pentacarbonyl{3-[1′,2′:3′,4′-di-*O*-isopropylidene-α-L-5′-arabinopyranosyl]-5-methylene-2-oxacyclopentylidene}-chromium(0) (4*R*).[29] Chromatography gave 251 mg (0.5 mmol, 50%) of **4*R*** as a red foam: R_f = 0.39 (petroleum ether/diethyl ether 3:1); ^{1}H NMR (400 MHz) δ 0.95 (s, 3H), 1.07 (s, 3H), 1.35 (s, 3H), 1.38 (s, 3H), 2.06 (dd, ^2J = 16.04 Hz, ^3J = 8.61 Hz, 1H), 2.71 (d, ^2J = 16.24 Hz, 1H), 3.91 (s, br, 1H), 3.98 (d, ^3J = 7.43 Hz, 1H), 4.02 (s, br, 1H), 4.38 (d, ^3J = 6.65 Hz, 1H), 4.76 (pt, ^3J = 4.21 Hz, 1H), 5.26 (d, ^3J = 3.91 Hz, 1H) 5.49 (s, br, 1H), 6.39 (s, br, 1 H); ^{13}C NMR (125.7 MHz) δ 24.58, 25.38, 26.55, 26.68, 29.22, 68.85, 71.49, 71.67, 71.75, 94.88, 97.16, 109.63, 110.23, 132.70, 159.18, 218.32, 225.41, 324.63; FT-IR (cm^{-1}, petroleum ether) ν (ν_{CO}) 2064 (*m*, A_1^1), 1987 (*w*, B), 1952 (*vs*, A_1^2, E); MS (EI, 70 eV) *m*/*z* (%) 502 (M^+, 17), 487 ($M^+ - CH_3$, 5), 474 ($M^+ - CO$, 1), 446 ($M^+ - 2CO$, 8), 431 ($M^+ - 2CO, - CH_3$, 14), 418 ($M^+ - 3CO$, 7), 403 ($M^+ - 3CO, - CH_3$, 1), 390 ($M^+ - 4CO$, 53), 362 ($M^+ - 5CO$, 68), 57 (100); HRMS calcd for M^+ 502.0568, found 502.0570.

3*S*-Pentacarbonyl{3-[1′,2′:3′,4′-di-*O*-isopropylidene-α-L-5′-arabinopyranosyl]-5-methylene-2-oxacyclopentylidene}-chromium(0) (4*S*).[29] Chromatography gave 226 mg (0.45 mmol, 45%) of **4*S*** as a red foam: R_f = 0.36 (petroleum ether/diethyl ether 3:1); ^{1}H NMR (500 MHz) δ 0.82−0.89 (m, 2H), 0.98 (s, 3H), 1.10 (s, 3H), 1.34 (s, 3H), 1.38 (s, 3H), 3.72 (dd, ^3J = 7.90 Hz, ^3J = 1.84 Hz, 1H), 3.76 (dd, ^3J = 7.85 Hz, ^3J = 1.99 Hz, 1H), 4.07 (dd, ^3J = 5.02 Hz, ^3J = 2.53 Hz, 1H), 4.38 (dd, ^3J = 7.85 Hz, ^3J = 2.48, 1H), 4.75 (pq, ^3J = 7.75 Hz, 1H), 5.40 (d, ^3J = 4.97 Hz, 1H), 5.43 (pt, J = 2.33, 1H), 6.37 (pt, J = 2.63 Hz, 1H); ^{13}C NMR (125.7 MHz) δ 24.80, 25.36, 26.57, 26.69, 29.52, 69.90, 71.18, 71.81, 71.81, 95.21, 97.16, 109.50, 110.44, 131.95, 158.31, 218.33, 225.51, 324.69; FT-IR (cm^{-1}, petroleum ether) ν (ν_{CO}) 2064 (*m*, A_1^1), 1987 (*w*, B), 1952 (*vs*, A_1^2, E); MS (EI, 70 eV) *m*/*z* (%) 502 (M^+, 7), 487 ($M^+ - CH_3$, 5), 474 ($M^+ - CO$, 2), 459 ($M^+ - CO, - CH_3$, 1), 446 ($M^+ - 2CO$, 4), 431 ($M^+ - 2CO, - CH_3$, 4), 418 ($M^+ - 3CO$, 4), 403 ($M^+ - 3CO, - CH_3$, 6), 390 ($M^+ - 4CO$, 22), 362 ($M^+ - 5CO$, 76), 52 (Cr^+, 100); HRMS calcd for M^+ 502.0568, found 502.0567.

General Procedure for the Diels−Alder Reactions of 4*R*/*S* with Cyclopentadiene. A 100 mg (0.2 mmol) portion of **4*R*** and **4*S*** was dissolved in 5 mL of cyclopentadiene each. After stirring for 30 min at room temperature, the diene was removed. In both reactions, only single stereoisomers were formed as determined by ^{1}H NMR of the crude product. The yellow residue was chromatographed on silica gel using petroleum ether/diethyl ether 3:1 as eluent.

3*R*,5*R*,1′*R*,4′*R*-Pentacarbonyl{3-(1″,2″:3″,4″-di-*O*-isopropylidene-α-L-5″-arabinopyranosyl)spiro[bicyclo[2.2.1]-hept-2′-ene-5′,5−2-oxacyclopent]-1-ylidene}chromium(0) (8).

(29) No clean ^{1}H NMR spectra for **4*R*/*S*** could be obtained because of the instability of these complexes.

Chromatography gave 50 mg (0.09 mmol, 44%) of **8** as a yellow solid, mp 127 °C. The NMR assignments were made by 2D-NMR spectroscopy: R_f = 0.43 (petroleum ether/diethyl ether 3:1); $[\alpha]^{20}_D$ −109° (*c* 0.0108, $CHCl_3$); ^{1}H NMR (250 MHz, C_6D_6) δ 0.82−0.90 (m, 1H, H-7′a), 1.01 (s, 3H, CH_3), 1.12 (s, 3H, CH_3), 1.35−1.44 (m, 1H, H-4a), 1.38 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 1.56−1.71 (m, 2H, H-4b, H-6′a), 2.27 (s, br, 1H, H-4′), 2.67 (d, ^2J = 8.79 Hz, 1H, H-6′b), 2.84 (s, br, 1H, H-1′), 3.09 (dd, ^2J = 12.51 Hz, ^3J = 3.60 Hz, 1H, H-7′b), 4.09 (dd, ^3J = 5.74 Hz, ^3J = 1.59 Hz, 1H, H-5″), 4.10 (dd, ^3J = 4.88 Hz, ^3J = 2.44 Hz, 1H, H-2″), 4.30 (dd, ^3J = 8.00 Hz, ^3J = 1.77 Hz, 1H, H-4″), 4.48 (dd, ^3J = 7.93 Hz, ^3J = 2.32 Hz, 1H, H-3″), 4.82 (ddd, ^3J = 8.76 Hz, ^3J = 6.87 Hz, ^3J = 5.83 Hz, 1H, H-3), 5.34 (d, ^3J = 5.00 Hz, 1H, H-1″), 5.61 (dd, ^3J = 5.62 Hz, ^3J = 3.05 Hz, 1H, H-3′), 5.92 (dd, ^3J = 5.34 Hz, ^3J = 3.11 Hz, 1H, H-2′); ^{13}C NMR (125.7 MHz) δ 24.64, 25.40, 26.64, 26.70 (4 × CH_3), 37.92 (C-4), 39.96 (C-6′), 44.53 (C-1′), 49.20 (C-7′), 51.76 (C-4′), 69.36 (C-5″), 71.63 (C-2″), 71.78 (C-3″), 71.86 (C-4″), 80.08 (C-5), 93.66 (C-1″), 97.34 (C-3), 110.31 (2 × C_q), 135.70, 142.21 (C-3′, C-2′), 217.98 (*cis*-CO), 224.50 (*trans*-CO), 354.83 (ylidene-C); FT-IR (cm^{-1}, *n*-hexane) ν (ν_{CO}) 2062 (*m*, A_1^1), 1985 (*w*, B), 1953 (*vs*, E), 1928 (*s*, A_1^2); MS (EI, 70 eV) *m*/*z* (%) 568 (M^+, 6), 553 ($M^+ - CH_3$, 17), 540 ($M^+ - CO$, 8), 525 ($M^+ - CO, - CH_3$, 11), 484 ($M^+ - 3CO$, 4), 469 ($M^+ - 3CO, - CH_3$, 4), 456 ($M^+ - 4CO$, 39), 441 ($M^+ - 4CO, - CH_3$, 7), 428 ($M^+ - 5CO$, 100); HRMS calcd for M^+ 568.1036, found 568.1041; HRMS calcd for $M^+ - CH_3$ 553.0802, found 553.0801.

3*S*,5*S*,1′*S*,4′*S*-Pentacarbonyl{3-(1″,2″:3″,4″-di-*O*-isopropylidene-α-L-5″-arabinopyranosyl)spiro[bicyclo[2.2.1]-hept-2′-ene-5′,5−2-oxacyclopent]-1-ylidene}chromium(0) (9). Chromatography gave 62 mg (0.11 mmol, 55%) **9** as a yellow solid, mp 122−123 °C. The NMR assignments were made by 2D-NMR spectroscopy: R_f = 0.34 (petroleum ether/diethyl ether 3:1); $[\alpha]^{20}_D$ −109° (*c* 0.0108, $CHCl_3$); ^{1}H NMR (500 MHz) δ 0.78 (dd, ^2J = 12.62 Hz, ^3J = 2.78 Hz, 1H, H-7′a), 0.94 (dd, ^2J = 12.91 Hz, ^3J = 10.93 Hz, 1H, H-4a), 1.04 (s, 3H, CH_3), 1.10 (s, 3H, CH_3), 1.36 (dd, ^2J = 8.89 Hz, ^3J = 1.74 Hz, 1H, H-6′a), 1.44 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 1.54 (dd, ^2J = 13.01 Hz, ^3J = 5.56 Hz, 1H, H-4b), 2.14 (s, br, 1H, H-1′), 2.66 (d, ^2J = 8.94 Hz, 1H, H-6′b), 2.88 (s, br, 1H, H-4′), 3.17 (dd, ^2J = 12.52 Hz, ^3J = 3.68 Hz, 1H, H-7′b), 3.61 (dd, ^3J = 7.95 Hz, ^3J = 1.79 Hz, 1H, H-4″), 3.78 (dd, ^3J = 8.20 Hz, ^3J = 1.64 Hz, 1H, H-5″), 4.13 (dd, ^3J = 4.92 Hz, ^3J = 2.53 Hz, 1H, H-2″), 4.40 (dd, ^3J = 7.95 Hz, ^3J = 2.48 Hz, 1H, H-3″), 4.85 (dd, ^3J = 10.73 Hz, ^3J = 8.25 Hz, ^3J = 5.56 Hz, 1H, H-3), 5.49 (d, ^3J = 4.97 Hz, 1H, H-1″), 5.55 (dd, ^3J = 5.56 Hz, ^3J = 3.18 Hz, 1H, H-2′), 5.92 (dd, ^3J = 5.61 Hz, ^3J = 3.03 Hz, 1H, H-3′); ^{13}C NMR (125.7 MHz) δ = 24.89, 25.47, 26.70, 26.72 (4 × CH_3), 37.30 (C-4), 39.45 (C-6′), 44.49 (C-1′), 49.04 (C-7′), 51.19 (C-4′), 71.32 (C-5″), 71.38 (C-2″), 71.56 (C-3″), 71.88 (C-4″), 79.22 (C-5), 95.01 (C-1″), 97.26 (C-3), 109.69 (C_q), 110.50 (C_q), 135.89, 142.03 (C-2′, C-3′), 217.80 (*cis*-CO), 224.64 (*trans*-CO), 353.70 (ylidene-C); FT-IR (cm^{-1}, *n*-hexane) ν (ν_{CO}) 2062 (*m*, A_1^1), 1985 (*w*, B), 1953 (*vs*, E), 1928 (*s*, A_1^2); MS (EI, 70 eV) *m*/*z* (%) 568 (M^+, 5), 553 ($M^+ - CH_3$, 15), 540 ($M^+ - CO$, 6), 525 ($M^+ - CO, - CH_3$, 11), 484 ($M^+ - 3CO$, 4), 469 ($M^+ - 3CO, - CH_3$, 4), 456 ($M^+ - 4CO$, 39), 441 ($M^+ - 4CO, - CH_3$, 10), 428 ($M^+ - 5CO$, 100); HRMS calcd for M^+ 568.1036, found 568.1040.

X-ray Crystallographic Studies of 9.[30] Crystallyzation of **9** from *n*-hexane at −30 °C provided yellow crystals which were subjected to single-crystal X-ray analysis. The structure was solved by direct methods (SHELXS-97).[31] The non-hydrogen atoms were refined anisotropically on F^2 (SHELXL-97).[32] Hydrogen atoms were refined using a riding model. The absolute structure was determined by refinement of Flack's parameter x.[33] Further details and selected bond lengths and bond angles are given in Tables 1 and 2.

Table 1. Crystallographic Data and Structure Refinement for 9

formula	$C_{26}H_{28}CrO_{11}$
dimensions, mm	0.35 × 0.30 × 0.20
crystal system	orthorhombic
space group	$P2_12_12_1$ (No. 19)
a, Å	10.6278(3)
b, Å	12.6851(3)
c, Å	20.2978(4)
V, Å^3	2736.44(11)
Z	4
ρ_{calcd}, g cm^{-3}	1.38
μ	0.476
F(000)	1184
diffractometer	Enraf−Nonius Kappa-CCD
radiation	Mo Kα
λ, Å	0.71073
T, K	123(2)
max 2θ, deg	56.5
no. of data	22824
no. of unique data	5944
no. of unique data [$I > 2\sigma(I)$]	5150
no. of variables	344
x	0.00(1)
$R(F)^a$	0.026
$wR_2(F^2)$	0.060

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

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 9

Cr(1)−C(1)	2.0518(16)	C(1)−O(2)	1.3144(14)
Cr(1)−C(1A)	1.8805(17)	C(3)−C(5″)	1.5063(19)
Cr(1)−C(1B)	1.8963(17)	C(5)−C(3′)	1.554(2)
Cr(1)−C(1C)	1.8996(18)	C(5)−C(1′)	1.607(2)
Cr(1)−C(1D)	1.9105(17)	C(3′)−C(4′)	1.556(2)
Cr(1)−C(1E)	1.9083(19)	C(5′)−C(6′)	1.317(2)
O(2)−C(1)−Cr(1)	114.38(10)	C(6′)−C(5′)−C(4′)	108.27(16)
O(2)−C(1)−C(5)	107.74(12)	C(5′)−C(6′)−C(1′)	107.44(15)
O(2)−C(3)−C(5″)	107.47(11)	C(4′)−C(7′)−C(1′)	93.77(11)

Acknowledgment. Support by the Graduiertenkolleg "Spektroskopie isolierter und kondensierter Moleküle", the Ministry of Science and Research (NRW), and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **2*R*/*S*−4*R*/*S***, **8**, and **9**. Crystal structure data for **9**, including tables of crystal data and refinement details, atomic parameters, and bond distances and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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(30) The numbering of the atoms of complex **9** used in the text is not in accordance with that used in the ORTEP plot. Atoms C/H-4′ (text) correspond to C/H-1′ (ORTEP), atoms C/H-5′ (text) correspond to C/H-2′ (ORTEP), and C/H-6′ (text) correspond to C/H-3′ (ORTEP).

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(32) Sheldrick, G. M. *SHELXL-97*; Universität Göttingen: Germany, 1997.
(33) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.