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Organotransition metal modified sugars☆ Part 21. Synthesis of organometallic disaccharides bearing two monosaccharide moieties linked by a chromium carbene spacer

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Dedicated to Professor Dieter Sellmann on the occasion of his 60th birthday.

Abstract

Organometallic disaccharides containing a chromium carbene spacer have been synthesized from tetramethylammonium acetyl(pentacarbonyl)chromate(-I) (**1**) in a two-step protocol. An acylation/alcoholysis sequence applying di(isopropylidene)-protected glucose, mannose, galactose and fructose afforded *O*-glycoside methylcarbene complexes **6**–**9** in 29–84% yield. Upon reaction with 1,2:3,4-di-*O*-isopropylidene-α-D-galacto-hexodiald-1,5-ose, activated by $TiCl_4$, they undergo a *trans*-selective aldol condensation to give a 53–89% yield of chromium vinylcarbene *O*,*C*-disaccharides (**10**–**13**) which are promising candidates for subsequent benzannulation, cyclopropanation, Diels–Alder- and Michael addition reactions. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbene complexes; Aldol condensation; *O*- and *C*-glycosides; Organometallic disaccharides

1. Introduction

In the past two decades metal carbenes have been developed to valuable reagents for stereoselective organic synthesis [2]. They have been applied to the synthesis of various natural products such as vitamins [3], antibiotics [4], amino acids and peptides [5]. Their impact on the elaboration of carbohydrates, however, is still limited but increasing [6]. The first incorporation of a sugar moiety into a carbene complex was based on the addition of carbohydrates to isonitrile complexes of gold and platinum to form (glycosyl)aminocarbene and neomycine B complexes [7,8]. A transition metal organometallic functionalization of the anomeric center has been known for glycosyl complexes of cobalt [9], iron [10] and manganese [11] which represent nucleophilic sugar synthons. It was only recently that electrophilic counterparts such as Fischer-type sugar metal carbenes have been synthesized [12]; they have been applied to diastereoselective ligand- or metal-centered cycloaddition such as Diels–Alder [13] and (3 + 2 + 1)benzannulation reactions [14] as well as to *O*- and *C*-glycosidation [15–17]. *O*-Glycosides play a pivotal role in the chemistry and biology of carbohydrates [18,19]; their *C*-analogues [20] are inherently stable towards hydrolysis and gain increasing importance as carbohydrate mimics [21] in antitumor, antibiotic, antiviral or antibacterial therapy [22]. We were interested in organometallic models of this type of reagents, and now report on the synthesis of a combined *O*- and *C*-disaccharide skeleton separated by a metal carbene spacer.

2. Glycosyloxycarbene complexes via acylation/alcoholysis

O-Glycosidated carbene complexes have been obtained by addition of suitably protected monodeproto-

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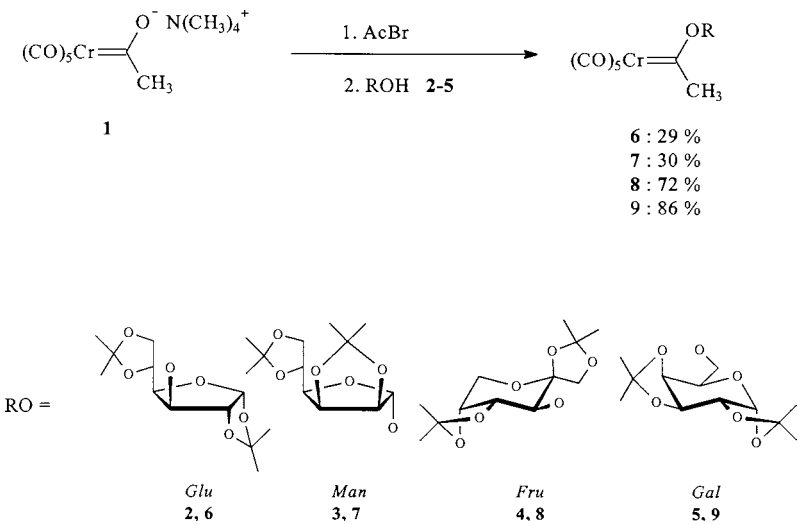
nated carbohydrates to cationic carbyne complexes of manganese and rhenium [23]. Another route was based on the conjugate addition of the sugar moiety to alkynylcarbene complexes of chromium and tungsten to give *O*-glycoside vinylcarbene complexes [24]. We focused on the introduction of the carbohydrate at the chromium carbene center, and applied a combined acylation/alcoholysis protocol previously used in the chiral modification of carbene ligands by amines [25] and terpene alcohols [26]. The low-temperature acylation of tetramethylammonium [acetyl(pentacarbonyl)]chromate (**1**) with acetyl bromide generated the acetoxycarbene complex intermediate which was subjected to an in situ alcoholysis with 1,2:5,6-di-*O*-isopropylidene glucofuranose (**2**), 2,3:5,6-di-*O*-isopropyli -dene mannofuranose (**3**), 1,2:4,5-di-*O*-isopropylidene fructopyranose (**4**) and 1,2:3,4-di-*O*-isopropylidene galactopyranose (**5**); low-temperature chromatographic workup afforded the *O*-glycoside methylcarbene complexes **6**–**9** in 29–86% yield (Scheme 1).

The alcoholysis of the acetoxycarbene intermediate by galactopyranose **5** proceeded smoothly within 3 h at −30°C as described previously for primary alcohols [27]. Under these standard conditions the more bulky secondary carbohydrate alcohols **2**, **3** and **4** gave only disappointingly low yields 5–15% after up to 18 h; previous deprotonation of the sugar by sodium hydride, proton sponge or *N*-ethyldiisopropyl amine resulted in no improvement. A carefully balanced protocol, however, taking into account both the thermolability of the acetoxycarbene intermediate which slowly decomposes above −30°C and the slow addition of secondary alcohols to the metal-coordinated carbene carbon atom [28] allowed for a dramatic increase of the yields. For instance, the yield of the fructopyranose-derived complex **8** raised to 72% within 3 h when a solution of the acetoxycarbene intermediate, generated at −35°C, was transferred via a cannula to the solution of the sugar at 0°C. The alcoholysis with furanoses **2** and **3** containing a less flexible sugar skeleton did not exceed a 30% yield as demonstrated for glucose and mannose complexes **6** and **7**. The chromium carbenes **6**–**9** were purified by flash chromatography at −15°C using dichloromethane to give yellow–orange oils.

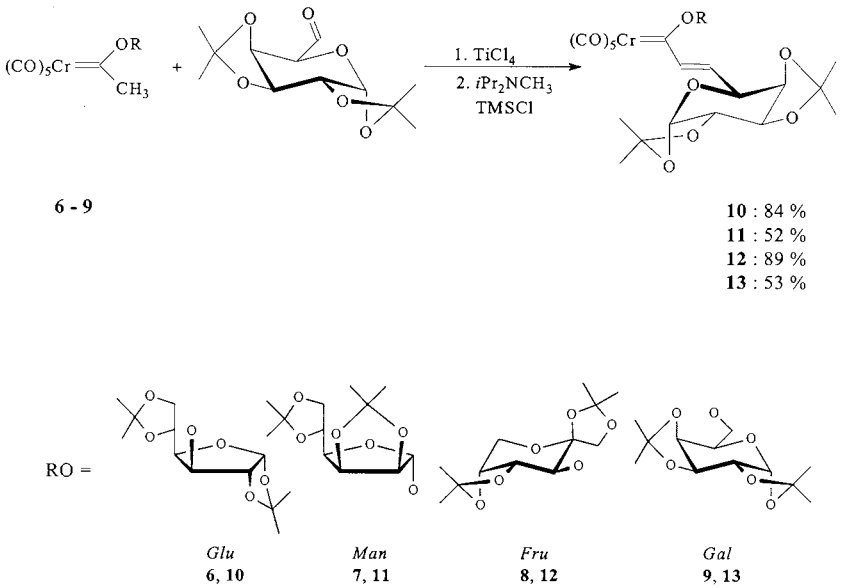
The elucidation of their molecular structure in solution was based on ^{1}H- and ^{13}C-NMR-spectroscopy; the incorporation of the metal carbene moiety into the sugar skeleton did not result in any significant variation of the chemical shifts exept for the CH-hydrogen atoms of the sugar skeleton next to the alkoxycarbene group. The alcoholysis of mannose **3** used as a mixture of anomers afforded the chromium carbene α-*O*-glycoside **7** as a single diastereomer as deduced from a singulet at 6.31 ppm assigned to H-1. The ^{13}C-NMR-spectra reveal a low-intensity (for **6**, **7**, **9**) or broadened (for **8**) signal for the methyl group attached to the carbene carbon atom indicating a restricted rotation around the C–O bond at ambient temperature as suggested for an *E*-configuration. This conclusion is further supported by a broadening of the signals for C-3 and C-6 in the less rigid fructose complex **8**.

3. Disaccharide vinylcarbene complexes via aldol condensation

The aldol condensation of methylcarbene complexes is a convenient route to alkenyl carbene complexes [29]. It was first applied to reactive non-enolizable aldehydes such as benzaldehyde in the presence of triethyl amine where it resulted in quantitative yields [30]. The scope of this methodology can be extended to various aldehydes and ketones if the carbonyl compound is acti-



Scheme 1. Synthesis of chromium carbene *O*-glycosides **6**–**9**.



Scheme 2. Chromium carbene *O*,*C*-disaccharides via aldol condensation.

vated by pre-complexation with a Lewis acid [31]. We applied this approach to the synthesis of vinylcarbene *C*-glycosides from sugar aldehydes. A major problem arose from the activation of 1,2:3,4-di-*O*-isopropylidene-α-D-galacto-hexodialid-1,5-ose by a Lewis acid which had to be compatible with the protective groups. We checked a series of Lewis acids ($SnCl_4$, $BF_3 \cdot Et_2O$, $TiCl_4$) and base/oxophile systems (Et_3N/TMSCl, (*i*-Pr)$_2$EtN/TMSCl, Et_3N/mesyl chloride, pyridine/mesyl chloride and (*i*-Pr)$_2$EtN/mesyl chloride) among which $TiCl_4$ applied at low temperature (-78°C) along with a combination of Hünig's Base (five equivalents) and trimethyl silyl chloride (five equivalents) turned out to be the reagents of choice. Chromium carbene disaccharides **10**–**13** including 1,2:3,4-di-*O*-isopropylidene-α-L-arabinopyranose as a new *C*-glycoside component were obtained as red oils in 52–89% yield after flash chromatography at -15°C using dichloromethane/*tert*-butyl methyl ether (10:1) as eluent (Scheme 2).

In contrast to the activation of sugar-based alkynols at a metal carbonyl template which affords moderate yields of a mixture of *E*/*Z*-isomers [32] the aldol protocol is *trans*-selective. NMR-spectroscopy and HPLC indicate the formation of a single diastereomer bearing an *E*-vinylcarbene C=C bond as established by a coupling constant of $^3J_{H,H} = 15$–16 Hz. The structural elucidation of the products **10**–**13** was mainly based on their ^{1}H- and ^{13}C-NMR-spectra. As already discussed for the fructose complex **8** a similar fluctional behaviour was observed for the D-fructose-L-arabinose disaccharide **12** (Fig. 1).

At room temperature the less rigid fructose skeleton in **12** reveals a restricted rotation around the carbene–oxygen bond as previously outlined for carbene complex **8**. The signals for H-3 and H-7′ appear as broad singlets; a similar broadening is observed for the resonances of H-6′ which appears as a doublet reflecting only the *E*-vicinal coupling across the olefinic C=C bond while the expected vicinal coupling to the adjacent L-arabinose hydrogen atom is not resolved. At a lower temperature (-20°C) well-resolved multiplets are observed for all these hydrogen atoms. The same phenomena, the hindered rotation at room temperature which is frozen at -20°C, is also evident from the ^{13}C-NMR signals for C-3, C-6′, C-7′ and the carbene C signal (Scheme 3). The chromium carbenes **10**, **11** and **13** bearing either a smaller furanose or one CH_2-containing pyranose *O*-glycoside component reveal only broadened signals for C-6′ and C-7′.

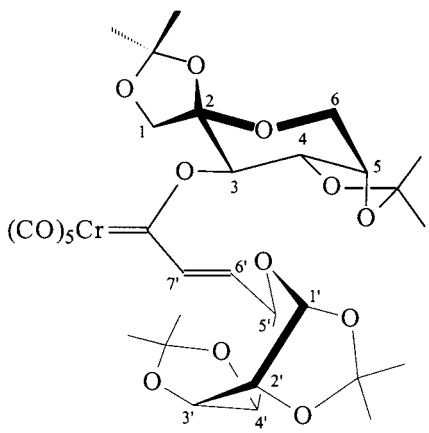
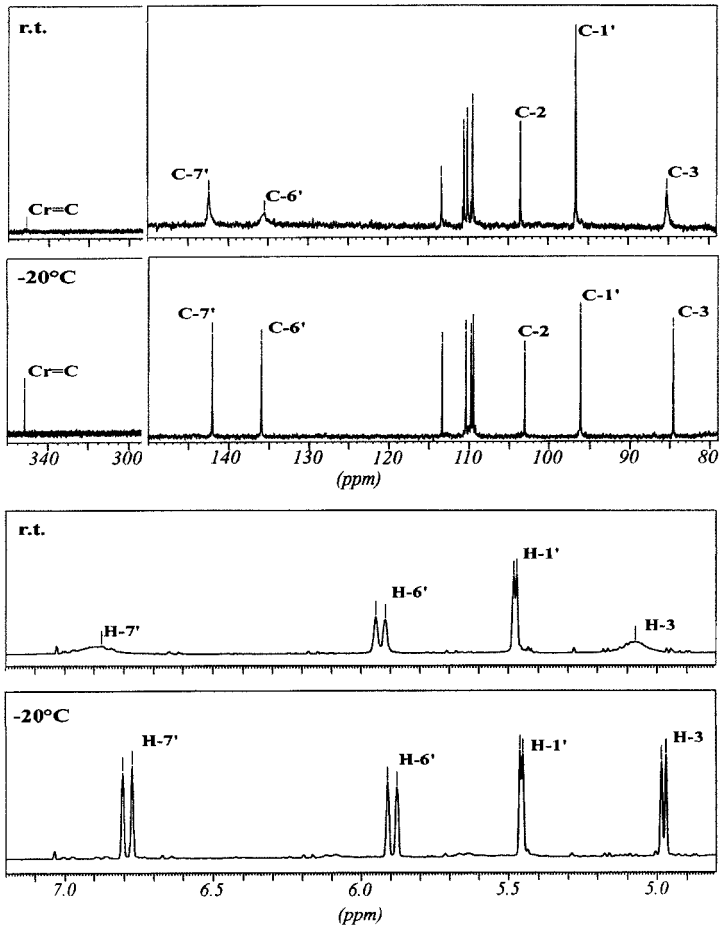


Fig. 1. Numbering of metal vinylcarbene *O*,*C*-disaccharides as shown for pentacarbonyl[1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranosyloxy-(1′,2′:3′,4′-di-*O*-isopropylidene-α-L-arabinopyranosyl-5′-propenylidene)]chromium (**12**).



Scheme 3. Temperature-dependent ^{1}H- and ^{13}C-NMR spectra of vinylcarbene disaccharide **12**.

4. Conclusions

The Lewis acid-assisted aldol condensation of methylcarbene chromium complexes and sugar aldehydes allows a *trans*-selective formation of vinylcarbene *C*-glycosides. It can be extended to a two-step synthesis of organometallic *O*,*C*-disaccharides in which both sugar components are linked by a vinylcarbene spacer. These chromium vinylcarbenes are thermostable and can be readily handled in solution under inert gas atmosphere. They are promising candidates for metal- and ligand-centered stereoselective C–C bond formation such as [3 + 2 + 1]-benzannulation, cyclopropanation, Diels–Alder and Michael addition reactions, and thus allow subsequent diastereoselective transformations directed towards non-natural oligosaccharides.

5. Experimental

5.1. General reaction conditions

All reactions were carried out under dry argon using Schlenk techniques. The solvents used for reactions and chromatography were dried by distillation from calcium hydride and saturated with argon. Silica gel (E. Merck, type 60, 0.63–0.200 mm) was degassed at high vacuum and stored under argon prior to use for chromatography.

5.2. Instruments

IR: Nicolet Magna 550 FT-IR. NMR: Bruker DRX-500, AM-400, AM-250. MS (FAB, EI): Kratos Instruments Concept 1H and MS 50 (70eV). HPLC: Knauer Wellchrom, injection valve A0258, pump K-1001, solvent organizer K-1500, UV detector K-2600, column Knauer Eurospher 100 Si (250 × 4 mm), Eurochrom 2000 for Windows.

5.3. Reagents

The following reagents were prepared according to literature procedures: tetramethylammonium [acetyl-(pentacarbonyl)]chromate(-I) (**1**) [33], 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**2**) [34], 2,3:5,6-di-*O*-isopropylidene-α/β-D-mannofuranose (**3**) [35], 1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranose (**4**) [36],

1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**5**) [37] and 1,2:3,4-di-*O*-isopropylidene-α-D-galacto-hexodiald-1,5-ose [38].

5.4. General procedure for the synthesis of pentacarbonyl[glycosiloxy(methyl)carbene]chromium complexes (6–8) with secondary carbohydrate alcohols

One equivalent of acetyl bromide was added at −35°C to a solution of 2.95 g (10 mmol) tetramethylammonium [acetyl(pentacarbonyl)]chromate (**1**) in 100 ml of CH_2Cl_2. The mixture was stirred for 30 min at this temperature while in a second flask a solution of the sugar (15 mmol) in 30 ml CH_2Cl_2 was cooled at 0°C. The dark red solution of pentacarbonyl[acetoxy(methyl)carbene]chromium was transferred to the sugar solution via cannula. After 3 h the solvent was evaporated, and the residue was purified by chromatography at −15°C using dichloromethane as eluent to give a yellow–orange oil.

5.4.1. Pentacarbonyl[1,2:5,6-di-O-isopropylidene-α-D-glucofuranosyloxy(methyl)carbene]chromium (6)

Yield: 1.37 g (2.87 mmol, 29%). $R_f = 0.58$ (CH_2Cl_2). IR (CH_2Cl_2): $\nu_{(C=O)} = 2063$ m, 1942 vs cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 1.34$ (s, 3H, CH_3), 1.38 (s, 6H, 2 CH_3), 1.51 (s, 3H, CH_3), 2.98 (s, 3H, CH_3), 4.06 (m, 1H, H-5), 4.30 (d, 1H, $^3J = 3.9$ Hz, H-2), 4.53 (dd, 1H, $^3J = 7.5/4.0$ Hz, H-4), 4.63 (d, 1H, $^3J = 3.7$ Hz, H-3), 4.94 (s, 2H, H-6b/H-6a), 6.03 (d, 1H, $^3J = 3.8$ Hz, H-1) ppm. ^{13}C-NMR (62.5 MHz, $CDCl_3$): $\delta = 24.3$, 24.6, 27.2, 27.8 (4 CH_3), 54.9 (CH_3), 68.8 (C-6), 71.2 (C-5), 75.9 (C-3), 81.2 (C-2), 84.6 (C-4), 102.1 (C-1), 107.2, 113.2 ($C(CH_3)_2$), 216.9 (*cis*-CO), 224.2 (*trans*-CO), 360.6 (Cr=C) ppm. MS (EI): m/z (%) = 478 (6) [M^+], 463 (3) [$M^+ - CH_3$], 435 (3) [$M^+ - CH_3$–CO], 422 (3) [$M^+ - 2CO$], 394 (7) [$M^+ - 3CO$], 366 (31) [$M^+ - 4CO$], 338 (58) [$M^+ - 5CO$], 323 (8) [$M^+ - CH_3 - 5CO$], 129 (24) [$C_6H_9O_3^+$], 113 (100) [$C_6H_9O_2^+$], 59 (26) [$C_3H_7O^+$]. HR-MS: Calc. for M^+: 478.0567; Found: 478.0560.

5.4.2. Pentacarbonyl[2,3:5,6-di-O-isopropylidene-α-D-mannofuranosyloxy(methyl)carbene]chromium (7)

Yield: 1.45 g (3.03 mmol, 30%). $R_f = 0.60$ (CH_2Cl_2). IR (CH_2Cl_2): $\nu_{(C=O)} = 2065$ m, 1945 vs cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 1.38$ (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 3.04 (s, 3H, CH_3), 3.99 (dd, 1H, $J = 8.8/4.6$ Hz, H-6b), 4.10 (dd, 1H, $J = 8.9/6.1$ Hz, H-6a), 4.18 (dd, 1H, $^3J = 7.4/3.2$ Hz, H-4), 4.44 (m, 1H, H-5), 5.04 (dd, 1H, $^3J = 8.1/4.9$ Hz, H-3), 5.07 (d, 1H, $^3J = 5.9$ Hz, H-2), 6.31 (s, 1H, H-1) ppm. ^{13}C-NMR (62.5 MHz, $CDCl_3$): $\delta = 24.5$, 25.1, 25.8, 26.7 (4 CH_3), 47.8 (CH_3), 66.5 (C-6), 72.6 (C-5), 79.3 (C-3), 83.3 (C-4), 85.2 (C-2), 109.4 (C-1), 110.3, 113.6 ($C(CH_3)_2$), 215.8 (*cis*-CO), 223.8 (*trans*-CO), 362.8 (Cr=C) ppm. MS (EI): m/z (%) = 478 (1) [M^+], 463 (4) [$M^+ - CH_3$], 435 (7) [$M^+ - CH_3$–CO], 422 (3) [$M^+ - 2CO$], 394 (12) [$M^+ - 3CO$], 366 (8) [$M^+ - 4CO$], 351 (9) [$M^+ - 4CO - CH_3$], 338 (19) [$M^+ - 5CO$], 323 (10) [$M^+ - CH_3 - 5CO$], 185 (76) [*Man*$^+ - (CH_3)_2CO$], 101 (100) [$C_5H_{11}O_2^+$], 85 (37) [$C_4H_5O_2^+$], 69 (29) [$C_4H_5O^+$], 59 (26) [$C_3H_7O^+$]. HR-MS: Calc. for M^+: 478.0567; Found: 478.0568.

5.4.3. Pentacarbonyl[1,2:4,5-di-O-isopropylidene-β-D-fructopyranosyloxy(methyl)carbene]chromium (8)

Yield: 3.45 g (7.23 mmol, 72%). $R_f = 0.64$ (CH_2Cl_2). IR (CH_2Cl_2): $\nu_{(C=O)} = 2064$ m, 1944 vs cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 1.36$ (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 3.09 (s, 3H, CH_3), 3.84 (d, 1H, $^2J = 8.94$ Hz, H-1b), 4.04 (d, 1H, $^2J = 8.94$ Hz, H-1a), 4.08 (d, 1H, $^3J = 13.41$ Hz, H-6b), 4.27 (dd, 1H, $J = 13.41/2.88$ Hz, H-6a), 4.37 (dd, 1H, $^3J = 5.96/2.48$ Hz, H-4), 4.55 (pt, 1H, $^3J = 6.35$ Hz, H-5), 5.06 (s, 1H, H-3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 26.3$, 26.7, 27.1, 28.2 (4 CH_3), 45.9 (CH_3), 61.5 (C-6), 72.6 (C-1), 74.2 (C-5), 75.6 (C-4), 84.1 (C-3), 103.4 (C-2), 110.6, 113.6 ($C(CH_3)_2$), 216.8 (*cis*-CO), 224.6 (*trans*-CO), 362.1 (Cr=C) ppm. MS (EI): m/z (%) = 478 (20) [M^+], 463 (4) [$M^+ - CH_3$], 435 (3) [$M^+ - CO - CH_3$], 422 (12) [$M^+ - 2CO$], 394 (10) [$M^+ - 3CO$], 366 (100) [$M^+ - 4CO$], 338 (35) [$M^+ - 5CO$], 323 (11) [$M^+ - 5CO - CH_3$], 59 (50) [$C_2H_3O_2^+$]. HR-MS: Calc. for M^+: 478.0567; Found: 478.0567.

5.5. Synthesis of pentacarbonyl[1,2:3,4-di-O-isopropylidene-α-D-galactopyranosyloxy(methyl)carbene]chromium (9)

One equivalent of acetyl bromide was added at −35°C to a solution of 2.95 g (10 mmol) tetramethylammonium [acetyl(pentacarbonyl)]chromate (**1**) in 100 ml of CH_2Cl_2. The mixture was stirred for 30 min at this temperature, and 1.5 equivalents of [1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**5**) in 30 ml CH_2Cl_2 were added dropwise to the dark red solution. After 3 h at −30°C the solvent was evaporated, and the residue was purified by chromatography at −15°C using dichloromethane as eluent to give an orange oil. Yield: 4.12 g (8.63 mmol, 86%). $R_f = 0.75$ (CH_2Cl_2). IR (CH_2Cl_2): $\nu_{(C=O)} = 2064$ m, 1942 vs cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 1.36$ (s, 6H, 2 CH_3), 1.46 (s, 3H, CH_3), 1.54 (s, 3H, CH_3), 2.98 (s, 3H, CH_3), 4.35–4.38 (m, 2H, H-5/H-4), 4.39 (dd, 1H, $^3J = 5.1/2.6$ Hz, H-2), 4.69 (dd, 1H, $^3J = 7.6/2.4$ Hz, H-3), 4.96 (s, 2H, H-6a/H-6b), 5.57 (d, 1H, $^3J = 5.0$ Hz, H-1) ppm. ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ = 24.8, 25.2, 26.3, 27.4 (4 CH_3), 49.9 (CH_3), 66.9 (C-5), 70.8 (C-2), 71.1 (C-4), 71.2 (C-3), 78.2 (C-6), 96.7 (C-1), 109.4, 110.4 ($C(CH_3)_2$), 216.7 (*cis*-CO), 224.0 (*trans*-CO), 360.4 (Cr=C) ppm. MS (EI): m/z (%) = 478 (20) [M^+], 463

(26) [$M^+ - CH_3$], 435 (18) [$M^+ - CO - CH_3$], 394 (28) [$M^+ - 3CO$], 366 (55) [$M^+ - 4CO$], 338 (100) [$M^+ - 5CO$], 323 (49) [$M^+ - 5CO - CH_3$], 245 (25) [$Gal^+ - CH_3$], 81 (43) [$C_4H_5O_2$], 69 (30) [$C_4H_5O^+$], 59 (39) [$C_2H_3O_2^+$]. HR-MS: Calc. for M^+: 478.0567; Found: 478.0560.

5.6. General procedure for the synthesis of vinylcarbene disaccharides (**10**–**13**)

A total of 1.00 g (2.09 mmol) of the carbohydrate carbene complex **6**–**9** was dissolved in 30 ml of *tert*-butyl methyl ether and deprotonated with one equivalent of *n*-BuLi at −78°C for 1 h. In a separate flask, a solution of $TiCl_4$ (4.18 mmol) in 5 ml CH_2Cl_2 was cooled to −78°C, and 1,2:3,4-di-*O*-isopropylidene-α-D-galacto-hexodialdo-1,5-ose (4.18 mmol) was quickly added. After 5 min the solution of the enolate of carbene complex **6**–**9** was transferred to the orange aldehyde/Lewis acid complex via cannula. The brown solution was allowed to warm to −60°C over 10 min. Then five equivalents of Hünig's Base and five equivalents of TMSCl were added, and the black solution was stirred for 1 h at −20°C. The reaction was monitored by IR-spectroscopy and TLC. After completion of the reaction the solution was filtrated and the solvent was evaporated. The residue was purified by chromatography at −15°C using *tert*-butyl methyl ether/dichloromethane (1:10) as eluent to give a red oil; as the methylcarbene complex precursor **6**–**9** it could not be completely freed from traces of solvent which hampered correct elemental analyses.

5.6.1. Pentacarbonyl[1,2:5,6-di-O-isopropylidene-α-D-glucofuranosyloxy-(1′,2′:3′,4′-di-O-isopropylidene-α-L-arabinopyranosyl-5′-propenylidene)]chromium (**10**)

Yield: 1.26 g (1.76 mmol, 84%). $R_f = 0.54$ (CH_2Cl_2). IR (CH_2Cl_2): $\nu_{(C=O)} = 2061$ m, 1948 vs cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 1.31$ (s, 3H, CH_3), 1.34 (s, 6H, 2 CH_3), 1.35 (s, 3H, CH_3), 1.37 (s, 6H, 2CH_3), 1.40 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 4.09 (td, 1H, $^3J = 7.3/3.3$ Hz, H-5), 4.26 (dd, 1H, $^3J = 7.8/2.1$ Hz, H-4′), 4.28 (d, 1H, $^3J = 3.9$ Hz, H-2), 4.35 (dd, 1H, $^3J = 5.1/2.5$ Hz, H-2′), 4.42 (m, 1H, H-5′), 4.50 (dd, 1H, $^3J = 7.5/3.8$ Hz, H-4), 4.61 (d, 1H, $^3J = 3.7$ Hz, H-3), 4.64 (dd, 1H, $^3J = 7.8/2.5$ Hz, H-3′), 4.99 (dd, 1H, $J = 11.0/6.9$ Hz, H-6b), 5.07 (dd, 1H, $J = 11.0/3.3$ Hz, H-6a), 5.60 (d, 1H, $^3J = 4.9$ Hz, H-1′), 6.03 (d, 1H, $^3J = 3.8$ Hz, H-1), 6.16 (dd, 1H, $^3J = 15.1/4.8$ Hz, H-6′), 7.45 (d, 1H, $^3J = 15.0$ Hz, H-7′) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 24.5$, 25.1, 25.5, 26.5, 26.8, 27.2, 27.6, 27.8 (8 CH_3), 68.2 (C-5′), 71.1, 71.4, 71.6 (C-2′/C-4′/C-5), 73.6 (C-3′), 75.8 (C-3), 79.4 (C-6), 80.0 (C-2), 84.6 (C-4), 97.0 (C-1′), 102.0 (C-1), 107.2, 109.4, 110.4, 113.1 (4 $C(CH_3)_2$), 130.7 (C-6′), 143.5 (C-7′), 216.9 (*cis*-CO), 225.0 (*trans*-CO), 337.6 (Cr=C) ppm. MS (FAB): m/z (%) = 718.1 (2) [M^+], 703 (2) [$M^+ - CH_3$], 520 (100) [$M^+ - 5CO - (CH_3)_2CO$], 501 (9) [$MH^+ - Ara - CH_3$], 462 (18) [$M^+ - 5CO - 2(CH_3)_2CO$], 245 (36) [$Glu^+ - CH_3$].

5.6.2. Pentacarbonyl[2,3:5,6-di-O-isopropylidene-α-D-mannofuranosyloxy-(1′,2′:3′,4′-di-O-isopropylidene-α-L-arabinopyranosyl-5′-propenylidene)]chromium (**11**)

Yield: 0.78 g (1.09 mmol, 52%). $R_f = 0.64$ (CH_2Cl_2). IR (CH_2Cl_2): $\nu_{(C=O)} = 2061$ m, 1954 vs cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 1.32$ (s, 6H, 2 CH_3), 1.34 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 4.01 (dd, 1H, $J = 8.9/4.6$ Hz, H-6b), 4.03 (dd, 1H, $J = 8.8/4.3$ Hz, H-6a), 4.16 (dd, 1H, $^3J = 7.8/3.5$ Hz, H-4), 4.29 (dd, 1H, $^3J = 7.7/2.0$ Hz, H-4′), 4.37 (dd, 1H, $^3J = 4.9/2.5$ Hz, H-5′), 4.45 (m, 1H, H-5), 4.48 (m, 1H, H-5′), 4.66 (dd, 1H, $^3J = 7.7/2.5$ Hz, H-3′), 5.01 (dd, 1H, $J = 5.8/3.5$ Hz, H-3), 5.05 (d, 1H, $J = 5.9$ Hz, H-2), 5.61 (d, 1H, $^3J = 4.9$ Hz, H-1′), 6.10 (dd, 1H, $^3J = 15.3/4.3$ Hz, H-6′), 6.46 (s, 1H, H-1), 7.49 (d, 1H, $^3J = 15.2$ Hz, H-7′) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 25.1$, 25.5, 25.9, 26.5, 26.6, 26.8, 27.5, 27.7 (8 CH_3), 67.5 (C-6), 68.0 (C-5′), 71.0, 71.6 (C-2′/C-4′), 73.2 (C-5), 73.4 (C-3′), 80.2 (C-3), 83.9 (C-4), 85.9 (C-2), 97.1 (C-1′), 109.5 (C-1), 110.2, 110.5, 111.6, 114.3 (4 $C(CH_3)_2$), 131.3 (C-6′), 143.7 (C-7′), 216.6 (*cis*-CO), 225.6 (*trans*-CO), 340.1 (Cr=C) ppm. FAB-MS: m/z (%) = 718 (1) [M^+], 703 (2) [$M^+ - CH_3$], 520 (100) [$M^+ - 5CO - (CH_3)_2CO$], 501 (27) [$MH^+ - Ara - CH_3$], 431 (26) [$M^+ - AraC_2H_2 - CO - 2CH_3$].

5.6.3. Pentacarbonyl[1,2:4,5-di-O-isopropylidene-β-D-fructopyranosyloxy-(1′,2′:3′,4′-di-O-isopropylidene-α-L-arabinopyranosyl-5′-propenylidene)]chromium (**12**)

Yield: 1.33 g (1.86 mmol, 89%). $R_f = 0.49$ (CH_2Cl_2). IR (CH_2Cl_2): $\nu_{(C=O)} = 2061$ m, 1952 vs cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 1.27$ (s, 3H, CH_3), 1.32 (s, 6H, 2 CH_3), 1.33 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 1.56 (s, 3H, CH_3), 3.74 (d, 1H, $^2J = 8.8$ Hz, H-1b), 3.88 (d, 1H, $^2J = 8.9$ Hz, H-1a), 4.02 (d, 1H, $^2J = 13.4$ Hz, H-6b), 4.18 (dd, 1H, $J = 13.5/2.7$ Hz, H-6a), 4.23 (dd, 1H, $J = 7.9/1.6$ Hz, H-2′/3′/4′), 4.29-4.31 (m, 2H, H-5, H-2′/3′/4′), 4.56 (d, 1H, $^3J = 7.3$ Hz, H-4), 4.59-4.62 (m, 2H, H-5′, H-2′/3′/4′), 5.08 (s, 1H, H-3), 5.47 (d, 1H, $^3J = 4.9$ Hz, H-1′), 5.93 (d, 1H, $^3J = 16.6$ Hz, H-6′), 6.87 (s, 1H, H-7′) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 24.7$, 25.5, 26.4, 26.7, 26.8, 27.3, 27.6, 28.1 (8 CH_3), 61.0 (C-6), 67.5 (C-5′), 71.1, 71.2 (C-2′/C-4′), 71.9 (C-1), 72.6, (C-3′), 74.1 (C-5), 75.3 (C-4), 85.2 (C-3), 96.6 (C-1′), 103.5 (C-2), 109.4, 110.1, 110.5, 113.6 (4 $C(CH_3)_2$), 135.5 (C-6′), 142.4 (C-7′), 216.7 (*cis*-CO), 225.5 (*trans*-CO), 350.8 (Cr=C) ppm. MS (FAB): m/z (%) = 718 (2) [M^+], 703 (2) [$M^+ - CH_3$], 662 (1) [$M^+ - 2CO$], 619 (0.6) [$M^+ - 3CO - CH_3$], 578 (45) [$M^+ - 5CO$], 520 (100)

$[M^+ - 5CO-(CH_3)_2CO]$, 518 (6) $[M^+ - 5CO-CH_3COOH]$, 462 (7) $[M^+_{578} - 2(CH_3)_2CO]$.

*5.6.4. Pentacarbonyl[1,2:3,4-di-O-isopropylidene-α-D-galactopyranosyloxy-(1′,2′:3′,4′-di-O-isopropylidene-α-L-arabinopyranosyl-5′-propenylidene)]chromium **(13)***

Yield: 0.79 g (1.10 mmol, 53%). $R_f = 0.52$ (CH_2Cl_2). IR (CH_2Cl_2): $\nu_{(C=O)} = 2061$ m, 1944 vs cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 1.31$ (s, 3H, CH_3), 1.34 (s, 9H, 3 CH_3), 1.40 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.52 (s, 6H, 2 CH_3), 4.29 (d, 1H, $^3J = 7.4$ Hz, H-4), 4.34-4.40 (m, 4H, H-2, H-5, H2′, H-4′), 4.44 (m, 1H, H-5′), 4.64 (d, 1H, $^3J = 7.2$ Hz, H-3′), 4.67 (d, 1H, $^3J = 6.8$ Hz, H-3), 5.00 (m, 1H, H-6b), 5.09 (m, 1H, H-6a), 5.56 (d, 1H, $^3J = 4.7$ Hz, H-1′), 5.60 (d, 1H, $^3J = 4.8$ Hz, H-1), 6.14 (dd, 1H, $^3J = 15.3/3.7$ Hz, H-6′), 7.50 (d, 1H, $^3J = 15.0$ Hz, H-7′) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 24.8$, 24.9, 25.2, 25.3, 26.2, 26.3, 26.4, 26.5 (8 CH_3), 67.0, 67.7 (C-5, C-5′), 70.8, 70.9, 71.1, 71.2, 71.3 (C-2, C-3, C-4, C-2′, C-4′), 73.1 (C-3′), 78.3 (C-6), 96.6, 96.8 (C-1, C-1′), 109.1, 109.3, 110.1, 110.3 (4 $C(CH_3)_2$), 129.7 (C-6′), 143.6 (C-7′), 216.6 (*cis*-CO), 224.8 (*trans*-CO), 336.9 (Cr=C) ppm. MS (FAB): m/z (%) = 718 (3) $[M^+]$, 703 (2) $[M^+ - CH_3]$, 648 (9) $[MH^+ - 2CO-CH_3]$, 628 (33) $[M^+ - CH_3CO_2H - 2CH_3]$, 578 (16) $[M^+ - 5CO]$, 558 (6) $[M^+_{578} - 2CH_3]$, 543 (12) $[M^+_{578} - 3CH_3]$, 520 (100) $[M^+ - 5CO-(CH_3)_2CO]$, 505 (8) $[M^+_{578} - CH_3COOH-CH_3]$, 462.1 (35) $[M^+_{578} - 2(CH_3)_2CO]$.

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