

Organotransition metal modified sugars

4. Carbene complex functionalized acyclic carbohydrates¹

K.H. Dötz^{a,*}, R. Ehlenz^a, W. Straub^a, J.C. Weber^a, K. Airola^a, M. Nieger^b

^a Institut für Organische Chemie und Biochemie der Universität Bonn, Gerhard-Domagk-Strasse 1, D-53121 Bonn, Germany

^b Institut für Anorganische Chemie der Universität Bonn, Gerhard-Domagk-Strasse 1, D-53121 Bonn, Germany

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Abstract

A synthetic strategy based on a combination of sugar electrophiles and transition metal nucleophiles allows the metal carbene functionalization of acyclic carbohydrates. Following this methodology the per-*O*-acetylated methoxycarbene complexes **8–14** are prepared in moderate to good yields. Upon reaction with ammonia they undergo aminolysis to give the aminocarbene complexes **16–18**. ¹H-NMR studies indicate that in solution the D-galacto and L-arabino complexes adopt extended planar zigzag conformations. A similar conformational preference is observed for the solid state as established by X-ray studies on the D-galacto derivatives **8** and **15**. © 1997 Elsevier Science S.A.

Keywords: Optically active carbene complexes; Carbohydrates; Glycosyl carbene complexes; Conformation of carbohydrates

1. Introduction

Fischer-type carbene complexes are of manifold use in stereoselective organic synthesis [2]. Their synthetic potential covers metal- and ligand-centered cycloaddition reactions, reactions based on photochemically generated ketene equivalents as well as their role as organometallic enolate analogs in aldol- and Michael-addition reactions. Transferring the synthetic potential of organometallic reagents onto carbohydrate chemistry still remains a challenge and essentially has been limited to stannylated and lithiated compounds. Transition metals have had only a minor impact on the modification of carbohydrates so far, and examples of transition metal functionalized sugars are very rare [3–5]. Glycosyl complexes of manganese [4] and iron [5] have been prepared and have been used as carbohydrate nucleophiles in synthesis; for instance, the manganese compounds have been applied to the synthesis of C-glycosides under high pressure conditions. We intend to incorporate the sugar skeleton into an electrophilic metal carbene functionality and thus to transfer the synthetic potential of Fischer-type complexes to the synthesis of carbohydrates [6].

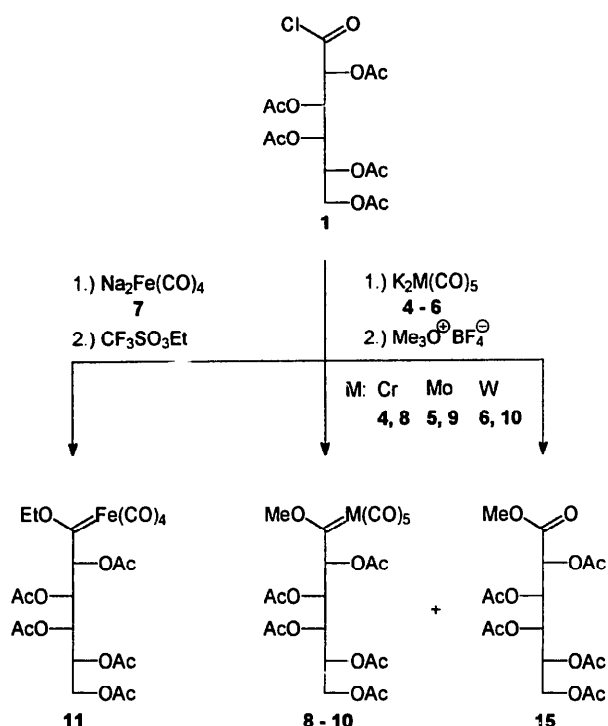
Recently, we reported the synthesis of group VIb and VIIIb metal carbene C-1 functionalized D-galacto sugars combining a galactonic acid chloride electrophile and carbonyl metalate nucleophiles [7]. During this work we became interested in whether the incorporation of the bulky organometallic fragment at the C-1 terminus might have an impact on the conformation along the carbohydrate skeleton. Generally, acyclic sugars prefer an extended planar zigzag conformation P unless severe *syn*-1,3-interactions enforce rotation around one or more C–C bonds to generate bent “sickle” conformations G [8–15] (for the G,P-terminology, see Ref. [16]). We now report on the synthesis of metal carbene functionalized acyclic carbohydrates and further present a comparative conformational study focusing on the D-galactose carbene complex **8** and the isolobal-analogous methyl galactonate **15** based on ¹H-NMR studies in solution and X-ray analysis in the solid state.

2. Synthesis of mono- and biscarbene complexes

The incorporation of the C-1 carbon atom of an acyclic carbohydrate into a metal carbene functionality is achieved by a combination of a sugar electrophile and a metalate nucleophile. The carbonyl chromate, molyb-

* Corresponding author.

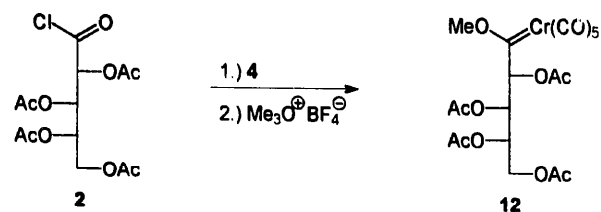
¹ For part 3, see Ref. [1].



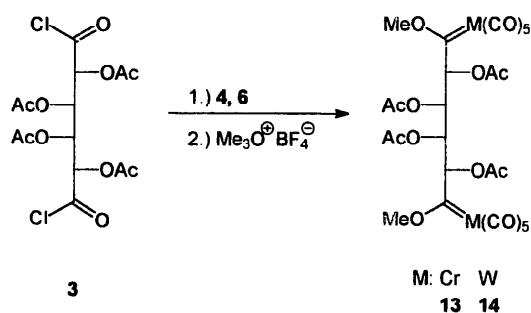
Scheme 1. Synthesis of D-galacto carbene complexes 8–11.

date, tungstate and ferrate 4–7 obtained by reduction of the binary metal carbonyl with graphite potassium or sodium [17] undergo addition to carbohydrate electrophiles such as 2,3,4,5,6-penta-*O*-acetyl-D-galactonyl chloride 1 at low temperature. The resulting acyl metalate intermediates are alkylated by trimethyloxonium tetrafluoroborate or ethyl trifluoromethanesulfonate to give the carbene complexes 8–11 in moderate to good yields (Scheme 1). In the iron series, alkylation is known to occur at the metal center to give Collman-type products and/or at the acyl oxygen to generate alkoxy-carbene complexes [18]. However, *O*-alkylation is favoured if ethyl trifluorosulfonate is used as alkylating agent in the presence of HMPA. The metal carbenes are fairly stable compounds; they can be handled in air for a limited period of time without any notable decomposition; nevertheless, if handled in solution application of inert gas and low temperature is required.

The synthetic approach can be extended to the preparation of pentose-derived metal carbenes as well as to carbohydrate-bridged biscarbene complexes. The reac-



Scheme 2. Synthesis of L-arabino chromium carbene complex 12.



Scheme 3. Synthesis of the biscarbene complexes 13 and 14.

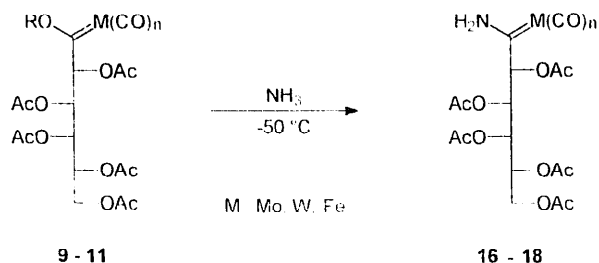
tion of pentacarbonylchromate 4 with 2,3,4,5-tetra-*O*-acetyl-L-arabinyloxy chloride 2 followed by alkylation yields the L-arabino-chromium carbene complex 12 (Scheme 2).

Similarly, the sugar electrophile/metalate nucleophile approach can be applied to bifunctional aldaric acid derivatives such as 2,3,4,5-tetra-*O*-acetyl-D-galactaroyl chloride 3. After alkylation the chromium and tungsten biscarbenes 13 and 14 are obtained even though the yields are much lower (Scheme 3).

In a first attempt to functionalize the sugar-modified carbene complexes, the metal alkoxycarbenes 9–11 were subjected to aminolysis. Upon reaction with ammonia under mild low temperature conditions the alkoxy substituent is replaced by NH_2 without affecting the acetyl protecting groups (Scheme 4). Simple evaporation of the solvent affords analytically and spectroscopically pure compounds 16–18; no chromatographic workup procedure is required.

3. Spectroscopic characterization

All compounds described above exhibit the spectroscopic properties characteristic for carbene complexes [19]. As a consequence of the coordination to the metal center their C-1 carbon atoms (and C-6, respectively, in metal biscarbenes 13 and 14) reveal a significant downfield shift in the ^{13}C -NMR spectra. The deshielding influence of the metal carbene moiety further effects the adjacent carbon atom. The better donor capacity of the amino substituent in 16–18 is reflected by a significant



Scheme 4. Aminolysis of D-galacto carbene complexes 9–11.

Table 1
Selected ^{13}C -NMR data of sugar metal carbenes **8–14** and **16–18**

Complex	$\text{C}_{\text{carbene}}$	<i>trans</i> -CO	<i>cis</i> -CO	C-2
8	355.0	223.0	215.5	84.5
9	346.2	212.5	204.8	84.4
10	328.2	202.5	196.6	86.0
11	327.6	212.5		85.0
12	355.4	223.0	215.4	84.6
13	354.7	223.0	215.5	84.3
14	328.4	203.1	196.6	86.2
16	272.2	212.1	205.7	81.8
17	261.0	201.8	197.2	84.0
18	270.1	214.9		81.3

upfield shift of the $\text{C}_{\text{carbene}}$ resonances compared with their alkoxy-carbene precursors **9–11**. (See Table 1.)

4. Conformational studies in solution

The conformation along the carbohydrate skeleton in solution has been studied by ^1H -NMR spectroscopy. Based on previous work vicinal coupling constants $^3J_{\text{HH}}$ of ~ 3 Hz indicate a *gauche* (*synclinal*) orientation whereas *trans*-periplana. hydrogen atoms give rise to coupling constants of ~ 9 Hz [20]. For the D-galactose derivatives an alternating small–large–small sequence is observed for the coupling constants $J_{2,3}$, $J_{3,4}$ and $J_{4,5}$ which indicates a *cis*–*trans*–*cis* relationship of hydrogen atoms H-2, H-3 and H-4 (Table 2). This suggests a planar extended zigzag conformation as depicted in Fig. 1 for the D-galacto chromium complex **8**. A similar conformational preference has been established previously for other *O*-peracetylated D-galactose compounds [12].

A similar consideration can be applied to the tetraacetylated pentose complex **12**. The L-arabino derivative exhibits a distinct small–large sequence of vicinal coupling constants ($J_{2,3} = 1.8$ Hz; $J_{3,4} = 9.2$ Hz) which is consistent with a *gauche* and *trans*-periplanar orientation of H-2–H-3 and H-3–H-4 (Fig. 2).

5. Conformational studies in the solid state

To compare the conformations in solution and in the solid state, the molecular structures of the chromium

Table 2
Spin coupling constants (in Hz) of D-galacto complexes **8**, **11**, **15** and **17**

	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$
8	n.d.	10.2	n.d.	4.5	8.3
9	1.6	10.1	n.d.	4.5	7.8
11	1.5	9.9	1.9	5.2	7.4
15	1.6	10.1	1.9	5.2	7.4
17	1.2	10.0	1.8	5.1	7.6

n.d. = not detected.

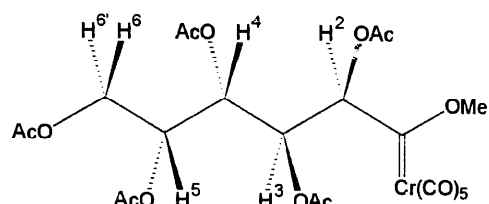


Fig. 1. Preferred P-conformation of D-galacto complex **8**.

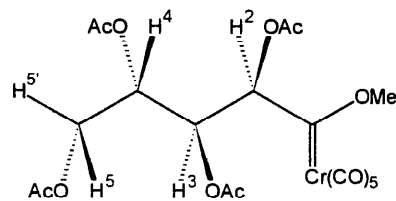


Fig. 2. Preferred conformation of L-arabino complex **12**.

carbene complex **8** and its isolobal analogue methyl galactonate **15** have been established by X-ray analysis. As depicted in Figs. 3 and 4 both compounds adopt an extended zigzag conformation as also indicated for chromium carbene **8** in solution. A comparison between **8** and **15** results in similar bond lengths and torsional angles suggesting a similar structure and conformation

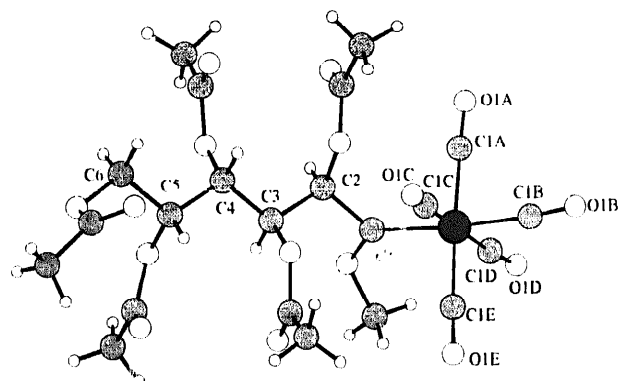


Fig. 3. Molecular structure of chromium complex **8** in the solid state (selected bond angles ($^\circ$), bond lengths (\AA) and torsional angles ($^\circ$)).

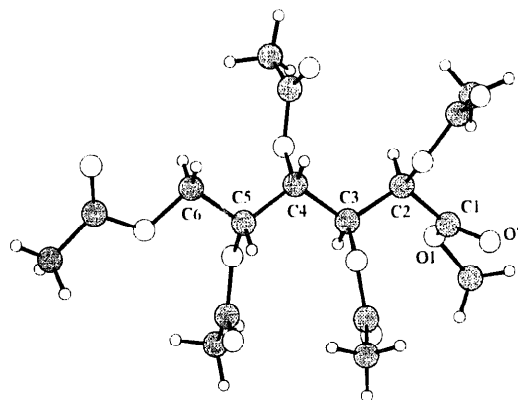


Fig. 4. Molecular structure of methyl-D-galactonate **15** in the solid state (selected bond lengths (\AA) and torsional angles ($^\circ$)).

along the sugar backbone. No significant structural changes are evident from the presence of the metal carbonyl fragment which only suffers a minor deviation from the octahedral environment of the metal center.

In summary, strongly electrophilic metal carbene analogues of acyclic carbohydrates are accessible in a straightforward synthetic approach based on a sugar electrophile/metalate nucleophile combination. Structural and conformational studies on D-galactose derivatives indicate that the preferred planar extended zigzag conformation along the sugar backbone—which is imposed by a minimization of *syn*-1,3-interactions arising from the protecting groups—is not affected by the incorporation of a bulky organometallic fragment at the C-1 terminus. This result may encourage the application of transition metal organometallics in stereoselective

synthesis involving the pronounced reactivity of the C-1 atom in carbohydrates.

6. Experimental

All organometallic transformations were performed under argon; solvents were dried by standard procedures. Chromatographic workup was carried out at 0°C on silica gel 60 (0.063–0.200, E. Merck) using dried solvents. ¹H- and ¹³C-NMR spectra were recorded on a Bruker AM-250, AM-400 or DRX-500 spectrometer. Chemical shifts refer to those of the residual solvent signal based on $\delta_{\text{TMS}} = 0.00$ ppm. FT-IR: Nicolet Magna 550. FABMS: Kratos Concept IH (matrix: *m*-nitrobenzyl alcohol). Elemental analysis: Elementar

Table 3
Crystallographic data and summary of data collection and refinement

	8	15
Crystal data		
Formula	C ₂₂ H ₂₄ CrO ₁₆	C ₁₇ H ₂₄ O ₁₂
<i>M</i>	596.4	420.4
Colour	orange	colourless
Dimension (mm)	0.10 × 0.20 × 0.35	0.25 × 0.30 × 0.40
Crystal system	orthorhombic	triclinic
Space group	P2 ₁ 2 ₁ 2 ₁ (No. 19)	P2 ₁ 2 ₁ 2 ₁ (No. 19)
<i>a</i> (Å)	8.017(4)	8.330(1)
<i>b</i> (Å)	15.918(6)	13.221(2)
<i>c</i> (Å)	21.639(11)	19.371(1)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
<i>V</i> (Å ³)	2761(2)	2133.3(4)
<i>Z</i>	4	4
ρ_{calc} (g cm ⁻³)	1.44	1.31
μ (mm ⁻¹)	0.49	0.97
<i>F</i> (000)	1232	888
Structure solution and refinement		
Full-matrix least-squares refinement on	<i>F</i> ²	<i>F</i> ²
Parameter/restraints	352/0	269/0
Measured reflections	4545	2351
Unique reflections used in refinement	3906	2064
<i>wR</i> ₂	0.104	0.185
<i>R</i> ₁ (for <i>I</i> > 2σ(<i>I</i>))	0.044	0.060
Flack's <i>x</i> -parameter largest diff.	−0.03(3)	0.3(6)
Peak and hole (e Å ⁻³)	0.30/−0.19	0.24/−0.22
Data collection parameter		
Diffractometer	Nicolet R3m	Enraf-Nonius CAD4
Radiation	Mo Kα	Cu Kα
(Å)	0.71073	1.54178
<i>T</i> (K)	293	293
2θ _{max} (°)	50	120
	−2 ≤ <i>h</i> ≤ 9	−9 ≤ <i>h</i> ≤ 1
	−2 ≤ <i>k</i> ≤ 18	−14 ≤ <i>k</i> ≤ 0
	−2 ≤ <i>l</i> ≤ 25	−21 ≤ <i>l</i> ≤ 0

Analysensysteme GmbH Vario EL. X-ray analysis: see Tables 3–5. The sugar acid chlorides **1**, **2** [21] and **3** [22] were prepared according to literature procedures.

6.1. Pentacarbonyl[2,3,4,5,6-penta-O-acetyl-D-galactohex-1-yl(methoxy)carbene]chromium **8**

At -60°C a solution of 2.16 g (5.1 mmol) D-galactonyl chloride **1** in 20 ml THF is added to dipotassium pentacarbonylchromate(-II) (**4**) prepared from 0.45 g (11.51 mmol) potassium, 1.10 g (92 mmol) graphite

Table 4
Data for Fig. 3 (compound **8**)

C1A-CR1-C1E	177.7(2)
C1C-CR1-C1D	173.9(2)
C1A-CR1-C1D	88.9(2)
C1A-CR1-C1C	93.7(2)
C1A-CR1-C1B	86.7(2)
C1D-CR1-C1B	86.5(2)
C1D-CR1-C1E	90.7(2)
C1B-CR1-C1C	88.1(2)
C1C-CR1-C1E	86.5(2)
C1-CR1-C1B	174.8(2)
C1-CR1-C1A	88.3(2)
C1-CR1-C1D	95.1(2)
C1-CR1-C1E	94.0(2)
C1-CR1-C1C	90.5(2)
CR1-C1	2.013(5)
CR1-C1A	1.885(6)
CR1-C1B	1.878(6)
CR1-C1C	1.915(6)
CR1-C1D	1.893(6)
CR1-C1E	1.911(6)
C1A-O1A	1.131(5)
C1B-O1B	1.152(6)
C1C-O1C	1.138(5)
C1D-O1D	1.146(6)
C1E-O1E	1.134(6)
C1-O11	1.310(5)
C1-C2	1.541(6)
C2-C3	1.534(6)
C3-C4	1.523(6)
C4-C5	1.522(6)
C5-C6	1.512(6)
C2-O21	1.434(5)
C3-O31	1.447(5)
C4-O41	1.439(5)
C5-O51	1.437(5)
C6-O61	1.442(5)
C1-C2-C3-C4	175.31
C2-C3-C4-C5	177.89
C3-C4-C5-C6	179.81
C4-C5-C6-O61	170.77
Cr-C1-C2-O21	0.88
O21-C2-C3-O31	66.14
O31-C3-C4-O41	176.75
O41-C4-C5-O51	60.7
O51-C5-C6-O61	67.46

Table 5
Data for Fig. 4 (compound **15**)

C1-C2-C3-C4	169.95
C2-C3-C4-C5	179.41
C3-C4-C5-C6	177.35
C4-C5-C6-O6	176.13
O7-C1-C2-O2	13.97
O2-C2-C3-O3	49.69
O3-C3-C4-O4	177.49
O4-C4-C5-O5	59.18
O5-C5-C6-O6	57.00
C1-O7	1.199(7)
C1-O1	1.321(7)
C1-C2	1.532(8)
C2-C3	1.515(8)
C3-C4	1.536(7)
C4-C5	1.500(8)
C5-C6	1.506(7)
C2-O2	1.421(7)
C3-O3	1.436(6)
C4-O4	1.450(7)
C5-O5	1.451(6)
C6-O6	1.441(7)

and 1.18 g (5.4 mmol) $\text{Cr}(\text{CO})_6$. After 30 min the solvent is evaporated, and the residue is dissolved in 120 ml dichloromethane. The resulting suspension is cooled to -30°C , 0.73 g (5.0 mmol) trimethyloxonium tetrafluoroborate are added, and the mixture is stirred for 5 h at $0-5^{\circ}\text{C}$. Another portion of trimethyloxonium tetrafluoroborate (0.44 g (3.0 mmol)) is added, and after an additional 5 h the mixture is recooled to -60°C and adsorbed on silica gel. The solvent is evaporated, and the residue is chromatographed at -15°C on silica gel using ether/petroleum ether/dichloromethane 1:1:1. The first fraction yields 1.93 g (64%) **8** as a yellow solid. (The second band contains 0.21 g (10%) of **15**.)

8: R_f (SiO_2 , ether/petroleum ether/dichloromethane 1:1:1): 0.70. M.p.: $113-115^{\circ}\text{C}$. IR (KBr): 2071s, 1994s, 1959vs, 1943vs, 1755s cm^{-1} . $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 5.46$ (d, $^3J_{3,4} = 10.2$ Hz, 1H, H-3), 5.41 (s, 1H, H-2), 5.34–5.26 (m, 2H, H-4/H-5), 4.82 (s, 3H, OCH_3), 4.30 (dd, $^2J_{6,6'} = 11.6$ Hz, $^3J_{5,6} = 4.5$ Hz, 1H, H-6), 3.72 (dd, $^2J_{6,6'} = 11.6$ Hz, $^3J_{5,6'} = 8.3$ Hz, 1H, H-6'), 2.31, 2.11, 2.04, 2.01, 1.99 (OCOCH_3). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): $\delta = 355.00$ (C=Cr), 222.95 (*trans*-CO), 215.46 (*cis*-CO), 170.47, 170.26, 170.13, 169.84, 169.28 (OCOCH_3), 84.54 (C-2), 68.92 (C-3), 67.97 (C-4), 67.72 (OCH_3), 67.53 (C-5), 62.41 (C-6), 20.87, 20.64, 20.64, 20.58, 20.50 (OCOCH_3). MS (FAB, *m*-NBA): m/z (%) = 596 (12) $[\text{M}^+]$, 456 (4) $[\text{M}^+ - 5 \text{CO}]$, 405 (12) $[\text{M}^+ + \text{H-Cr}(\text{CO})_5]$, 230 (100) $[\text{M}^+ + \text{H-Cr}(\text{CO})_5 - \text{Ac}_2\text{O} - \text{CH}_2\text{OAc}]$.

Anal. Found: C, 44.01; H, 4.23. $\text{C}_{22}\text{H}_{24}\text{CrO}_{16}$ (596.43) calcd.: C, 44.30; H, 4.06%.

6.2. Pentacarbonyl[2,3,4,5,6-penta-O-acetyl-D-galactohex-1-yl(methoxy)carbene]molybdenum 9

2.06 g (4.9 mmol) **1** are allowed to react with **5** as described for **8**. Yield 1.40 g (44%) **9**, yellow solid. R_f (SiO₂, ether/petroleum ether/dichloromethane 1:1:1): 0.71. M.p.: 115–117°C. IR (KBr): 2078s, 1992s, 1968vs, 1944vs, 1933vs, 1749s cm⁻¹. ¹H-NMR (400 MHz, CDCl₃): δ = 5.48 (dd, ³ $J_{3,4}$ = 10.1 Hz, ³ $J_{2,3}$ = 1.6 Hz, 1H, H-3), 5.40 (d, ³ $J_{2,3}$ = 1.6 Hz, 1H, H-2), 5.34–5.29 (m, 2H, H-4/H-5), 4.69 (s, 3H, OCH₃), 4.29 (dd, ² $J_{6,6'}$ = 11.8 Hz, ³ $J_{5,6}$ = 4.5 Hz, 1H, H-6), 3.87 (dd, ² $J_{6,6'}$ = 11.8 Hz, ³ $J_{5,6'}$ = 7.8 Hz, 1H, H-6'), 2.26, 2.10, 2.03, 2.01, 1.99 (OCOCH₃). ¹³C-NMR (100 MHz, CDCl₃): δ = 346.24 (C=Mo), 212.48 (*trans*-CO), 204.78 (*cis*-CO), 170.30, 170.08, 170.01, 169.61, 169.00 (OCOCH₃), 84.43 (C-2), 69.12 (OCH₃), 68.75 (C-3), 67.78 (C-4), 67.25 (C-5), 62.19 (C-6), 20.72, 20.49, 20.46, 20.46, 20.37 (OCOCH₃). MS (FAB, *m*-NBA, ⁹⁸Mo): m/z (%) = 642 (14) [M⁺], 558 (50) [M⁺–3 CO], 405 (38) [M⁺ + H–Mo(CO)₅], 243 (100) [M⁺ + H–Mo(CO)₅–Ac₂O–OAc].

Anal. Found: C, 40.99; H, 3.79. C₂₂H₂₄MoO₁₆ (640.36) calcd.: C, 41.26; H, 3.78%.

6.3. Pentacarbonyl[2,3,4,5,6-penta-O-acetyl-D-galactohex-1-yl(methoxy)carbene]tungsten 10

1.68 g (4.0 mmol) **1** are allowed to react with **6** as described for **8**. Yield 1.19 g (42%) **10**, red solid. R_f (SiO₂, ether/petroleum ether/dichloromethane 1:1:1): 0.72. M.p.: 130–132°C. IR (KBr): 2074s, 1986s, 1963vs, 1937vs, 1927vs, 1756s cm⁻¹. ¹H-NMR (400 MHz, CDCl₃): δ = 5.47 (d, ³ $J_{3,4}$ = 10.2 Hz, 1H, H-3), 5.33–5.27 (m, 2H, H-4/H-5), 5.25 (s, 1H, H-2), 4.57 (s, 3H, OCH₃), 4.26 (dd, ² $J_{6,6'}$ = 11.6 Hz, ³ $J_{5,6}$ = 4.4 Hz, 1H, H-6), 3.78 (dd, ² $J_{6,6'}$ = 11.6 Hz, ³ $J_{5,6'}$ = 7.7 Hz, 1H, H-6'), 2.23, 2.10, 2.02, 1.99, 1.98 (OCOCH₃). ¹³C-NMR (100 MHz, CDCl₃): δ = 328.18 (C=W), 202.52 (*trans*-CO), 196.04 (*cis*-CO), 170.30, 170.08, 169.92, 169.62, 169.13 (OCOCH₃), 86.01 (C-2), 69.89 (OCH₃), 68.41 (C-3), 67.77 (C-4), 67.37 (C-5), 62.17 (C-6), 20.75, 20.40, 20.40, 20.49, 20.49 (OCOCH₃). MS (FAB, *m*-NBA, ¹⁸⁴W): m/z (%) = 728 (10) [M⁺], 644 (54) [M⁺–3 CO], 405 (77) [M⁺ + H–W(CO)₅], 318 (100), 243 (97).

Anal. Found: C, 36.10; H, 3.45. C₂₂H₂₄O₁₆W (728.27) calcd.: C, 36.28; H, 3.32%.

6.4. Methyl 2,3,4,5,6-penta-O-acetyl-D-galactonate 15

M.p.: 127–128°C. R_f (SiO₂, ether/petroleum ether/dichloromethane 1:1:1): 0.54. ¹H-NMR (400 MHz, CDCl₃): δ = 5.45 (dd, ³ $J_{2,3}$ = 1.6 Hz, ³ $J_{3,4}$ = 10.1 Hz, H-3), 5.36 (dd, ³ $J_{3,4}$ = 10.1 Hz, ³ $J_{4,5}$ = 1.9 Hz, H-4), 5.25 (pseudo-sept, ³ $J_{5,6'}$ = 7.2 Hz, ³ $J_{5,6}$ = 5.4 Hz,

³ $J_{4,5}$ = 1.9 Hz, H-5), 5.00 (d, ³ $J_{2,3}$ = 1.6 Hz, H-2), 4.18 (dd, ³ $J_{5,6}$ = 5.2 Hz, ² $J_{6,6'}$ = 11.5 Hz, H-6), 3.70 (dd, ³ $J_{5,6'}$ = 7.4 Hz, ² $J_{6,6'}$ = 11.5 Hz, H-6'), 3.62 (s, 3H, OCH₃), 2.10, 2.03, 2.00, 1.93, 1.89 (OCOCH₃). ¹³C-NMR (100 MHz, CDCl₃): δ = 170.25, 170.04, 170.04, 169.27, 169.13 (OCOCH₃), 167.32 (C-1), 69.02 (C-2), 67.57 (C-3), 67.39 (C-4), 67.30 (C-5), 61.76 (C-6), 52.61 (OCH₃), 20.54, 20.49, 20.34, 20.26, 20.26 (OCOCH₃).

6.5. Tetracarbonyl[2,3,4,5,6-penta-O-acetyl-D-galactohex-1-yl(ethoxy)carbene]iron 11

0.72 ml (5.4 mmol) pentacarbonyliron are reduced according to the literature procedure to give white solid ferrate **7** which is mixed with 75 ml THF. The mixture is cooled to –60°C, and 2.29 g (5.4 mmol) **1** in 15 ml THF are added. After 3 h the resulting red solution is evaporated to dryness, and the residue is dissolved in a mixture of 15 ml ether und 2.5 ml HMPA. 1.05 ml (8.1 mmol) ethyl trifluoromethanesulfonate are added at –70°C, and the reaction mixture is stirred for 16 h. Column chromatography (ether/petroleum ether/dichloromethane 1:1:1) yields 0.9 g (1.5 mmol, 28.5%) **9** as a red solid. R_f (SiO₂, ether/petroleum ether/dichloromethane 1:1:1): 0.71. M.p.: 91–93°C. IR (KBr): 2060m, 1996m, 1989m, 1960vs, 1942vs, 1751s cm⁻¹. ¹H-NMR (400 MHz, CDCl₃): δ = 5.56 (dd, ³ $J_{3,4}$ = 9.9 Hz, ³ $J_{2,3}$ = 1.5 Hz, 1H, H-3), 5.48 (dd, ³ $J_{3,4}$ = 9.9 Hz, ³ $J_{4,5}$ = 1.9 Hz, 1H, H-4), 5.40 (d, ³ $J_{2,3}$ = 1.5 Hz, 1H, H-2), 5.30 (ddd, ³ $J_{5,6'}$ = 7.4 Hz, ³ $J_{5,6}$ = 5.2 Hz, ³ $J_{4,5}$ = 1.9 Hz, 1H, H-5), 5.03 (q, ³ J = 7.1 Hz, 1H, OCH₂CH₃), 5.02 (q, ³ J = 7.1 Hz, 1H, CH₂CH₃), 4.25 (dd, ² $J_{6,6'}$ = 11.5 Hz, ³ $J_{5,6}$ = 5.2 Hz, 1H, H-6), 3.84 (dd, ² $J_{6,6'}$ = 11.5 Hz, ³ $J_{5,6'}$ = 7.4 Hz, 1H, H-6'), 2.18, 2.09, 2.05, 2.00, 1.99 (OCOCH₃), 1.58 (t, ³ J = 7.1 Hz, 3H, OCH₂CH₃). ¹³C-NMR (100 MHz, CDCl₃): δ = 327.62 (C=Fe), 212.50 (CO), 170.32, 170.17, 169.75, 169.50, 168.88 (OCOCH₃), 84.95 (C-2), 78.21 (OCH₂CH₃), 68.03 (C-4), 67.72 (C-3), 67.27 (C-5), 61.78 (C-6), 20.59, 20.52, 20.32, 20.29 (OCOCH₃), 14.19 (OCH₂CH₃). MS (FAB, *m*-NBA): m/z (%) = 587 (4) [M⁺ + H], 558 (9) [M⁺–CO], 502 (72) [M⁺–3 CO], 474 (55) [M⁺–4 CO], 431 (55) [M⁺–Ac–4 CO], 313 (100) [M⁺–OAc–Ac₂O–4 CO].

Anal. Found: C, 44.72; H, 4.57. C₂₂H₂₆FeO₁₅ (586.29) calcd.: C, 45.07; H, 4.47%.

6.6. Pentacarbonyl[2,3,4,5-tetra-O-acetyl-L-arabinopent-1-yl(methoxy)carbene]chromium 12

1.26 g (3.6 mmol) **2** are allowed to react with **4** as described for the preparation of **8**. Yield 0.86 g (46%) **12**, red solid. R_f (SiO₂, ether/petroleum ether/dichloromethane 1:2:1): 0.63. M.p.: 91–93°C. IR (KBr): 2071s, 1993s, 1962vs, 1938vs, 1755s cm⁻¹. ¹H-NMR

(250 MHz, CDCl_3): $\delta = 5.60$ (d, $^3J_{3,4} = 9.2$ Hz, $^3J_{2,3} = 1.8$ Hz, 1H, H-3), 5.56 (bs, 1H, H-2), 5.08 (bm, $^3J_{3,4} = 9.2$ Hz, $^3J_{4,5} = 2.6$ Hz, 1H, H-4), 4.83 (s, 3H, OCH_3), 4.22 (dd, $^2J_{5,5'} = 12.7$ Hz, $^3J_{4,5} = 2.6$ Hz, 1H, H-5), 4.17 (dd, $^2J_{5,5'} = 12.7$ Hz, $^3J_{4,5'} = 3.7$ Hz, 1H, H-5'), 2.23, 2.06, 2.04, 2.01 (OCOCH_3). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): $\delta = 355.36$ (C=Cr), 222.95 (*trans*-CO), 215.36 (*cis*-CO), 170.41, 169.72, 169.68, 168.87 (OCOCH_3), 84.57 (C-2), 69.61 (C-3), 67.92 (C-4), 67.53 (OCH_3), 61.19 (C-5), 20.70, 20.67, 20.51, 20.31 (OCOCH_3). MS (FAB, *m*-NBA): m/z (%) = 524 (7) $[\text{M}^+]$, 496 (1) $[\text{M}^+ - \text{CO}]$, 440 (3) $[\text{M}^+ - 3 \text{CO}]$, 412 (5) $[\text{M}^+ - 4 \text{CO}]$, 384 (3) $[\text{M}^+ - 5 \text{CO}]$, 282 (52) $[\text{M}^+ - \text{Ac}_2\text{O} - 5 \text{CO}]$, 251 (10), 230 (100) $[\text{M}^+ - \text{Cr}(\text{CO})_5 - \text{Ac}_2\text{O}]$.

Anal. Found: C, 43.17; H, 4.07. $\text{C}_{19}\text{H}_{20}\text{CrO}_{14}$ (524.36) calcd.: C, 43.52; H, 3.84%.

6.7. 1,6-Bis-pentacarbonyl[2,3,4,5-tetra-*O*-acetyl-*D*-galactaroyl-bis(methoxycarbene)]chromium 13

0.73 g (1.8 mmol) **3** are allowed to react with two equivalents of **4** as described for the preparation of **8**. Yield 0.15 g (11%) **13**, yellow solid. R_f (SiO_2 , petroleum ether/ether/dichloromethane 5:1:5): 0.62. M.p.: 128°C (decomposition). IR (KBr): 2064 (m), 1979sh, 1963s, 1949sh, 1925vs, 1761m cm^{-1} . MS (FAB, *m*-NBA): m/z (%) = 758.1 (57) $[\text{M}^+]$, 730.1 (3) $[\text{M}^+ - \text{CO}]$, 674.1 (10) $[\text{M}^+ - 3 \text{CO}]$, 613.3 (10), 582.1 (20), 567.0 (20), 460.2 (10), 340.0 (20). $^1\text{H-NMR}$ (250 MHz, CDCl_3): $\delta = 5.47$ (s, 2 H, H-2/H-5), 5.45 (s, 2 H, H-3/H-4), 4.84 (s, 6 H, OCH_3), 2.25 (s, 6 H, OCOCH_3), 2.03 (s, 6 H, OCOCH_3). $^{13}\text{C-NMR}$ (62.5 MHz, CDCl_3): $\delta = 354.74$ (C=Cr), 222.99 (*trans*-CO), 215.49 (*cis*-CO), 170.08 (OCOCH_3), 169.31 (OCOCH_3), 84.30 (C-2/C-5), 69.43 (C-3/C-4), 67.78 (OCH_3), 20.87 (OCOCH_3), 20.56 (OCOCH_3).

Anal. Found: C, 41.08; H, 3.16. $\text{C}_{26}\text{H}_{22}\text{O}_{20}\text{Cr}_2$ (758.44) calcd.: C, 41.17, H: 2.92%.

6.8. 1,6-Bis-pentacarbonyl[2,3,4,5-tetra-*O*-acetyl-*D*-galactaroyl-bis(methoxycarbene)]tungsten 14

1.26 g (3.6 mmol) **2** are allowed to react with **6** as described for the preparation of **8**. Yield 0.13 g (7%) **14**, yellow-orange solid. R_f (SiO_2 , petroleum ether/ether/dichloromethane 5:1:5): 0.62. M.p.: 142°C (decomposition). IR (KBr): 2072m, 1977sh, 1947sh, 1919vs, 1759s, 1751m cm^{-1} . $^1\text{H-NMR}$ (500 MHz, CDCl_3): $\delta = 5.47$ (s, 2 H, H-2/H-5), 5.26 (s, 2 H, H-3/H-4), 4.63 (s, 6 H, OCH_3), 2.26 (s, 6 H, OCOCH_3), 2.04 (s, 6 H, OCOCH_3). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): $\delta = 328.39$ (C=W), 203.08 (*trans*-CO), 196.56 (*cis*-CO), 170.41 (OCOCH_3), 169.61 (OCOCH_3), 86.16 (C-2/C-5), 70.44 (C-3/C-4), 69.43 (OCH_3), 21.26 (OCOCH_3), 20.91 (OCOCH_3). MS (FAB, *m*-NBA, ^{184}W): m/z (%) = 1022.1 (25) $[\text{M}^+]$,

994.1 (40) $[\text{M}^+ - \text{CO}]$, 938.1 (65) $[\text{M}^+ - 3 \text{CO}]$, 910 (5) $[\text{M}^+ - 4 \text{CO}]$.

Anal. Found: C, 30.04; H, 2.21. $\text{C}_{26}\text{H}_{22}\text{O}_{20}\text{W}_2$ (1022.15) calcd.: C, 30.55; H, 2.17%.

6.9. General procedure for the aminolysis of **9**, **10** and **11**

A 0.013M solution of the methoxycarbene complex in dichloromethane is treated with gaseous ammonia at -50°C . After several minutes the reaction mixture turns pale yellow, and evaporation of the solvent affords pure aminocarbene complexes **16–18**.

6.10. Pentacarbonyl[2,3,4,5,6-penta-*O*-acetyl-*D*-galactohex-1-yl(amino)carbene]molybdenum 16

0.20 g (0.31 mmol) **9** are allowed to react with ammonia as described above. Column chromatography (SiO_2 , 0°C , dichloromethane/petroleum ether/methanol 5:2:1) yields 0.16 g (0.26 mmol, 85%) **19** as a yellow oil. R_f (dichloromethane/petroleum ether/methanol 2:5:1): 0.73. IR (CH_2Cl_2): 2070w, 1981w, 1935vs, 1751s cm^{-1} . $^1\text{H-NMR}$ (250 MHz, CDCl_3): $\delta = 9.02$ (br s, 1H, NH_2), 8.92 (br s, 1H, NH_2), 6.01 (s, 1H, H-2), 5.89 (dd, $^3J_{3,4} = 10.0$ Hz, $^3J_{2,3} = 1.1$ Hz, 1H, H-3), 5.31 (dd, $^3J_{3,4} = 10.0$ Hz, $^3J_{4,5} = 1.8$ Hz, 1H, H-4), 5.20 (ddd, $^3J_{5,6'} = 7.4$ Hz, $^3J_{5,6} = 5.2$ Hz, $^3J_{4,5} = 1.8$ Hz, 1H, H-5), 4.26 (dd, $^2J_{6,6'} = 11.5$ Hz, $^3J_{5,6'} = 7.4$ Hz, 1H, H-6'), 2.18, 2.14, 2.05 (3 s, 9 H, OCOCH_3), 2.00 (s, 6H, OCOCH_3). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): $\delta = 273.16$ (C=Mo), 212.06 (*trans*-CO), 205.73 (*cis*-CO), 170.73, 170.03, 169.29, 168.37 (OCOCH_3), 81.83 (C-2), 68.01 (C-3), 67.31 (C-4), 66.09 (C-5), 62.11 (C-6), 20.69, 20.64, 20.50, 20.46, 20.38 (OCOCH_3). MS (FAB, *m*-NBA, ^{98}Mo): m/z = 627 (1) $[\text{M}^+]$, 599 (6) $[\text{M}^+ - \text{CO}]$, 568 (4), 543 (24) $[\text{M}^+ - 3 \text{CO}]$, 390 (55).

Anal. Found: C, 39.91; H, 3.85; N, 2.24. $\text{C}_{21}\text{H}_{23}\text{MoNO}_{15}$ (625.35) calcd.: C, 40.19; H, 3.70; N, 2.23%.

6.11. Pentacarbonyl[2,3,4,5,6-penta-*O*-acetyl-*D*-galactohex-1-yl(amino)carbene]tungsten 17

0.18 g (0.25 mmol) **10** are allowed to react as described above. Evaporation of dichloromethane yields **17** as a yellow solid. IR (CH_2Cl_2): 2070w, 1976sh, w, 1927vs, 1754m cm^{-1} . $^1\text{H-NMR}$ (250 MHz, CDCl_3): $\delta = 9.02$ (s, 1H, NH), 8.63 (s, 1H, NH), 6.06 (s, 1H, H-2), 5.85 (dd, $^3J_{3,4} = 10.0$ Hz, $^3J_{2,3} = 1.2$ Hz, 1H, H-3), 5.34 (dd, $^3J_{3,4} = 10.0$ Hz, $^3J_{4,5} = 1.8$ Hz, 1H, H-4), 5.22 (sept, $^3J_{5,6'} = 7.6$ Hz, $^3J_{5,6} = 5.1$ Hz, $^3J_{4,5} = 1.8$ Hz, 1H, H-5), 4.28 (dd, $^2J_{6,6'} = 11.6$ Hz, $^3J_{5,6} = 5.1$ Hz, H-6), 3.85 (dd, $^2J_{6,6'} = 11.6$ Hz, $^3J_{5,6'} = 7.6$ Hz, 1H,

H-6'), 2.18, 2.14, 2.07, 2.06, 2.02 (OCOCH₃). ¹³C-NMR (100 MHz, CDCl₃): δ = 260.95 (C=W), 201.80 (*trans*-CO), 197.20 (s, d, ²J_{CW} = 126.38 Hz, *cis*-CO), 170.49, 170.42, 169.87, 168.93, 168.17 (OCOCH₃), 83.95 (C-2), 67.80 (C-3), 67.12 (C-4), 65.91⁻ (C-5), 61.95 (C-6), 20.54, 20.48, 20.34, 20.28 (OCOCH₃). MS (FAB, *m*-NBA, ¹⁸⁴W): *m/z* = 713 (26) [M⁺], 685 (78) [M⁺-CO], 654 (38) [M⁺-OAc], 629 (35) [M⁺-3 CO], 601 (10) [M⁺-4 CO], 573 (3) [M⁺-5 CO], 513 (16), 390.1 (47).

Anal. Found: C, 34.20; H, 3.36; N, 1.74. C₂₁H₂₃NO₁₅W (713.26) calcd.: C, 35.36; H, 3.25; N, 1.96%.

6.12. Tetracarbonyl[2,3,4,5,6-penta-O-acetyl-D-galactohex-1-yl(amino)carbene]iron 18

0.03 g (0.06 mmol) **11** are treated as described above. After evaporation of the solvent **18** is obtained as a yellow solid. IR (CH₂Cl₂): 2052m, 1977m, 1940s, 1753vs cm⁻¹. ¹H-NMR (400 MHz, CDCl₃): δ = 8.86 (s, 1H, NH), 8.58 (s, 1H, NH), 6.20 (s, 1H, H-2), 6.04 (d, ³J_{3,4} = 10.0 Hz, 1H, H-3), 5.32 (d, ³J_{3,4} = 10.0 Hz, 1H, H-4), 5.13 (m, 1H, H-5), 4.26 (dd, ²J_{6,6'} = 11.3 Hz, ³J_{5,6} = 5.5 Hz, 1H, H-6), 3.86 (dd, ²J_{6,6'} = 11.3 Hz, ³J_{5,6'} = 7.2 Hz, 1H, H-6'), 2.19, 2.15, 2.12, 2.02, 2.01 (OCOCH₃). ¹³C-NMR (100 MHz, CDCl₃): δ = 270.06 (br, C=Fe), 214.90 (CO), 170.64, 170.53, 170.06, 168.88, 168.14 (OCOCH₃), 81.27 (C-2), 68.06 (C-3), 67.44 (C-4), 67.30⁻ (C-5), 61.92 (C-6), 20.79, 20.66, 20.48 (OCOCH₃).

6.13. X-ray crystallographic studies of **8** and **15**²

The structures were solved by direct methods. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were localized by difference electron density determination and refined using a riding model. In **15** an extinction correction was applied. The absolute structure was determined by Flack's *x*-refinement (in **15** the absolute structure could not be determined reliably) [23]. Details of data collection and refinement are given in Table 3. Programs used: SHELXTL-Plus [24] and SHELXL-93 [25].

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References

- [1] Organotransition Metal Modified Sugars, Part 4. —For Part 3, see: R. Ehlenz, M. Nieger, K. Airola, J. Carbohydr. Chem. (in print).
- [2] Reviews: a) K.H. Dötz, *Angew. Chem. Int. Ed. Engl.* 23 (1984) 587; b) W.D. Wulff, in: B.M. Trost, I. Fleming (Eds.), *Comprehensive Organic Synthesis*, vol. 5, Pergamon, New York, 1991, p. 1065; c) H.-U. Reissig, in: *Organometallics in Organic Synthesis* 2, Springer, Berlin, 1989, p. 311; d) D.F. Harvey, D.M. Sigano, *Chem. Rev.* 96 (1996) 271; e) L.S. Hegedus, *Pure Appl. Chem.* 62 (1990).
- [3] a) T. Kametani, K. Kawamura, T. Honda, *J. Am. Chem. Soc.* 109 (1987) 3010; b) J.C.-Y. Cheng, G.D. Daves, *J. Org. Chem.* 52 (1987) 3083; c) A. Rosenthal, H.J. Koch, *Tetrahedron Lett.* (1967) 871.
- [4] a) P. DeShong, G.A. Slough, V. Elango, *Carbohydr. Res.* 171 (1987) 342; b) P. DeShong, G.A. Slough, V. Elango, G.L. Trainor, *J. Am. Chem. Soc.* 107 (1985) 7788.
- [5] a) J.W. Krajewski, P. Gluzinski, Z. Pakulski, A. Zamojski, A. Mishnev, A. Kemme, *Carbohydr. Res.* 252 (1994) 97; b) H.H. Baer, H.R. Hanna, *Carbohydr. Res.* 102 (1982) 169; c) G.L. Trainor, B.E. Smart, *J. Org. Chem.* 48 (1983) 2447.
- [6] a) K.H. Dötz, O. Neuss, M. Nieger, *Synlett* 995 (1996); b) T. Pill, K. Polborn, W. Beck, *Chem. Ber.* 123 (1990) 11; c) H. Fischer, J. Schleu, G. Roth, *Chem. Ber.* 128 (1995) 373; d) H. Fischer, J. Schleu, *Chem. Ber.* 129 (1996) 385; e) R. Aumann, *Chem. Ber.* 125 (1992) 2773; f) R. Aumann, *Chem. Ber.* 127 (1994) 725.
- [7] K.H. Dötz, W. Straub, R. Ehlenz, K. Peseke, R. Meisel, *Angew. Chem. Int. Ed.* 37 (1995) 1856.
- [8] C. Ortiz Mellet, J.L.J. Blanco, J.M. García Fernández, J. Fuentes, *J. Carbohydr. Chem.* 14 (1995) 1133.
- [9] M. Benazza, M. Massoui, R. Uzan, G. Demailly, *J. Carbohydr. Chem.* 13 (1994) 967.
- [10] N.B. D'Accorso, I.M.E. Thiel, *Carbohydr. Res.* 167 (1987) 301.
- [11] D. Horton, Z. Walaszek, I. Ekiel, *Carbohydr. Res.* 119 (1983) 263.
- [12] M. Blanc-Muesser, J. Defaye, D. Horton, *Carbohydr. Res.* 87 (1980) 71.
- [13] L.M. Sweeting, B. Coxon, R. Varma, *Carbohydr. Res.* 72 (1979) 43.
- [14] D. Horton, J.D. Wander, *Carbohydr. Res.* 13 (1970) 33.
- [15] D. Horton, J.D. Wander, *Carbohydr. Res.* 10 (1969) 279.
- [16] D. Horton, J.D. Wander, *J. Org. Chem.* 39 (1974) 1859.
- [17] a) M.F. Semmelhack, G.R. Lee, *Organometallics* 6 (1987) 1839; b) M.A. Schwindt, T. Lejon, L.S. Hegedus, *Organometallics* 9 (1990) 2814.
- [18] M.F. Semmelhack, R. Tamura, *J. Am. Chem. Soc.* 105 (1983) 4099.
- [19] B.E. Mann, B.F. Taylor, ¹³C-NMR Data for Organometallic Compounds, Academic Press, London, 1981.
- [20] M. Blanc-Muesser, J. Defaye, D. Horton, *J. Org. Chem.* 43 (1978) 3053.
- [21] M.L. Wolfrom, A. Thompson, in: *Methods in Carbohydrate Chemistry II*, Academic Press, New York, 1963.
- [22] a) Z.H. Skrap, *Monatsh. Chem.* 14 (1893) 488; b) O. Diels, F. Löflund, *Chem. Ber.* 47 (1914) 2351.
- [23] H.D. Flack, *Acta Cryst. A* 39 (1983) 876.
- [24] G.M. Sheldrick, SHELXTL-Plus, Siemens Analytical X-ray Instruments, Madison, WI, USA, 1989.
- [25] G.M. Sheldrick, SHELXL-93, University of Göttingen, 1993.

² Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository numbers CSD 406729 (**8**) and CSD 406730 (**15**), the publication and the names of the authors.