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Part 16. Diastereoselective synthesis of carbohydrate-derived spirocyclic 2-oxacyclohexylidene chromium and tungsten complexes

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Abstract

Carbohydrate-derived 4-pentyn-1-ols have been synthesized from spirocyclic oxirane precursors upon reaction with allenylmagnesium bromide. They undergo cycloisomerization at low-valent chromium or tungsten templates to give spirocyclic 2-oxacyclohexylidene metal complexes. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Spirocyclic ring systems represent an important structural feature in a series of natural products and biologically active compounds. They are encountered in many different classes of compounds ranging from simple bicyclic systems in the dactyloxenes [2] to very complicated molecules as in polyether antibiotics [3]. Recently, we have started a program aiming at the combination of carbohydrates and Fischer-type ylidene complexes [4] in order to investigate the influence of the chiral information provided by the carbohydrate moiety on the stereoselectivity of cycloaddition reactions [1,5] and to evaluate the potential of these organometallic sugars in the synthesis of natural products. Up to now there are only a few examples reported for the chiral modification of the ylidene ligand using carbohydrates [6]. Herein we now report on the synthesis of carbohydrate-derived spirocyclic 2-oxacyclohexylidene chromium and tungsten complexes based on the cycloisomerization of carbohydrate-modified 4-pentyn-1-ols at a coordinatively unsaturated metal template [7].

2. Results and discussion

Recently, we successfully applied the cycloisomerization of carbohydrate-derived butynols at low valent metal templates to the synthesis of metal 2-oxacyclo*pentylidene*-functionalized spirocyclic carbohydrates [8]. In order to extend this methodology to the synthesis of metal 2-oxacyclo*hexylidene*-homologs we aimed at the preparation of suitable carbohydrate-modified 4-pentyn-1-ols which are most conveniently synthesized by reaction of allenylmagnesium bromide [9] with carbohydrate-derived spirocyclic oxiranes **1**–**3** (Scheme 1).

Nucleophilic ring-opening of oxiranes **1**–**3** by γ-addition of allenylmagnesium bromide to the methylene carbon atom (C-1′) afforded the 4-pentyn-1-ols **4**–**6** in moderate to excellent yields. The reaction of allenylmagnesium bromide with **1** and **2** afforded pentynols **4** and **5** as the only isolable reaction products after chromatographic workup as a viscous colorless oil and a white solid, respectively. In contrast, reaction of allenylmagnesium bromide with the spirocyclic oxirane

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[☆] For Part 15, see Ref. [1].

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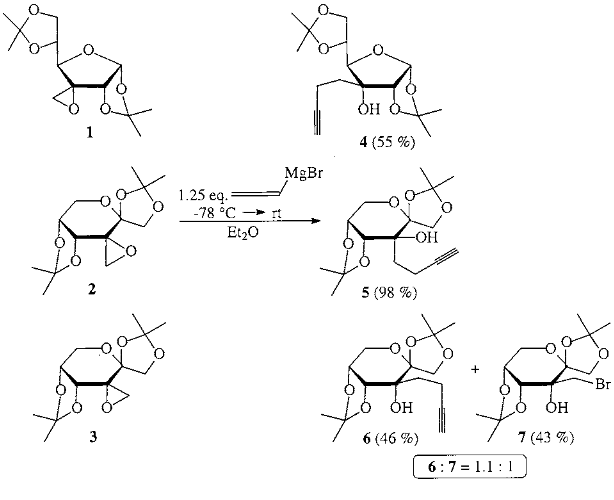
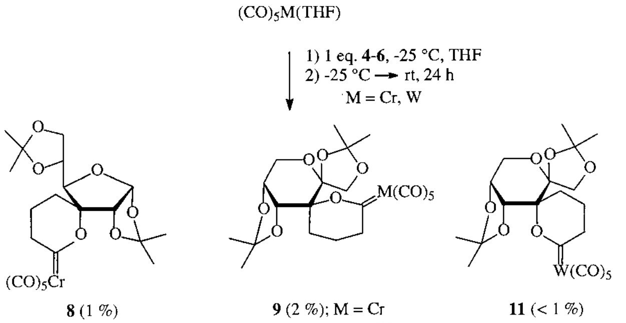
3 gave a 1.1:1 mixture of pentynol **6** and the 3-*C*-bromomethyl-β-D-psicopyranose derivative **7** which was separated using chromatographic techniques to give **6** as a white solid and **7** as a highly viscous colorless oil. The formation of **7** can be rationalized in terms of a nucleophilic ring-opening of the oxirane by a bromide anion.

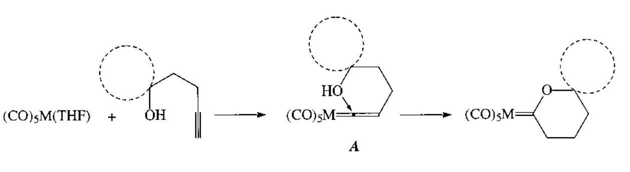
The pentynols **4**–**6** were treated with pentacarbonyl(tetrahydrofuran)chromium and -tungsten generated by UV-irradiation of the corresponding metal hexacarbonyl in tetrahydrofuran at −10°C. The glucose-based pentynol **4** was cyclized at the chromium template in tetrahydrofuran at room temperature (r.t.). After 24 h chromatographic workup of the reaction mixture on silica gel using a 1:1 mixture of petroleum ether–diethyl ether as eluent gave a mixture of complex **8** and pentynol **4** which was separated by a second column chromatography on silica gel using a 1:2 mixture of petroleum ether–methylene chloride as eluent to afford the spirocyclic 2-oxacyclohexylidene complex **8** as a viscous yellow oil in 1% yield (Scheme 2). Following the same procedure the cyclization of the fructose-based pentynol **5** using chromium and tungsten templates gave complexes **9** in 2% and **10** in 5% yield, respectively, as viscous yellow oils.



Scheme 1.



Scheme 2.

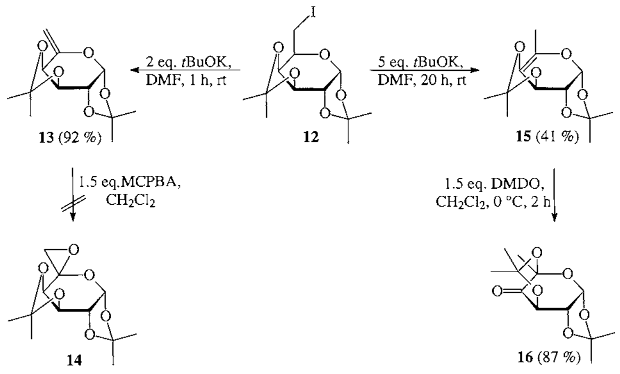


Scheme 3.

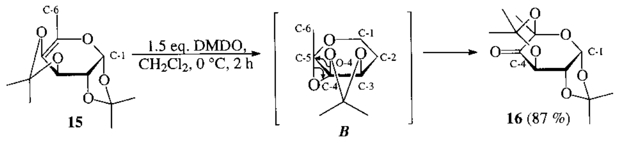
Although in general the cycloisomerization of 4-pentyn-1-ols gives lower yields than the cyclization of 3-butyn-1-ols, the yields obtained for complexes **8**–**11** were very disappointing. Attempts to further optimize the reaction conditions by gentle warming resulted in increased decomposition suggesting an only limited thermostability of the intermediates proposed. This outcome might be rationalized in terms of a slower intramolecular nucleophilic attack of the hydroxy function at the α-carbon atom of the vinylidene complex intermediate *A* (Scheme 3) as a result of a higher flexibility of the hydroxyalkyl substituent combined with a lower thermal stability of the vinylidene complex intermediate. The idea that the length and thereby the flexibility of the alkyl chain of the vinylidene complex intermediate plays an important role in the subsequent cyclization has been supported by the isolation and characterization of a few rare examples of hydroxyalkylvinylidene complexes [10].

It is noteworthy that in contrast to the reaction of the psicose-based 3-butyn-1-ol with pentacarbonyl(tetrahydrofuran)chromium(0) [5], the reaction with the psicose-based 4-pentyn-1-ol neither yielded the desired 2-oxacyclohexylidene complex nor its formation during the reaction could be detected by IR-spectroscopy. On the other hand, using the more reactive tungsten template the formation of the psicose-derived spirocyclic 2-oxacycloalkylidene complex **11** could be monitored by a decrease of the A_1^1-band of pentacarbonyl(tetrahydrofuran)tungsten at 2074 cm^{-1} along with an increasing intensity of the A_1^1-band of 2-oxacyclohexylidene complex **11** at 2068 cm^{-1}; after 24 h a small amount of **11** was isolated by column chromatography, but could not be purified sufficiently. Attempts to warm the reaction mixture to 40°C did not result in any improvement, but only led to decomposition of the solvent-stabilized tungsten template without formation of **11**. It is remarkable that only a few examples of 2-oxacyclohexylidene group 6 metal complexes have been prepared via cycloisomerization of the corresponding pentynols so far [10a,11,12]. No additional information on the low cycloisomerization reactivity of pentynol **6** could be deduced from its molecular structure which was established by single-crystal X-ray analysis.

In order to synthesize carbohydrate-derived 2-oxacyclohexylidene metal complexes containing a spiroketal structure we chose 6-deoxy-6-iodo-1,2:3,4-di-*O*-isopropylidene-α-D-galacto-1,5-pyranose (**12**) [13] which can be readily dehydrohalogenated to its *exo*-methylene



Scheme 4.



Scheme 5.

derivative **13** [14] upon treatment with potassium *tert*-butoxide in *N*,*N*-dimethylformamide at r.t. [15]. Oxidation of **13** with MCPBA was expected to yield the spirocyclic oxirane **14** (Scheme 4). However, epoxidation of **13** could not be achieved under our standard conditions. On the other hand, we found that a larger excess of potassium *tert*-butoxide (five versus two equivalents) combined with a longer reaction time (20 versus 1 h) for the dehydrohalogenation of **12** gave rise to the formation of the galacto-1,5-pyranose derivative **15** in moderate yield (Scheme 4).

We suggest that under these conditions the *exo*-methylene derivative **13** is formed first and subsequently undergoes a base-induced isomerization to give the thermodynamically more stable enol ether **15** bearing an endocyclic (C=C)-double bond. After extractive workup and chromatographic purification, **15** was obtained as a pale yellow solid in 41% yield. Following the procedure for the preparation of 1,2-anhydro-pyranoses from the corresponding glycals [16], treatment of **15** with 1.5 equivalents of DMDO in methylene chloride at 0°C afforded compound **16** as a colorless solid in 87% yield after column chromatography.

The formation of **16** is supposed to involve an initial epoxidation of the endocyclic (C=C)-double bond. The resulting intermediate ***B*** (Scheme 5)[1] in which C-4 is a constituent part of three adjacent rings may reduce its ring strain by opening of the oxirane generating a carbonyl group at C-4 and by a concomitant 1,2-shift of the oxygen atom O-4 from C-4 to C-5. The structure of **16** has been confirmed by single-crystal X-ray analysis.

3. Conclusions

The cycloisomerization of pentynols **4**–**6** provides an approach to carbohydrate-derived spirocyclic 2-oxa-cyclohexylidene group 6 metal complexes containing the novel α,β-spirocyclic connectivity[2]. To the best of our knowledge this type of structure is unprecedented whereas α,α-connection is a structural feature of many natural products [17]. Moreover, some examples of β,β-connected spirocycles have also been reported in the literature [18].

4. Experimental

4.1. 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 (diethyl ether), calcium hydride (petroleum ether, b.p. 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. ^{1}H-NMR: Bruker AM-250 (250 MHz) and Bruker DRX-500 (500 MHz). ^{13}C-NMR: AM-250 (62.8 MHz), Bruker AM-400 (100.6 MHz) and Bruker DRX-500 (125.7 MHz). NMR spectra were recorded in C_6D_6 with C_6H_6 at $\delta_H = 7.16$ or $CDCl_3$ with $CHCl_3$ at $\delta_H = 7.26$ as internal standard. FT-IR: Nicolet Magna 550. Elemental analysis: Heraeus CHN-Rapid. MS: Kratos MS 50 (EI, 70 eV). M.p.: Büchi SMP 20, the reported melting points are uncorrected. TLC: 0.25 mm Merck silica gel plates 60 F_{254}. $[\alpha]^{20}_{D}$: Perkin–Elmer 341 polarimeter. 3,1′-Anhydro-3-*C*-(1′-hydroxymethyl)-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**1**) [19], 3,1′-anhydro-3-*C*-(1′-hydroxymethyl)-1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranose (**2**) [20], 3,1′-anhydro-3-*C*-(1′-hydroxymethyl)-1,2:4,5-di-*O*-isopropylidene-β-D-psicopyranose (**3**) [20] and allenylmagnesium bromide [9] were prepared according to methods reported previously.

*4.2. General procedure for the preparation of 4-pentyn-1-ols **4**–**6***

A total of 2 ml of a 2.5 M solution of allenylmagnesium bromide in diethyl ether was added at −78°C dropwise to a solution of 4 mmol of 3,1′-anhydro-3-*C*-

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[1] The 1,2-acetonide unit is not shown in the intermediate ***B***.

[2] The term ‘α,β’ refers to the distance of the ring-oxygen atoms from the spirocyclic center of the dioxaspiroalkanes. For the β-position there is a methylene group between the ring oxygen atom and the spirocyclic center whereas for the α-position the ring oxygen atom is directly connected to the spirocyclic carbon atom.

(1′-hydroxymethyl)-sugars **1**–**3** in 50 ml of diethyl ether. After stirring for 1 h at −78°C the cooling bath was removed and stirring was continued for another hour. Then, a 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 diethyl ether. The combined organic extracts were washed twice with 50 ml portions of water, dried over magnesium sulfate, and the solvent was removed. Column chromatography on silica gel gave the pure 4-pentyn-1-ols **4**–**6**.

*4.2.1. 1,2:5,6-Di-O-isopropylidene-3-C-(4′-but-1′-ynyl)-α-D-allofuranose (**4**)*

Column chromatography on silica gel using petroleum ether–ethyl acetate–diethyl ether (2:1:1) as eluent gave 687 mg (2.2 mmol, 55%) of **4** as white crystalline solid, m.p. 90°C. $R_f = 0.61$ (petroleum ether–ethyl acetate–diethyl ether, 2:1:1); $[\alpha]_D^{20} = 45°$ ($c = 0.0884$, $CHCl_3$); ^{1}H-NMR (250 MHz, C_6D_6): $\delta =$ 1.07 (s, 3 H, CH_3), 1.23 (s, 3 H, CH_3), 1.33 (s, 6 H, 2 CH_3), 1.57 (t, $^4J = 1.95$ Hz, 1 H, H-1′), 1.81 (s, br, 1 H, OH), 2.06–2.25 (m, 2 H, H-3′a/b), 2.29–2.42 (m, 1 H, H-4′a), 2.45–2.60 (m, 1 H, H-4′b), 3.93 (d, $^3J = 4.87$ Hz, 1 H, H-4), 4.02–4.06 (m, 2 H, H-6a/b), 4.11 (d, $^3J = 3.54$ Hz, 1 H, H-2), 4.33 (dpt, $^3J = 7.81$ Hz, $^3J = 5.92$ Hz, 1 H, H-5), 5.81 (d, $^3J = 3.54$ Hz, 1 H, H-1); ^{13}C-NMR (62.8 MHz, C_6D_6): $\delta = 14.52$ (C-4′), 26.10, 27.16, 27.51, 27.87 (4 CH_3), 32.95 (C-3′), 68.66 (C-6), 70.32 (C-1′), 74.09 (C-5), 83.02 (C-2′), 84.91 (C-4), 85.26 (C-3), 86.29 (C-2), 105.77 (C-1), 110.32, 113.05 (2 C_q); FT-IR (KBr): $\nu = 3490$ cm^{-1} (*s*, ν_{O-H}), 3280 (*vs*, $\nu_{C\equiv CH}$), 2990 (*s*, ν_{C-H}), 2974 (*s*, ν_{C-H}), 2941 (*s*, ν_{C-H}), 2918 (*m*, ν_{C-H}), 2893 (*w*, ν_{C-H}), 2859 (*w*, ν_{C-H}), 2116 (*w*, $\nu_{C\equiv C}$); MS (EI, 70 eV); *m*/*z* (%): 312 (1) [M^+], 297 (45) [M^+–CH_3], 101 (100) [2,2-dimethyl-1,3-dioxacyclopentyl$^+$]; HRMS Calc. for M^+: 312.1573. Found: 312.1578. Anal. Calc. for $C_{16}H_{24}O_6$: C, 61.52; H, 7.74. Found: C, 61.24; H, 7.71%.

*4.2.2. 1,2:4,5-Di-O-isopropylidene-3-C-(4′-but-1′-ynyl)-β-D-fructopyranose (**5**)*

Column chromatography on silica gel using petroleum ether–ethyl acetate (4:1) as eluent gave 1.22 g (3.9 mmol, 98%) of **5** as colorless oil. $R_f = 0.41$ (petroleum ether–ethyl acetate, 4:1). $[\alpha]_D^{20} = -66°$ ($c =$ 0.044, $CHCl_3$); ^{1}H-NMR (500 MHz, C_6D_6): $\delta = 1.10$ (s, 3 H, CH_3), 1.27 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3), 1.80 (t, $^4J = 2.60$ Hz, 1 H, H-1′), 1.92 (ddd, $^2J = 13.89$ Hz, $^3J = 10.07$ Hz, $^3J = 5.33$ Hz, 1 H, H-4′a), 2.24 (ddd, $^2J = 13.89$ Hz, $^3J = 10.07$ Hz, $^3J = 6.10$ Hz, 1 H, H-4′b), 2.37 (dddd, $^2J = 16.48$ Hz, $^3J = 10.07$ Hz, $^3J = 6.11$ Hz, $^4J = 2.59$ Hz, 1 H, H-3′a), 2.45 (dddd, $^2J = 16.48$ Hz, $^3J = 10.08$ Hz, $^3J = 5.49$ Hz, $^4J = 2.75$ Hz, 1 H, H-3′b), 2.56 (s, 1 H, OH), 3.67 (dd, $^2J = 11.91$ Hz, $^3J = 0.92$ Hz, 1 H, H-6a), 3.96 (d, $^2J =$ 9.76 Hz, 1 H, H-1a), 3.97 (dd, $^3J = 7.43$ Hz, $^3J = 1.37$ Hz, 1 H, H-5), 4.19 (dd, $^2J = 12.20$ Hz, $^3J = 2.44$ Hz, 1 H, H-6b), 4.20 (d, $^3J = 7.63$ Hz, 1 H, H-4), 4.25 (d, $^2J = 10.07$ Hz, 1 H, H-1b); ^{13}C-NMR (100.6 MHz, C_6D_6): $\delta = 13.17$ (C-4′), 25.31, 25.94, 27.03, 27.35 (4 CH_3), 34.15 (C-3′), 64.73 (C-6), 69.84 (C-1′), 73.07 (C-3), 73.68 (C-5), 73.93 (C-1), 74.37 (C-4), 85.44 (C-2′), 106.36 (C-2), 109.96, 110.34 (2 C_q); FT-IR (film): $\nu =$ 3534 cm^{-1} (*s*, ν_{O-H}), 3289 (*s*, $\nu_{C\equiv C-H}$), 2982 (*vs*, ν_{C-H}), 2938 (*vs*, ν_{C-H}), 2899 (*s*, ν_{C-H}), 2878 (*m*, ν_{C-H}), 2120 (*w*, $\nu_{C\equiv C}$); MS (FAB, *m*-NBA); *m*/*z* (%): 313 (32) [M^+ + H], 297 (80) [M^+–CH_3], 255 (100) [(M^+ + H)–$(CH_3)_2C{=}O$], 194 (93).

*4.2.3. 1,2:4,5-Di-O-isopropylidene-3-C-(4′-but-1′-ynyl)-β-D-psicopyranose (**6**)*

Column chromatography on silica gel using petroleum ether–diethyl ether (1:1) as eluent gave 575 mg (1.8 mmol, 46%) of **6** as white solid, m.p. 96–97°C, and 607 mg (1.7 mmol, 43%) of **7** as viscous colorless oil. **6**: $R_f = 0.87$ (petroleum ether–diethyl ether, 1:1); $[\alpha]_D^{20} = -78°$ ($c = 0.66$, $CHCl_3$); ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 1.34$ (s, 3 H, CH_3), 1.42 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3), 1.55 (s, 3 H, CH_3), 1.83 (pt, $J = 8.24$ Hz, 2 H, H-4′a/b), 1.91 (t, $^4J = 2.62$ Hz, 1 H, H-1′), 2.39–2.49 (m, 2 H, H-3′a/b), 2.64 (s, br, 1 H, OH), 3.93 (d, $^2J = 9.52$ Hz, 1 H, H-1a), 4.03–4.24 (m, 4 H, H-4, H-5 and H-6a/b), 4.33 (d, $^2J = 9.52$ Hz, 1 H, H-1b); ^{13}C-NMR (62.8 MHz, $CDCl_3$): $\delta = 13.16$ (C-4′), 25.38 (2 C, 2 CH_3), 25.85, 26.31 (2 CH_3), 34.99 (C-3′), 59.63 (C-6), 67.80 (C-1′), 71.04 (C-3), 71.55 (C-5), 72.23 (C-1), 75.15 (C-4), 85.14 (C-2′), 106.88 (C-2), 108.79, 112.37 (2 C_q); FT-IR (KBr): $\nu = 3491$ cm^{-1} (*vs*, ν_{O-H}), 3315 (*s*, $\nu_{C\equiv C-H}$), 3297 (*s*, $\nu_{C\equiv C-H}$), 2995 (*vs*, ν_{C-H}), 2943 (*s*, ν_{C-H}), 2898 (*m*, ν_{C-H}), 2127 (*w*, $\nu_{C\equiv C}$); MS (EI, 70 eV); *m*/*z* (%): 312 (1) [M^+], 297 (29) [M^+–CH_3], 81 (100); HRMS Calc. for M^+–CH_3: 297.1338. Found: 297.1345. Anal. Calc. for $C_{16}H_{24}O_6$: C, 61.52; H, 7.74. Found: C, 61.25; H, 7.66%.

*4.2.4. 1,2:4,5-Di-O-isopropylidene-3-C-bromomethyl-β-D-psicopyranose (**7**)*

$R_f = 0.56$ (petroleum ether–diethyl ether, 1:1); $[\alpha]_D^{20} = -111°$ ($c = 0.27$, $CHCl_3$); ^{1}H-NMR (250 MHz, C_6D_6): $\delta = 1.14$ (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3), 2.13 (d, $^2J = 5.96$ Hz, 1 H, H-1′a), 3.02 (d, $^2J = 5.09$ Hz, 1 H, H-1′b), 3.49 (dd, $^2J = 13.01$ Hz, $^3J = 1.79$ Hz, 1 H, H-6a), 3.64 (d, $^2J = 13.11$ Hz, 1 H, H-6b), 3.65 (d, $^3J = 7.45$ Hz, 1 H, H-4), 3.78 (dd, $^3J = 7.50$ Hz, $^3J = 1.04$ Hz, 1 H, H-5), 4.27 (d, $^2J = 9.14$ Hz, 1 H, H-1a), 4.51 (d, $^2J = 9.14$ Hz, 1 H, H-1b); ^{13}C-NMR (62.8 MHz, C_6D_6): $\delta = 25.32$, 26.28, 26.30, 26.49 (4 CH$_3$), 48.06 (C-1′), 56.70 (C-3), 64.14 (C-6), 74.27, 75.53, 76.30 (C-1, C-4 and C-5), 103.90 (C-2), 110.36, 110.73 (2 C$_q$); MS (EI, 70 eV); *m*/*z* (%): 337 (3) [M$^+$–CH$_3$], 81 (100); HRMS Calc. for M$^+$–CH$_3$: 337.0287. Found: 337.0292.

4.3. General procedure for the synthesis of carbohydrate-derived spirocyclic 2-oxacyclohexylidene metal complexes ***8–11***

A solution of 1.5 mmol of metal carbonyl [Cr(CO)$_6$ or W(CO)$_6$] in 50 ml of tetrahydrofuran was irradiated for 5 h at − 10°C using a mercury vapor lamp (Philips 125 HPK) and quartz glassware while a color change to orange occurred. Then the solution of the pentacarbonyl(tetrahydrofuran)metal complex was cooled to − 25°C. After addition of 1.5 mmol of 4-pentyn-1-ol the cooling bath was removed and the solution was concentrated to one third before the reaction mixture was stirred at r.t. for 24 h. The solvent was stripped off and the dark brown residue was chromatographed on silica gel using mixtures of petroleum ether–diethyl ether as eluent affording mixtures of complexes **8**–**11** and pentynols **4**–**6**. A second column chromatography was performed to separate the ylidene complexes from the starting pentynols.

4.3.1. Pentacarbonyl{1′,2′:5′,6′-di-O-isopropylidene-spiro[α-D-allopyranos-3,3′-oxacyclohex]-1-ylidene}-chromium ***(8)***

Column chromatography on silica gel using petroleum ether–methylene chloride (1:2) as eluent gave 11 mg (0.02 mmol, 1%) of **8** as a viscous yellow oil. $R_f = 0.74$ (petroleum ether–diethyl ether, 1:1); $R_f = 0.26$ (petroleum ether–methylene chloride, 1:2); ^{1}H-NMR (500 MHz, C$_6$D$_6$): $\delta = 0.72–0.80$ (m, 1 H, H-5a), 0.82–0.89 (m, 1 H, H-5b), 0.99 (s, 3 H, CH$_3$), 1.20 (s, 3 H, CH$_3$), 1.26 (s, 3 H, CH$_3$), 1.29 (s, 3 H, CH$_3$), 1.93–2.00 (m, 2 H, H-4a/b), 2.78 (ddd, $^2J = 20.74$ Hz, $^3J = 10.60$ Hz, $^3J = 6.83$ Hz, 1 H, H-6a), 3.47 (d, br, $^2J = 20.36$ Hz, 1 H, H-6b), 3.96 (d, $^3J = 8.84$ Hz, 1 H, H-4′), 3.98 (d, $^3J = 3.68$ Hz, 1 H, H-2′), 4.00 (dd, $^2J = 8.98$ Hz, $^3J = 5.17$ Hz, 1 H, H-6′a), 4.04 (dd, $^2J = 8.79$ Hz, $^3J = 6.21$ Hz, 1 H, H-6′b), 4.60 (dpt, $^3J = 8.91$ Hz, $^3J = 5.49$ Hz, 1 H, H-5′), 5.95 (d, $^3J = 3.68$ Hz, 1 H, H-1′); ^{13}C-NMR (125.7 MHz, C$_6$D$_6$): $\delta = 15.69$ (C-5), 23.34 (C-4), 25.49, 27.26, 27.52, 27.76 (4 CH$_3$), 55.61 (C-6), 69.18 (C-6′), 73.73 (C-5′), 84.34, 85.10 (C-2′, C-4′), 85.23 (C-3), 105.98 (C-1′), 110.76, 113.93 (2 C$_q$), 217.75 (*cis*-CO), 224.58 (*trans*-CO), 356.89 (*ylidene*-C); FT-IR (petroleum ether): $\nu_{CO} = 2064$ cm^{-1} (*w*, A$_1^1$), 1983 (*m*, B), 1962 (*m*, A$_1^2$), 1949 (*s*, E); MS (EI, 70 eV): *m*/*z* (%): 504 (1) [M$^+$], 489 (1) [M$^+$–CH$_3$], 476 (1) [M$^+$–CO], 461 (1) [M$^+$–CO, –CH$_3$], 448 (1) [M$^+$–2CO], 420 (1) [M$^+$–3CO], 392 (1) [M$^+$–4CO], 364 (1) [M$^+$–5CO], 101 (100) [2,2-dimethyldioxacyclopentyl$^+$]; HRMS Calc. for M$^+$: 504.0724. Found: 504.0722.

4.3.2. Pentacarbonyl{1′,2′:4′,5′-di-O-isopropylidene-spiro[β-D-fructopyranos-3,3′-oxacyclohex]-1-ylidene}-chromium ***(9)***

Column chromatography on silica gel using petroleum ether–methylene chloride (2:1) as eluent gave 15 mg (0.03 mmol, 2%) of **9** as a viscous yellow oil. $R_f = 0.74$ (petroleum ether–diethyl ether 3:1); $R_f = 0.23$ (petroleum ether–methylene chloride, 2:1); ^{1}H-NMR (500 MHz, C$_6$D$_6$): $\delta = 0.71–0.78$ (m, 1 H), 0.80–0.88 (m, 2 H), 1.06 (s, 3 H, CH$_3$), 1.29 (s, 3 H, CH$_3$), 1.35 (s, 3 H, CH$_3$), 1.43 (s, 3 H, CH$_3$), 1.69–1.75 (m, 1 H), 2.56 (ddd, $^2J = 19.97$ Hz, $^3J = 9.84$ Hz, $^3J = 5.86$ Hz, 1 H, H-6a), 3.53 (d, br, $^2J = 19.77$ Hz, 1 H, H-6b), 3.82 (d, $^2J = 12.81$ Hz, 1 H, H-6′a), 3.90 (d, $^3J = 9.83$ Hz, 1 H, H-1′a), 3.94 (d, $^3J = 9.83$ Hz, 1 H, H-1′b), 4.09 (d, $^3J = 7.25$ Hz, 1 H, H-4′), 4.18 (dd, $^3J = 7.25$ Hz, $^3J = 2.38$ Hz, 1 H, H-5′), 4.47 (dd, $^2J = 12.67$ Hz, $^3J = 2.33$ Hz, 1 H, H-6′b); ^{13}C-NMR (125.7 MHz, C$_6$D$_6$): $\delta = 14.20$ (C-5), 26.00 (C-4), 25.67, 26.85, 26.89, 27.20 (4 CH$_3$), 55.01 (C-6), 64.46 (C-6′), 73.98 (C-1′), 74.22, 76.11 (C-4′, C-5′), 90.73 (C-3), 105.66 (C-2′), 110.56, 111.84 (2 C$_q$), 217.85 (*cis*-CO), 224.75 (*trans*-CO), 357.81 (*ylidene*-C); FT-IR (petroleum ether): $\nu_{CO} = 2067$ cm^{-1} (*w*, A$_1^1$), 1989 (*vw*, B), 1964 (*m*, A$_1^2$), 1953 (*vs*, E), 1942 (*s*); MS (EI, 70 eV); *m*/*z* (%): 504 (15) [M$^+$], 420 (19) [M$^+$–3CO], 392 (49) [M$^+$–4CO], 364 (3) [M$^+$–5CO], 218 (100); HRMS Calc. for M$^+$: 504.0724. Found: 504.0722.

4.3.3. Pentacarbonyl{1′,2′:4′,5′-di-O-isopropylidene-spiro[β-D-fructopyranos-3,3′-oxacyclohex]-1-ylidene}-tungsten ***(10)***

Column chromatography on silica gel using petroleum ether–ethylene chloride (1:2) as eluent gave 51 mg (0.08 mmol, 5%) of **10** as a viscous yellow oil. $R_f = 0.46$ (petroleum ether–diethyl ether, 3:1); $R_f = 0.43$ (petroleum ether–methylene chloride, 2:1); ^{1}H-NMR (250 MHz, C$_6$D$_6$): $\delta = 0.75–0.89$ (m, 2 H, H-5a/b), 1.07 (s, 3 H, CH$_3$), 1.29 (s, 3 H, CH$_3$), 1.35 (s, 3 H, CH$_3$), 1.42 (s, 3 H, CH$_3$), 1.46–1.56 (m, 1 H, H-4a), 1.78 (ddpt, $^2J = 14.24$ Hz, $^3J = 5.10$ Hz, $^4J = 1.67$ Hz, 1 H, H-4b), 2.24 (ddd, $^2J = 20.32$ Hz, $^3J = 9.22$ Hz, $^3J = 6.29$ Hz, 1 H, H-6a), 3.28 (ddpt, $^2J = 20.37$ Hz, $^3J = 4.23$ Hz, $^2J = 1.91$ Hz, 1 H, H-6b), 3.80 (d, $^2J = 12.94$ Hz, H-6′a), 3.81–3.91 (m, 2 H, H-1′a/b), 4.06 (d, $^3J = 7.32$ Hz, 1 H, H-4′), 4.13 (dd, $^3J = 7.32$ Hz, $^3J = 2.56$ Hz, 1 H, H-5′), 4.38 (dd, $^2J = 12.88$ Hz, $^3J = 2.56$ Hz, 1 H, H-6′b); ^{13}C-NMR (62.8 MHz, C$_6$D$_6$): $\delta = 14.09$ (C-5), 26.70 (C-4), 25.68, 25.99, 26.85, 27.22 (4 CH$_3$), 56.86

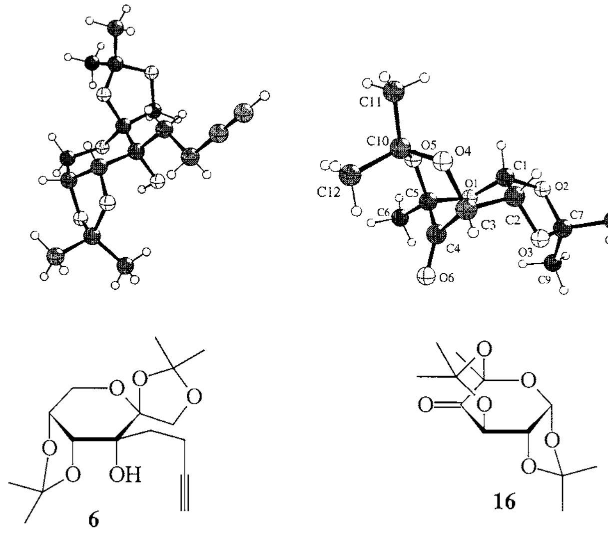

Fig. 1.

(C-6), 64.44 (C-6′), 73.95 (C-1′), 74.15 (C-5′), 76.09 (C-4′), 90.34 (C-3), 105.62 (C-2′), 110.59, 111.87 (2 C_q), 199.06 (t, $J_{CW} = 61.03$ Hz, *cis*-CO), 206.15 (*trans*-CO), 329.91 (*ylidene*-C); FT-IR (petroleum ether): $\nu_{CO} = 2071$ cm^{-1} (*w*, A_1^1), 1981 (*w*, B), 1952 (*vs*, E), 1937 (*s*, A_1^2); MS (EI, 70 eV): *m/z* (%): 634 (20) [M$^+$], 621 (11) [M$^+$–CH$_3$], 496 (6) [M$^+$–5CO], 268 (17) [W(CO)$_3^+$], 43 (100) [C$_2$H$_3$O$^+$]; $C_{21}H_{24}O_{11}$ ^{182}W; HRMS Calc. for M$^+$; $C_{21}H_{24}O_{11}$ ^{182}W: 634.081. Found: 634.0795.

4.3.4. *Pentacarbonyl{1′,2′:4′,5′-di-O-isopropylidene-spiro[β-D-psicopyranos-3,3′-oxacyclohex]-1-ylidene}-tungsten (**11**)*

After the first column chromatography using petroleum ether–diethyl ether (3:1) as eluent a few milligrams (yield < 1%) of **11** were obtained. Further purification was not attempted. $R_f = 0.34$ (petroleum ether–diethyl ether, 3:1); ^{13}C-NMR (125.6 MHz, C_6D_6): $\delta = 196.98$ (t, $J_{CW} = 61.03$ Hz, *cis*-CO), 204.54 (*trans*-CO), 328.21 (*ylidene*-C); FT-IR (petroleum ether): $\nu_{CO} = 2070$ cm^{-1} (*w*, A_1^1), 1983 (*w*, B), 1965 (*w*), 1950 (*s*, A_1^2), 1942 (*vs*, E), 1934 (*s*).

4.4. *6-Desoxy-1,2:3,4-di-O-isopropylidene-α-D-galacto-4-ene-1,5-pyranose (**15**)*

A total of 1.7 g (15 mmol) of potassium *tert*-butoxide was added at r.t. to a solution of 1.1 g (3 mmol) of 6-desoxy-6-iodo-1,2:3,4-di-*O*-isopropylidene-α-D-galacto-1,5-pyranose (**12**) in 55 ml of *N*,*N*-dimethylformamide. After 20 h the reaction mixture was treated with 100 ml of water. 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, dried over magnesium sulfate, and the solvent was removed. Column chromatography of the crude product, an orange oil, on silica gel using a mixture of petroleum ether–diethyl ether (3:1) gave 300 mg (1.24 mmol, 41%) of **15** as a pale yellow solid, m.p. 33°C. $R_f = 0.52$ (petroleum ether–diethyl ether, 3:1); $[\alpha]_D^{20} = -96°$ ($c = 0.3504$, CHCl$_3$); ^{1}H-NMR (500 MHz, CDCl$_3$): $\delta = 1.39$ (s, 3 H, CH$_3$), 1.44 (s, 3 H, CH$_3$), 1.49 (s, 3 H, CH$_3$), 1.54 (s, 3 H, CH$_3$), 1.80 (d, $^4J = 2.28$ Hz, 3 H, CH$_3$-6), 4.41 (dd, $^3J = 4.27$ Hz, $^4J = 2.78$ Hz, 1 H, H-2), 4.58 (pqui, $J = 2.41$ Hz, 1 H, H-3), 5.19 (d, $^3J = 4.27$ Hz, 1 H, H-1); ^{13}C-NMR (125.7 MHz, CDCl$_3$): $\delta = 13.78$ (C-6), 25.02, 26.35, 26.43, 27.76 (4 CH$_3$), 76.38 (C-3), 85.09 (C-2), 99.33 (C-1), 112.83, 112.98 (2 C_q), 123.66 (C-5), 137.96 (C-4); FT-IR (KBr): $\nu = 2996$ cm^{-1} (*s*, ν_{C-H}), 2936 (*s*, ν_{C-H}), 1386 (*vs*, δ_{C-H}), 1382 (*vs*, δ_{C-H}), 1127 (*vs*), 1025 (*vs*, ν_{C-O}); MS (EI, 70 eV): *m/z* (%): 242 (18) [M$^+$], 227 (8) [M$^+$–CH$_3$], 184 (18) [M$^+$–(CH$_3$)$_2$C=O], 169 (29) [M$^+$–CH$_3$, –(CH$_3$)$_2$C=O], 84 (100), 59 (98); HRMS Calc. for M$^+$: 242.1154. Found: 242.1144; Anal. Calc. for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 59.48; H, 7.46%.

4.5. *6-Desoxy-1,2:3,5-di-O-isopropylidene-α-D-threo-4,5-hexodiulo-1,5-pyranose (**16**)*

A total of 25 ml of a 0.06 M solution of DMDO in acetone was added at 0°C to a solution of 242 mg (1 mmol) of **15** in 10 ml of methylene chloride. After 2 h, all of the starting material had reacted. Starting material **15** and product **16** have the same R_f-value, but the product does not decolorize a solution of potassium permanganate. The solvent was evaporated, and the residue was chromatographed on silica gel using a mixture of petroleum ether–diethyl ether (3:1) as eluent to afford 225 mg (0.87 mmol, 87%) of **16** as a colorless solid, m.p. 94°C. $R_f = 0.52$ (petroleum ether–diethyl ether, 3:1); $[\alpha]_D^{20} = -18°$ ($c = 0.07$, CHCl$_3$); ^{1}H-NMR (250 MHz, CDCl$_3$): $\delta = 1.31$ (s, 3 H, CH$_3$), 1.34 (s, 3 H, CH$_3$), 1.37 (s, 6 H, 2 CH$_3$), 1.45 (s, 3 H, C-6, CH$_3$), 4.32 (d, $^3J = 4.15$ Hz, 1 H, H-3), 4.61 (dd, $^3J = 3.85$ Hz, $^3J = 2.75$ Hz, 1 H, H-2), 5.79 (d, $^3J = 2.56$ Hz, 1 H, H-1); ^{13}C-NMR (62.8 MHz, CDCl$_3$): $\delta = 21.28$ (CH$_3$), 26.16 (2 CH$_3$), 27.38 (CH$_3$), 28.98 (C-6), 72.77 (C-3), 85.98 (C-2), 95.55 (C-1), 96.52 (C-5), 99.35, 113.31 (2 C_q), 201.59 (C-4); FT-IR (KBr): $\nu = 3002$ cm^{-1} (*s*, ν_{C-H}), 2943 (*m*, ν_{C-H}), 2885 (*w*, ν_{C-H}), 1767 (*vs*, $\nu_{C=O}$); MS (EI, 70 eV): *m/z* (%): 243 (15) [M$^+$–CH$_3$], 215 (2) [M$^+$–C$_2$H$_3$O], 200 (3) [M$^+$–(CH$_3$)$_2$C=O], 185 (42) [M$^+$–C$_3$H$_5$O$_2$], 171 (34), 101 (61), 59 (100) [HO = C(CH$_3$)$_2^+$]; HRMS Calc. for M$^+$–CH$_3$: 243.0869. Found: 243.0857; Anal. Calc. for $C_{12}H_{18}O_5$: C, 55.81; H, 7.02. Found: C, 56.14; H, 7.14%.

4.6. X-Ray crystallographic studies of **6** and **16** (Fig. 1)

Colorless needles of **6** grown from a solution of **6** in petroleum ether–diethyl ether (1:1) upon cooling from 50°C to r.t. were subjected to single crystal X-ray analysis. Crystallization of **16** from petroleum ether by slow evaporation of the solvent at r.t. provided colorless crystals which were subjected to single-crystal X-ray analysis. The structures were solved by direct methods (SHELXS-97) [21]. The non-hydrogen atoms were refined anisotropically on F^2 (SHELXL-97) [22]. Hydrogen atoms were refined using a riding model. The absolute structures were determined by refinement of Flack's parameter x [23]. An empirical absorption correction on the basis of ψ-scans was applied for **6** and an extinction correction for **16**. Further details are given in Table 1.

5. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 138141 for **6** and CCDC no. 138140 for **16**. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Rd., Cambridge CB2 1EX, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.com.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 1
Crystallographic data and summary of data collection and refinement of **6** and **16**

	6	**16**
Formula	$C_{16}H_{24}O_6$	$C_{12}H_{18}O_6$
M_r	312.35	258.26
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$ (no.19)	$P2_12_12_1$ (no.19)
a (Å)	10.099(1)	9.127(1)
b (Å)	18.296(2)	11.684(1)
c (Å)	18.294(5)	12.526(1)
V (Å^3)	3380(1)	1335.8(2)
Z	8	4
Crystal size (mm^3)	$0.15\times0.40\times0.60$	$0.25\times0.43\times0.60$
ρ_{calc} (g cm^{-3})	1.23	1.28
μ (mm^{-1})	0.776	0.873
$F(000)$	1344	552
Diffractometer	Enraf-Nonius MACH3	
Radiation	Cu–K$_\alpha$	Cu–K$_\alpha$
λ (Å)	1.54178	1.54178
T (K)	293(2)	293(2)
Scan type	$2\theta/\omega$	$2\theta/\omega$
Max 2θ (°)	140	140
Index range	$0\leq h\leq 12$	$-11\leq h\leq 11$
	$0\leq k\leq 22$	$-6\leq k\leq 14$
	$-22\leq l\leq 22$	$-2\leq l\leq 15$
No. of data	7406	3956
No. of unique data	6384	2503
R_{int}	0.022	0.093
Parameters/restraints	396/23	165/0
x	0.26(18)	0.0(3)
$R(F)$ for $I>2\sigma(I)$	0.046	0.060
$wR_2(F^2)$ for all data	0.126	0.171
Goodness-of-fit on F^2	1.02	1.07

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References

[1] C. Jäkel, K.H. Dötz, Tetrahedron 56 (2000) 2167.

[2] (a) F.J. Schmitz, F.J. McDonald, D.J. Vanderah, J. Org. Chem. 43 (1978) 4220. (b) M.D. Lord, J.T. Negri, L.A. Paquette, J. Org. Chem. 60 (1995) 191.

[3] J.A. Robinson, Fortschr. Chem. Org. Naturst. 58 (1991) 1.

[4] For reviews, see: (a) K.H. Dötz, H. Fischer, P. Hofmann, F.R. Kreißl, U. Schubert, K. Weiss, Transition Metal Carbene Complexes, Verlag Chemie, Weinheim, 1983. (b) K.H. Dötz, Angew. Chem. Int. Ed. Engl. 23 (1984) 587. (c) W.D. Wulff, in: B.M. Trost, I. Fleming, L.A. Paquette (Eds.), Comprehensive Organic Synthesis, vol. 5, Pergamon Press, Oxford, 1991, p. 1065. (d) W.D. Wulff, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon Press, Oxford, 1995, p. 469. (e) L.S. Hegedus, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon Press, Oxford, 1995, p. 549. (f) M.J. Winter, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 5, Pergamon Press, Oxford, 1995, p. 155. (g) D.F. Harvey, D.M. Sigano, Chem. Rev. 96 (1996) 271. (h) A. de Meijere, Pure Appl. Chem. 68 (1996) 61. (i) J. Barluenga, Pure Appl. Chem. 68 (1996) 543.

[5] (a) B. Weyershausen, M. Nieger, K.H. Dötz, Organometallics 17 (1998) 1602. (b) B. Weyershausen, M. Nieger, K.H. Dötz, J. Org. Chem. 64 (1999) 4206.

[6] (a) For a review on carbohydrate-modified metal carbene complexes, see: K.H. Dötz, R. Ehlenz, Chem. Eur. J. 3 (1997) 1751 and Refs. therein. (b) T. Pill, K. Polborn, W. Beck, Chem. Ber. 123 (1990) 11. (c) R. Aumann, Chem. Ber. 125 (1992) 2773. (d) R. Aumann, Chem. Ber. 127 (1994) 725. (e) H. Fischer, J. Schleu, G. Roth, Chem. Ber. 128 (1995) 373. (f) K.H. Dötz, W. Straub, R. Ehlenz, K. Peseke, R. Meisel, Angew. Chem. Int. Ed. Engl. 34 (1995) 1856. (g) H. Fischer, J. Schleu, G. Roth, Chem. Ber. 129 (1996) 385. (h) S. Krwielitzki, W. Beck, Chem. Ber./Recueil 130 (1997) 1659. (i) H. Fischer, K. Weißenbach, C. Karl, A. Geyer, Eur. J. Inorg. Chem. (1998) 339.

[7] For a review on the cycloisomerization of alkynols, see: B. Weyershausen, K.H. Dötz, Eur. J. Inorg. Chem. (1999) 1057.

[8] For the synthesis of spirocyclic carbohydrate-derived 2-oxacyclo*pentylidene* chromium and tungsten complexes, see: K.H. Dötz, O. Neuß, M. Nieger, Synlett (1996) 995.

[9] L. Brandsma, H. Verkruijsse, Preparative Polar Organometallic Chemistry I, Berlin, Springer, 1987, p. 63.

[10] (a) R.L. Beddoes, R.W. Grime, Z.I. Hussain, M.W. Whiteley, J. Chem. Soc. Dalton Trans. (1996) 3893. (b) See citation 8 in:

M.P. Gamasa, J. Gimeno, M. Gonzalez-Cueva, E. Lastra, J. Chem. Soc. Dalton Trans. (1996) 2547. (c) C. Bianchini, A. Marchi, N. Mantovanti, L. Marvelli, D. Masi, M. Peruzzini, R. Rossi, Eur. J. Inorg. Chem. (1998) 211.

[11] (a) F.E. McDonald, J.L. Bowman, Tetrahedron Lett. 37 (1996) 4675. (b) F.E. McDonald, H.Y.H. Zhu, Tetrahedron 53 (1997) 11061. (c) K.-W. Liang, W.-T. Li, S.-M. Peng, S.-L. Wang, R.-S. Liu, J. Am. Chem. Soc. 119 (1997) 4404. (d) J.L. Bowman, F.E. McDonald, J. Org. Chem. 63 (1998) 3680.

[12] For the synthesis of group 6 metal 2-oxacyclohexylidene complexes by other methodologies than metal-assisted alkynol cycloisomerization, see: (a) C.A. Merlic, D.J. Xu, Am. Chem. Soc. 113 (1991) 9855. (b) S. Aoki, T. Fujimura, E.J. Nakamura, J. Am. Chem. Soc. 114 (1992) 2985.

[13] (a) P.J. Garegg, B.J. Samuelson, Chem. Soc. Chem. Commun. (1979) 978. (b) P.J. Garegg, B.J. Samuelson, Chem. Soc. Perkin Trans. I (1980) 2866.

[14] (a) K. Freudenberg, K. Raschig, Ber. 62 (1929) 373. (b) B. Helferich, E. Himmen, Ber. 62 (1929) 2136, (c) T. Iimori, H. Takahashi, S. Ikegami, Tetrahedron Lett. 37 (1996) 649.

[15] I. Frappa, Unpublished results, Universität Bonn, Germany, 1997.

[16] R.L. Halcomb, S.J.J. Danishefsky, Am. Chem. Soc. 111 (1989) 6661.

[17] F. Perron, K.F. Albizati, Chem. Rev. 89 (1989) 1617.

[18] (a) D.H.R. Barton, P.G. Sammes, M.V. Taylor, E.J. Werstiuk, Chem. Soc. 14 (1970) 1977. (b) T. Harrison, P.L. Myers, G. Pattenden, Tetrahedron 45 (1989) 5247. (c) A. Talab, C. Cave, S. Menager, M. Miocque, O. Lafont, Ann. Pharm. Fr. 47 (1990) 304.

[19] (a) A. Kirrmann, P. Duhamel, R. Nouri-Bimorghi, Justus Liebigs Ann. Chem. 691 (1966) 33. (b) D.C. Baker, D.K. Brown, D. Horton, R.G. Nikol, Carbohydr. Res. 32 (1974) 299.

[20] B.E. Maryanoff, A.B. Reitz, S.O Nortey, Tetrahedron 44 (1988) 3093.

[21] G.M. Sheldrick, SHELXS-97, Acta Crystallogr. A46 (1990) 467.

[22] G.M. Sheldrick, SHELXL-97, Universität Göttingen, Germany, 1997.

[23] H.D. Flack, Acta Crystallogr. A39 (1983) 876.