Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 669 (2003) 1–5
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Organotransition metal modified sugars
Part 23. Synthesis of vinylcarbene chromium complexes containing a *C*-monosaccharide ligand☆

Erik Janes, Karl Heinz Dötz *

Kekulé-Institut für Organische Chemie und Biochemie der Rheinischen, Friedrich-Wilhelms Universität, Gerhard-Domagk-Strasse 1, D-53121 Bonn, Germany

Received 21 October 2002; accepted 2 December 2002

Abstract

Organometallic *C*-glycosides containing a chromium carbene functionality have been synthesized from pentacarbonyl[(methoxy)methylcarbene]chromium (**1**) in a $TiCl_4$-assisted aldol condensation with formyl glycosides. The condensation is *trans*-selective to give a 54–82% yield of chromium vinylcarbene *C*-glycosides **5**, **6** and **8** which are promising candidates for subsequent Diels–Alder, Michael addition, benzannulation and cyclopropanation reactions.

Keywords: Bioorganometallic chemistry; Chromium carbene complexes; Aldol condensation; *C*-glycosides; Organometallic monosaccharides

1. Introduction

Due to the ubiquitous role carbohydrates play in biology, carbohydrate analogues are valuable tools for the study of biochemical systems. Since the chemistry of sugars is dominated by the reactivity of the glycosidic bond, a great deal of effort has been devoted to the synthesis and study of *C*-glycosides in which the acetal linkage is replaced by a carbon–carbon bond stable towards hydrolysis. The synthesis of *C*-glycosides has become a well established area of carbohydrate chemistry [2]. Several *C*-glycosides are potent carbohydrate mimics [3] in antitumor, antibiotic, antiviral or antibacterial therapy [4].

In the past decades metal carbenes have been developed to valuable reagents for stereoselective organic synthesis [5]. Their impact on the elaboration of carbohydrates 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]. We were interested in organometallic models of this type of reagents, and recently reported on the synthesis of a combined *O*- and *C*-disaccharide skeleton separated by a metal carbene spacer [18]. We now concentrate on the flexibility of the aldol condensation with formyl glycosides for the synthesis of organometallic *C*-glycosides.

2. Results and discussion

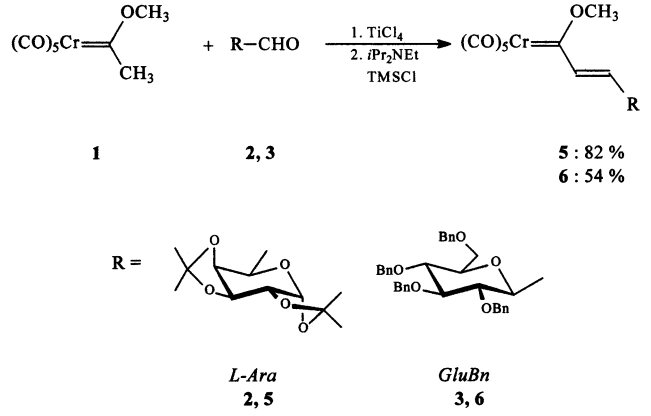
The aldol condensation of methylcarbene complexes is a convenient route to alkenyl carbene complexes [19]. It was first applied to reactive non-enolizable aldehydes

☆ For Part 22, see Ref. [1].

* Corresponding author. Tel.: +49-228-73-5609; fax: +49-228-73-5813.
E-mail address: doetz@uni-bonn.de (K.H. Dötz).

0022-328X/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0022-328X(02)02160-5

such as benzaldehyde in the presence of triethyl amine where it resulted in quantitative yields [20]. The scope of this methodology can be extended to various aldehydes and ketones if the carbonyl compound is activated by pre-complexation with a Lewis acid [21]. Recently, we have applied this approach to the synthesis of vinylcarbene disaccharides from sugar aldehydes [18]. The major problem of this route was the activation of 1,2:3,4-di-*O*-isopropylidene-α-D-galactohexodialdo-1,5-pyranose (**2**) by a Lewis acid which had to be compatible with the protective groups. After an extensive series of tests it became clear that $TiCl_4$ applied at low temperature (−78 °C) along with a combination of Hünig's base (five equivalents) and trimethylsilyl chloride (five equivalents) turned out to be the reagents of choice. We explored whether these conditions are generally applicable to the reaction of pentacarbonyl[(methoxy)-methylcarbene]chromium **1** with formyl glycosides bearing different protecting groups such as in 1,2:3,4-di-*O*-isopropylidene-α-D-galactohexadialdo-1,5-pyranose (**2**) and 2,3,4,6-tetra-*O*-benzyl-1-formyl-D-glucopyranose (**3**). The aldol condensation afforded chromium carbene monosaccharides **5** and **6** based on 1,2:3,4-di-*O*-isopropylidene-α-L-arabinopyranose and 1-deoxy-2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranose as novel *C*-glycoside components; these complexes were obtained as red oils in 54–82% yield after flash chromatography at −20 °C using dichloromethane as eluent (Scheme 1).

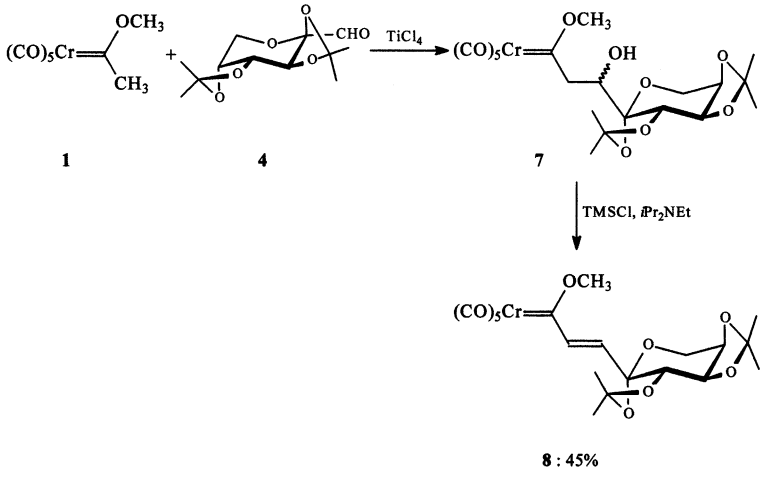


Scheme 1. Synthesis of chromium carbene *C*-saccharides **5** and **6** via aldol condensation.

These results demonstrated that the reaction conditions are compatible with glycosides bearing a 'primary' aldehyde group even at the anomeric center as well as with protective groups stable towards base.

We then focused our interest on the synthesis of sugar aldehydes bearing less flexible carbohydrate skeletons and turned to a sugar containing a 'tertiary' aldehyde functionality such as 2,3:4,5-di-*O*-isopropylidene-β-D-fructohexadialdo-2,6-pyranose (**4**). Surprisingly, the reaction with 'fructose aldehyde' **4** stopped at the aldol addition stage **7** which was isolated in 82% yield (Scheme 2); HPLC indicated that complex **7** was formed as a mixture of diastereomers. Obviously, this product was unable to undergo elimination to the aldol condensation product. Variation of the condensation conditions using other bases like triethyl amine did not result in any significant improvement. However, elimination could be achieved starting from the in situ generated-aldol addition product **7** at room temperature over a period of 26 h using our standard base–oxophile system to give 1,2:3,4-di-*O*-isopropylidene-α-D-arabinopyranose derivative **8** as a red oil in 45% yield (Scheme 2). This experimental result indicates the limitation of the aldol condensation procedure with formyl glycosides: The presence of a severely sterically hindered unflexible sugar skeleton attached to the formyl group renders the elimination step extremely difficult.

In contrast to the activation of sugar-based alkynols at a metal carbonyl template [22] this variant of aldol



Scheme 2. Synthesis of pentacarbonyl[methoxy(1,2:3,4-di-*O*-isopropylidene-α-D-arabinopyranosyl-1-propenylidene)]chromium **8** via aldol condensation.

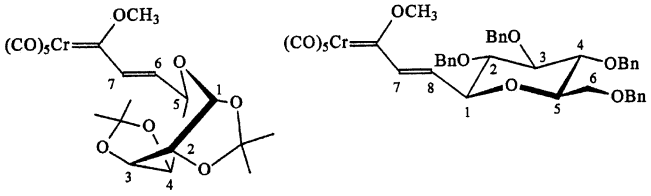


Fig. 1. Atom-numbering in metal vinylcarbene *C*-glycosides pentacarbonyl[methoxy-(1,2:3,4-di-*O*-isopropylidene-α-L-arabinopyranosyl-5-propenylidene)]chromium (**5**) and pentacarbonyl-[methoxy(1-deoxy-2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl-1-propenylidene)]-chromium (**6**).

condensation is *trans*-selective. The structural elucidation of the products **5**, **6** and **8** was mainly based on their ^{1}H- and ^{13}C-NMR spectra. The ^{1}H-NMR spectrum of the compound **7** reveals signals of a methylene group (H-7/H-7a) and of H-6 appearing as a broad singlet. Another significant indication for a saturated carbene complex such as **7** is the ^{13}C-NMR absorption at 362 ppm revealing a down field shift of 22 ppm as compared with its unsaturated analogue **8**. 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 $^{3}J_{H,H} = 15$ Hz. The ^{1}H-NMR signal of H-7 next to the carbene carbon atom appears as a doublet reflecting only the *E*-vicinal coupling across the olefinic C=C bond and resonates at 7.50–7.60 ppm; with the exception of complex **8** the signals for H-6 or H-8, respectively, are observed as a doublet of doublets resulting from the additional vicinal coupling to the adjacent glycosidic hydrogen atom. In contrast to the flexible chair conformation of the benzyl-protected glucose skeleton in complex **8** the isopropylidene-protected arabinose (in **5** and **8**) adopts a rigid boat conformation (Fig. 1).

3. Conclusion

The Lewis acid-assisted aldol condensation of the methoxy(methyl)carbene chromium complex **1** and sugar aldehydes bearing various protective groups provides a general synthetic method for the *trans*-selective formation of vinylcarbene *C*-glycosides. These chromium vinylcarbenes are thermostable compounds 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.

4. Experimental

4.1. 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.

4.2. Instruments

IR: Nicolet Magna 550 FTIR. NMR: Bruker DRX-500, DPX-300, AM-250. MS (FAB): Kratos Instruments Concept 1H. HPLC: Knauer Wellchrom, Injection valve A0258, pump K-100, solvent organizer K-1500, UV detector K-2600, column Knauer Eurospher 100 Si (250 × 4ø), EUROCHROM 2000 for Windows.

4.3. Reagents

The following reagents were prepared according to literature procedures: Pentacarbonyl[methoxy-(methyl)carbene]chromium (**1**) [23], 1,2:3,4-di-*O*-isopropylidene-α-D-galactohexadialdo-1,5-pyranose (**2**) [24], 2,3,4,6-tetra-*O*-benzyl-1-formyl-D-glucopyranose (**3**) [25] and 2,3:4,5-di-*O*-isopropylidene-β-D-fructohexadialdo-2,6-pyranose (**4**) [26].

4.4. General procedure for the synthesis of vinylcarbene monosaccharides 5 and 6

Methoxy(methyl)carbene chromium complex **1** (0.73 g, 2.90 mmol) was dissolved in 20 ml of *tert*-butyl methyl ether and deprotonated with one equivalent of *n*-BuLi (1.6 M) at −78 °C for 1 h. In a separate flask, a solution of $TiCl_4$ (5.80 mmol) in 5 ml CH_2Cl_2 was cooled to −78 °C, and two equivalents of the formyl glycoside were quickly added. After 5 min the solution of the carbene complex anion derived from **1** 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 filtered, and the solvent was evaporated. The residue was purified by chromatography at −20 °C using dichloromethane as eluent to give an oil, which could not be completely freed from traces of solvent hampering to obtain correct elemental analyses.

*4.4.1. Pentacarbonyl[methoxy-(1,2:3,4-di-O-isopropylidene-α-L-arabinopyranosyl-5-propenylidene)]-chromium (**5**)*

Red oil; yield: 1.17 g (2.39 mmol, 82%). $R_f = 0.71$ (CH_2Cl_2). IR (CH_2Cl_2): $\nu_{(C=O)}$ (cm^{-1}) = 2062 m, 1984 sh, 1944 vs. ^{1}H-NMR (250 MHz, $CDCl_3$): δ (ppm) = 1.31 (s, 3H, CH_3); 1.32 (s, 3H, CH_3); 1.40 (s, 3H, CH_3); 1.49 (s, 3H, CH_3); 4.26 (dd, 1H, ^3J = 7.75/2.08 Hz, H-4); 4.34 (dd, 1H, ^3J = 5.00/2.57 Hz, H-2); 4.41 (m, 1H, H-5); 4.64 (dd, 1H, ^3J = 7.75/2.57 Hz, H-3); 4.73 (s, 3H, OCH_3); 5.58 (d, 1H, ^3J = 5.00 Hz, H-1); 6.09 (dd, 1H, ^3J = 15.1/4.64 Hz, H-6); 7.55 (dd, 1H, J = 15.1/1.53 Hz, H-7). ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 25.0, 25.4, 26.4, 26.6 ($4CH_3$); 67.2 (C-5); 67.9 (OCH_3); 71.0, 71.5 (C-2, C-4); 73.5 (C-3); 97.0 (C-1); 109.3, 110.4 ($2C(CH_3)_2$); 128.2 (C-6); 143.8 (C-7); 217.0 (*cis*-CO); 224.8 (*trans*-CO); 337.6 (Cr=C). FABMS: *m/z* (%) = 490.0 (4.7) [M^+]; 475.0 (1.9) [$M^+ - CH_3$]; 459.9 (7.2) [$M^+ - OCH_3$]; 378.0 (15.7) [$M^+ - 4CO$]; 350.1 (100) [$M^+ - 5CO$]; 335.1 (9.4) [$M^+ - 5CO - CH_3$]; 292.0 (45.6) [$M^+ - 5CO - (CH_3)_2CO$].

*4.4.2. Pentacarbonyl[methoxy-(1-deoxy-2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl-1-propenylidene)]-chromium (**6**)*

Red oil; yield: 1.24 g (1.58 mmol, 54%). $R_f = 0.80$ (CH_2Cl_2). IR (CH_2Cl_2): $\nu_{(C=O)}$ (cm^{-1}) = 2062 m, 1986 sh, 1942 vs. ^{1}H-NMR (250 MHz, $CDCl_3$): δ (ppm) = 3.51–3.80 (m, 6H, H-2, H-3, H-4, H-5, H-6, H-6a); 3.91 (dd, 1H, ^3J = 9.77/5.13 Hz, H-1); 4.57–4.51 (m, 1H, $PhCH_2$); 4.62 (d, 1H, ^2J = 12.5 Hz, $PhCH_2$); 4.65 (d, 1H, ^2J = 12.5 Hz, $PhCH_2$); 4.74 (d, 1H, ^2J = 12.7 Hz, $PhCH_2$); 4.75 (s, 3H, OCH_3); 4.83 (d, 1H, ^2J = 11.0 Hz, $PhCH_2$); 4.85 (d, 1H, ^2J = 11.2 Hz, $PhCH_2$); 4.87 (d, 1H, ^2J = 11.0 Hz, $PhCH_2$); 4.97 (d, 1H, ^2J = 11.2 Hz, $PhCH_2$); 6.15 (dd, 1H, ^3J = 15.1/5.13 Hz, H-8); 7.14–7.37 (m, 20H, $PhCH_2$); 7.59 (d, 1H, ^3J = 15.1 Hz, H-7). ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 67.2 (OCH_3); 69.6 (C-6); 74.1, 74.4, 75.9, 76.4 ($4C\underline{H}_2Ph$); 78.7, 79.7 (C-2, C-4); 82.6 (C-3); 87.7 (C-5); 94.2 (C-1); 128.2–129.5 (20 CBn); 130.4 (br, C-8); 138.3, 138.7, 138.8, 139.0 (4*ipso*-CBn); 143.8 (C-7); 217.0 (*cis*-CO); 224.6 (*trans*-CO); 337.8 (Cr=C). FABMS: *m/z* (%) = 784.1 (3.4) [M^+]; 732.3 (10.0) [$M^+ - C_4H_4$]; 695.1 (3.1) [$MH^+ - C_7H_6$]; 670.2 (12.9) [$MH^+ - 3CO - OCH_3$]; 644.2 (100) [$M^+ - 5CO$]; 554.1 (13.7) [$M^+ - 5CO - C_7H_6$]; 446.1 (6.5) [$M^+ - 5CO - C_7H_7 - C_7H_7O$]; 391.3 (7.3) [$M^+ - 5CO - 2C_7H_7O - C_3H_3$]; 386.1 (10.5) [$M^+ - 5CO - C_7H_7O - HCOC_7H_7 - OCH_3$]; 307.0 (83.9) [$M^+ - 5CO - 2C_7H_7 - C_7H_6 - C_5H_5$].

*4.4.3. Pentacarbonyl[methoxy-(1,2:3,4-di-O-isopropylidene-α-D-arabinopyranosyl-6-hydroxy-8-propylidene)]chromium (**7**)*

Orange oil; yield: 5.28 g (10.4 mmol, 82%). $R_f = 0.44$ (CH_2Cl_2). IR (CH_2Cl_2): $\nu_{(C=O)}$ (cm^{-1}) = 2064 m, 1942 vs. ^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.34 (s, 3H, CH_3); 1.40 (s, 3H, CH_3); 1.48 (s, 3H, CH_3); 1.53 (s, 3H, CH_3); 3.72 (d, 1H, ^2J = 13.2 Hz, H-5); 3.73 (d, br, 1H, ^2J = 12.4 Hz, H-7); 3.88 (d, br, 1H, ^2J = 12.8 Hz, H-7a); 4.12 (d, 1H, ^2J = 13.3 Hz, H-5a); 4.21 (d, br, 1H, ^3J = 7.95 Hz, H-6); 4.40 (d, 1H, ^3J = 2.18 Hz, H-2); 4.53–4.62 (m, 2H, H-3, H-4); 4.81 (s, 3H, OCH_3). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 24.5, 26.3, 26.4, 27.3 ($4CH_3$); 60.7 (C-7); 62.1 (C-5); 68.4 (OCH_3); 70.7, 71.3 (C-2, C-4); 76.5 (C-3); 78.6 (C-6); 104.2 (C-1); 109.4, 109.6 ($2C(CH_3)_2$); 216.9 (*cis*-CO); 224.1 (*trans*-CO); 362.4 (Cr=C). FABMS: *m/z* (%) = 508.1 (1.5) [M^+]; 481.1 (2.9) [$MH^+ - CO$]; 425.0 (7.3) [$MH^+ - 3CO$]; 408.0 (25.5) [$M^+ - C_5H_8O_2$]; 396.1 (4.0) [$M^+ - 4CO$]; 368.1 (5.8) [$M^+ - 5CO$].

*4.5. Procedure for the synthesis of pentacarbonyl[methoxy-(1,2:3,4-di-O-isopropylidene-α-D-arabinopyranosyl-1-propenylidene)]chromium (**8**)*

Methoxy(methyl)carbene chromium complex **1** (3.17 g, 12.7 mmol) was dissolved in 50 ml of *tert*-butyl methyl ether and deprotonated with one equivalent of *n*-BuLi (1.6 M) at −78 °C for 1 h. In a second flask, a solution of $TiCl_4$ (two equivalents) in 5 ml CH_2Cl_2 was also cooled to −78 °C, and two equivalents of the 2,3:4,5-di-*O*-isopropylidene-β-D-fructohexadialdo-2,6-pyranose (**4**) were quickly added. After 5 min the solution of the carbene complex anion 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 26 h at room temperature. The reaction was monitored by IR-spectroscopy and TLC. After completion of the reaction the solution was filtered and the solvent was evaporated. The residue was purified by chromatography at −20 °C using dichloromethane as eluent to give a red oil from which traces of solvent could not be removed completely.

Yield: 2.82 g (5.75 mmol, 45%). $R_f = 0.72$ (CH_2Cl_2). IR (CH_2Cl_2): $\nu_{(C=O)}$ (cm^{-1}) = 2062 m, 1942 vs. ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.36 (s, 3H, CH_3); 1.42 (s, 3H, CH_3); 1.50 (s, 3H, CH_3); 1.59 (s, 3H, CH_3); 3.79 (dd, 1H, J = 13.0/0.75 Hz, H-5); 3.91 (dd, 1H, J = 13.0/1.88 Hz, H-5a); 4.23 (d, 1H, ^3J = 2.64 Hz, H-2); 4.24 (ddd, 1H, ^3J = 7.91/1.88/0.75 Hz, H-4); 4.62 (dd, 1H, ^3J = 7.91/2.64 Hz, H-3); 4.77 (s, 3H, OCH_3); 6.03 (d, 1H, ^3J = 15.3 Hz, H-6); 7.63 (d, 1H, ^3J = 15.3 Hz, H-7). ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 24.9, 25.5, 26.7, 26.8 ($4CH_3$); 62.2 (C-5); 67.3 (OCH_3); 70.8, 71.2 (C-2, C-4); 74.4 (C-3); 102.4 (C-1); 109.7, 110.0 ($2C(CH_3)_2$); 130.3 (C-6); 142.5 (C-7); 216.9 (*cis*-CO); 224.8 (*trans*-CO); 340.4 (Cr=C). FABMS: *m/z* (%) = 491.1 (11.1) [MH^+]; 490.1 (6.6) [M^+]; 475.0 (1.9) [$M^+ - CH_3$]; 431.0 (1.8) [$M^+ - CO - OCH_3$]; 378.0 (9.5) [$M^+ - 4CO$]; 350.1

(100) [$M^+ - 5CO$]; 335.1 (5.1) [$M^+ - 5CO - CH_3$]; 289.0 (4.7) [$M^+ - 5CO - OCH_3 - 2CH_3$].

Acknowledgements

Financial support from the Fonds der Chemischen Industrie and the Ministry of Science and Research NRW is gratefully acknowledged.

References

[1] C. Jäkel, K.H. Dötz, J. Organomet. Chem. 624 (2001) 172.
[2] (a) P. Sinaÿ, Carbohydr. Res. 171 (1987) special issue;
(b) M.H.D. Postema, Tetrahedron 48 (1992) 8545;
(c) M.H.D. Postema, *C*-Glycoside Synthesis, CRC press, Boca Raton, 1995;
(d) D.E. Levy, C. Tang, The Chemistry of *C*-Glycosides, Pergamon, Oxford, 1995;
(e) J.-M. Beau, T. Gallagher, Top. Curr. Chem. 187 (1997) 1;
(f) P. Sinaÿ, Pure Appl. Chem. 69 (1997) 459;
(g) F. Nicotra, Top. Curr. Chem. 187 (1997) 55;
(h) K. Toshima, Carbohydr. Res. 327 (2000) 15.
[3] Y. Chapleur, Carbohydrate Mimics—Concepts and Methods, Wiley-VCH, Weinheim, 1999.
[4] (a) U. Hacksell, G.D. Daves, Prog. Med. Chem. 22 (1985) 1;
(b) K. Suzuki, Pure Appl. Chem. 66 (1994) 2175.
[5] (a) For reviews, see: Carbene Complexes in Organic Chemistry, J.W. Herndon (Guest Ed.), Tetrahedron Symposium-in-Print Tetrahedron, 56 (2000) 4893;
(b) K.H. Dötz, Angew. Chem. 96 (1984) 573;
(c) K.H. Dötz, Angew. Chem. Int. Ed. Engl. 23 (1984) 587;
(d) W.D. Wulff, in: B.M. Trost, I. Fleming, L.A. Paquette (Eds.), Comprehensive Organic Synthesis, vol. 5, Pergamon Press, Oxford, 1991, p. 1065;
(e) L.S. Hegedus, Tetrahedron 53 (1997) 4105;
(f) J. Barluenga, Pure Appl. Chem. 68 (1996) 543;
(g) R. Aumann, H. Nienaber, Adv. Organomet. Chem. 41 (1997) 161;
(h) F. Zaragoza-Dörwald, Metal Carbenes in Organic Synthesis, Wiley-VCH, Weinheim, 1999;
(i) A. de Meijere, H. Schirmer, M. Duetsch, Angew. Chem. 112 (2000) 4124;
(j) A. de Meijere, H. Schirmer, M. Duetsch, Angew. Chem. Int. Ed. Engl. 39 (2000) 3964.
[6] (a) K.H. Dötz, R. Ehlenz, Chem. Eur. J. 6 (1997) 1751;
(b) I. Frappa, D. Sinou, J. Carbohydr. Chem. 16 (1997) 255;
(c) O. Jarreton, T. Skrydstrup, J.-F. Espinosa, J. Jiménez-Barbero, J.-M. Beau, Chem. Eur. J. 5 (1999) 430;
(d) K.H. Dötz, C. Jäkel, W.-C. Haase, J. Organomet. Chem. 617–618 (2001) 119.
[7] T. Pill, K. Polborn, W. Beck, Chem. Ber. 123 (1990) 11.
[8] S. Krawielitzki, W. Beck, Chem. Ber./Recueil. 130 (1997) 1659.
[9] A. Rosental, H.J. Koch, Tetrahedron Lett. (1967) 871.
[10] G.L. Trainor, B.E. Smart, J. Org. Chem. 48 (1983) 2447.
[11] (a) P. DeShong, G.A. Slough, V. Elango, G.L. Trainor, J. Am. Chem. Soc. 107 (1985) 7788;
(b) P. DeShong, V. Elango, Carbohydr. Res. 171 (1987) 342.
[12] (a) K.H. Dötz, W. Straub, R. Ehlenz, R. Meisel, K. Peseke, Angew. Chem. 107 (1995) 2023;
(b) K.H. Dötz, W. Straub, R. Ehlenz, R. Meisel, K. Peseke, Angew. Chem. Int. Ed. Engl. 34 (1995) 1856.
[13] B. Weyershausen, M. Nieger, K.H. Dötz, J. Org. Chem. 64 (1999) 4206.
[14] (a) K.H. Dötz, R. Ehlenz, D. Paetsch, Angew. Chem. 109 (1997) 2473;
(b) K.H. Dötz, R. Ehlenz, D. Paetsch, Angew. Chem. Int. Ed. Engl. 36 (1997) 2376;
(c) F. Otto, M. Nieger, K.H. Dötz, J. Organomet. Chem. 621 (2001) 77.
[15] W.-C. Haase, M. Nieger, K.H. Dötz, Chem. Eur. J. 5 (1999) 2014.
[16] C. Jäkel, K.H. Dötz, Tetrahedron 56 (2000) 2167.
[17] K.H. Dötz, M. Klumpe, M. Nieger, Chem. Eur. J. 5 (1999) 691.
[18] E. Janes, K.H. Dötz, J. Organomet. Chem. 622 (2001) 251.
[19] For a review, see: W.D. Wulff, in: W.E. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon Press, Oxford, 1995.
[20] (a) C.P. Casey, R.A. Boggs, R.L. Anderson, J. Am. Chem. Soc. 94 (1972) 8947;
(b) R. Aumann, H. Heinen, Chem. Ber. 120 (1987) 537.
[21] (a) W.D. Wulff, S.R. Gilbertson, J. Am. Chem. Soc. 107 (1985) 503;
(b) W.D. Wulff, Y.C. Xu, J. Org. Chem. 52 (1987) 3263;
(c) T.S. Powers, Y. Shi, K.J. Wilson, W.D. Wulff, A.L. Rheingold, J. Org. Chem. 59 (1994) 6882.
[22] K.H. Dötz, D. Paetsch, H. Le Bozec, J. Organomet. Chem. 589 (1999) 11.
[23] B.C. Söderberg, L.S. Hegedus, M.A. Sierra, J. Am. Chem. Soc. 112 (1990) 4364.
[24] (a) D.H. Hollenberg, R.S. Klein, J.J. Fox, Carbohydr. Res. 67 (1978) 491;
(b) S. Hanessian, A. Ugolini, Carbohydr. Res. 130 (1984) 261.
[25] M.E. Lasterra Sánchez, V. Michelet, I. Besnier, J.P. Genêt, Synlett (1994) 705.
[26] R.E. Arrick, D.C. Baker, D. Horton, Carbohydr. Res. 26 (1973) 441.