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Organotransition metal modified sugars 14. Activation of sugar-based alkynols at a metal carbonyl template: a metal vinyl carbene functionalization of carbohydrates and non-conventional route to organometallic disaccharides☆

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Dedicated to Professor Edgar Niecke on the occasion of his 60th birthday.

Abstract

Chromium and tungsten alkenyl carbene modified carbohydrates have been synthesized by activation of sugar-based propargylic alcohols with pentacarbonyl–THF complexes followed by addition of methanol. This method has also been exploited in disaccharide synthesis. Higher functionalized carbohydrate skeletons are accessible by Diels–Alder and Michael-type addition reactions. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Carbene complexes; Carbohydrates; Diels–Alder Reactions; Disaccharides

1. Introduction

Since their discovery [2] metal carbenes have been developed as valuable reagents for stereoselective organic synthesis [3–5]. They have been used in both metal-centered cycloaddition reactions [3] like benzannulation and cyclopropanation, and in ligand-centered carbon–carbon bond formation [4] such as aldol and Michael-type addition reactions as well as in the photoinduced generation of ketene equivalents [5]. Double bonds in α,β-position to metal carbene fragments are significantly activated, allowing distinctly milder conditions for Diels–Alder reactions than encountered with analogous carbonyl compounds [6]. Examples in which organometallic synthetic methodology is applied to the elaboration of carbohydrate skeletons are still rare, albeit increasing [7]. We became interested in metal carbene modified sugars aiming at their synthetic potential in carbohydrate synthesis and in non-conventional routes to C-glycosides and oligosaccharides [8].

Recently, we applied the Group VIb metal carbonyl assisted cycloisomerization of butynols to the synthesis of carbohydrate functionalized oxacyclopentylidene complexes [9]. Apart from this intramolecular process [10], the activation of alkynols may be further exploited in an intermolecular reaction with alcohols to give acyclic α,β-unsaturated carbene complexes [11]. In order to incorporate the highly reactive vinyl carbene fragment into a carbohydrate skeleton using a one-pot protocol, we extended this methodology to sugar-derived propargylic alcohols. We now report on the synthesis of metal vinyl carbene functionalized carbohydrates and their application in disaccharide synthesis, Diels–Alder and Michael-type addition reactions.

2. Results and discussion

Activation of propargylic alcohols **1** and **2**, accessible from D-arabinose and D-ribose by addition of ethynyl

☆ For Part 13, see Ref. [1].

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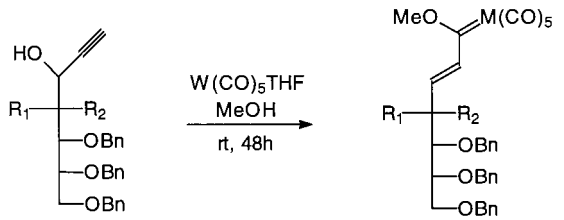


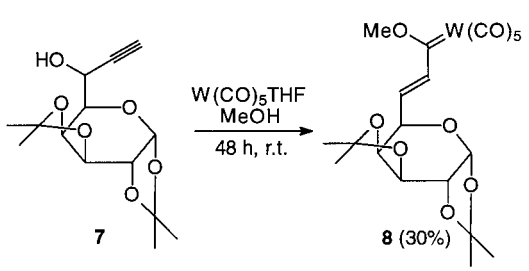
1: R_1 = OBn, R_2 = H
2: R_1 = H, R_2 = OBn

3 (1%): R_1 = OBn, R_2 = H, M = Cr
4 (60%): R_1 = OBn, R_2 = H, M = W
5 (3%): R_1 = H, R_2 = OBn, M = Cr
6 (20%): R_1 = H, R_2 = OBn, M = W

Scheme 1. Synthesis of metal sugar vinyl carbenes **3**–**6** by activation of alkynols **1** and **2** at a pentacarbonyl metal template.

magnesium bromide [12], at a $M(CO)_5THF$ template (M = Cr, W) generated metal allenylidene intermediates [10] that were trapped in the presence of methanol to give sugar-derived metal vinyl carbenes **3**–**6** (Scheme 1). The stereoselective formation of the resulting C=C bonds was established by vicinal coupling constants $^3J_{H,H} \approx 15$–16 Hz indicative of an *E*-configuration. The choice of the metal template is crucial for the isomerization/addition sequence: while the chromium complexes **3** and **5** were obtained only in trace amounts (1–3%), their tungsten analogues could be isolated in more satisfactory yields (**4**: 60%; **6**: 20%, Scheme 1). This observation reflects the reduced thermal stability of the $(CO)_5CrTHF$ complex which is more liable to decomposition during prolonged reaction times.

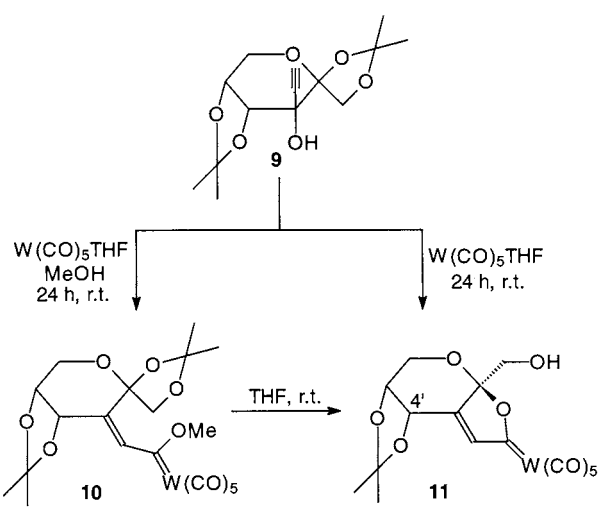
A similar protocol can be applied to the activation of pyranose alkynols. D-Galactose-derived alkynol **7**—the major product resulting from the moderately selective ethynylation of the sugar aldehyde precursor—afforded exclusively the *E*-isomer of methoxycarbene complex **8** (Scheme 2). The reaction sequence could be further exploited to introduce exocyclic double bonds. The activation of the psicose-derived alkynol **9** by $(CO)_5WTHF$ gave a 30% yield of the *Z*-vinyl carbene complex **10**. This complex can be stored at −30°C for months and handled at room temperature in solution for shorter periods of time; however, it undergoes partial deprotection in 1,2-position to form the annulated sugar metal carbene **11**. The structure of **11** was elucidated by NMR spectroscopy; a strong NOE enhancement was observed for H-4′ upon irradiation in =CH and vice versa, which is indicative of a *Z*-C=C double bond in the oxacyclopentylidene ring. In agreement with earlier observations, the formation of a six-membered 2-oxacyclohexenylidene ring is disfavored [8b] as demonstrated by upfield NMR absorptions for the geminal protons H_1 and H_1' (3.84 and 3.75 ppm, respectively, in benzene-d_6) which support the presence of a terminal hydroxymethyl group. If no methanol was added to the reaction mixture the bicyclic complex **11** was formed directly (Scheme 3).



Scheme 2. Synthesis of D-galactose vinyl carbene complex **8**.

We speculated whether the metal-promoted activation of sugar alkynols could be applied to the synthesis of organometallic disaccharides combining two monosaccharide moieties by a metal carbene spacer. If methanol was replaced as the trapping nucleophile by a selectively unprotected sugar derivative such as 1,2:3,4-diisopropylidene-α-D-galactopyranose (**12**) the metal carbene linked digalactose derivative **13** was obtained in moderate yield (Scheme 4). NMR spectroscopy and analytical HPLC indicate the formation of a single diastereomer bearing an *E*-vinyl carbene C=C bond as established by a characteristic coupling constant of $^3J_{HH} = 15.3$ Hz. Starting from the isopropylidene-protected D-galactose the organometallic disaccharide was accessible in three steps. A similar metal-linked acyclic arabinose–galactopyranose derivative **14** could be obtained in 21% yield as a 9:1 mixture of *E*/*Z* isomers. The two isomers could be observed by analytical HPLC and identified by their coupling constants $^3J_{HH} = 15.0$ Hz (*E*-**14**) and 5.50 Hz (*Z*-**14**).

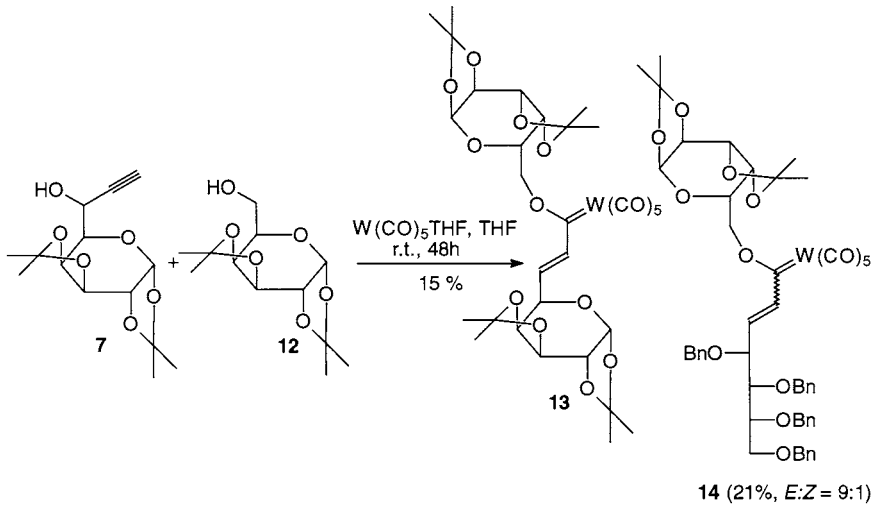
The synthetic potential of the metal vinyl carbene functionalized carbohydrates is demonstrated by Diels–Alder and Michael-type addition reactions. Addition of cyclopentadiene to complexes **4** and **8** afforded the norbornyl complexes **15** and **16** in high yields (Scheme



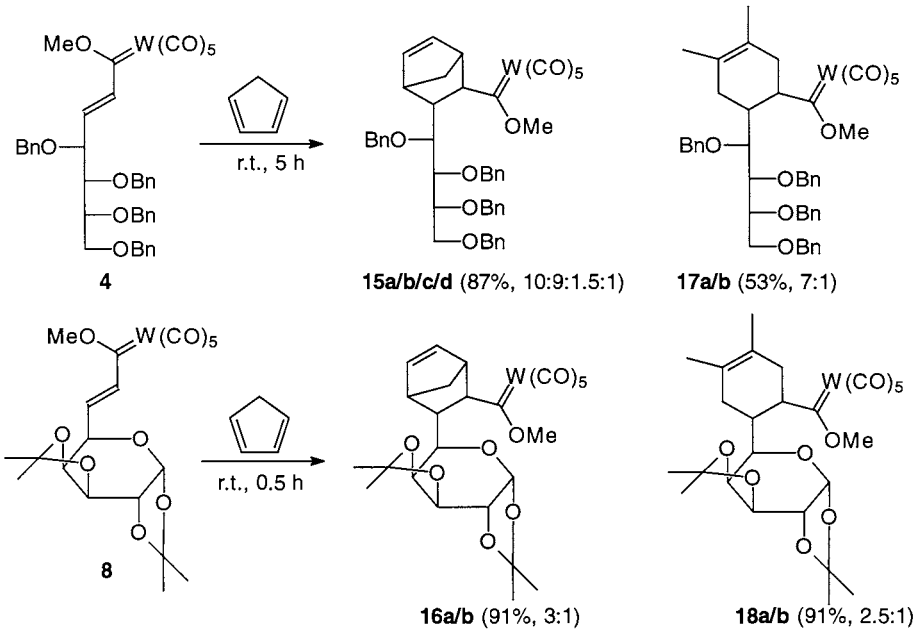
Scheme 3. Synthesis of the psicose-derived complex **10** and rearrangement to tungsten oxacyclopentenylidene **11**.

5). The reactions proceeded at room temperature within 0.5 h (**16**) and 5 h (**15**), while Diels–Alder reactions of comparable esters required 22 h in refluxing toluene [13]. This demonstrates the significant activation of the C=C bond by the metal carbene fragment, which might be exploited in the functionalization of carbohydrates bearing sensitive groups. Due to the competition of *endo* versus *exo* and *si* versus *re* attack, four isomers were to be expected. Whereas the reaction of **4** gave all possible isomers of **15a**/**b**/**c**/**d** in a 10:9:1.5:1 ratio, complex **8** reacted more selectively affording only two isomers (**16a**/**b** = 3:1) (Scheme 5). In both cases the isomers could be separated and isolated by HPLC. As determined by analysis of the characteristic coupling constants the major isomers **15a**, **16a** and **16b** result from *endo* attack. The decision between *re* and *si* face attack, so far, was hampered by the oily consistency of the compounds, which prevented crystal growth for X-ray analysis. A similar trend in diastereoselectivity was observed with 1,3-dimethylbutadiene. The arabino-derived complex **4** formed the Diels–Alder products **17a**/**b** in a 7:1 ratio while the galactopyranose-congener **8** underwent a less selective cycloaddition to give a 2.5:1 ratio of complexes **18a**/**b**.

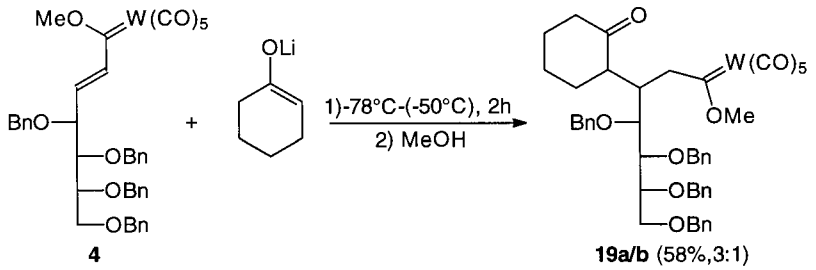
The reactivity of the arabinose-derived complex **4** was further demonstrated by 1,4-addition of lithium cyclohexanone enolate. After protonation with methanol, complex **19** was obtained as a 3:1 mixture of two isomers, which could be separated by column chromatography (Scheme 6).



Scheme 4. Synthesis of the metal carbene linked disaccharides **13** and **14**.



Scheme 5. Diels–Alder reactions of ribose and galactopyranose complexes **4** and **8**.



Scheme 6. Michael-type addition of enolates to ribose complex **4**.

3. Conclusions

We have demonstrated that the metal-assisted activation of sugar propargylic alcohols allows a metal vinylcarbene functionalization at C-1, C-3 or C-6 of the carbohydrate skeleton. This methodology can be applied to the assembly of two monosaccharides linked by a metal carbene spacer to give non-conventional organometallic disaccharides. Subsequent cycloaddition or conjugate addition reactions may be conceived for further elaboration of more complex structures. It should be mentioned that all metal carbene functionalized carbohydrates described above are stable compounds which can be stored for months under an argon atmosphere at -30°C and can be handled even in air for short periods of time.

4. Experimental

4.1. General reaction conditions

All reactions were carried out under argon. The solvents used for reactions and chromatography were dried and distilled. Chromatography was performed with E. Merck Silica Gel 60 (0.63–0.200). For photochemical reactions mercury lamps were used (Philipps 125 HPK and Heraeus TQ 159). D.e. values were determined by ^{1}H-NMR spectroscopy.

4.2. Instruments

IR: Nicolet Magna 550 FT-IR. NMR: Bruker DRX 500. AM 400. MS (FAB, EI): Kratos Instruments Concept 1H and MS-50. Elemental analysis: Elementar Analysensysteme Vario EL.

4.3. Reagents

4.3.1. Synthesis of alkynols *1,2,7,9*

4.3.1.1. General procedure A. Sugar aldehyde or ketone (10 mmol) [14] was dissolved in 50 ml THF. At -78°C two equivalents of a 1 M solution of ethynyl magnesium bromide were added. The solution was stirred for 2 h at this temperature and for another 10 min at room temperature (r.t.). Then a saturated solution of ammonium chloride was added. The mixture was extracted three times with diethyl ether. The combined organic extracts were dried with magnesium sulfate. Removal of the solvent under reduced pressure and column chromatography (light petroleum–diethyl ether or light petroleum–ethyl acetate mixtures) afforded pure products.

*4.3.1.2. 1,2-Dideoxy-(R/S)-hydroxy-4,5,6,7-tetra-O-benzyl-D-arabino-hept-1-initol (**1a**/**b**).* Chromatographic separation gave 320 mg (6.0 mmol, 60%) of **1** as a colorless oil containing a 3:1 mixture of isomers **1a**:**b**. IR (KBr): ν(C≡C) 3287 m, ν(≡CH) 2114 w, ν(OH) 3410 vs cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.75–3.80 (m), 3.89–3.99 (m), 4.11 (pt, 1 H), 4.14–4.31 (m), 4.34 (dd, $^3J = 5.47$, $^3J = 3.91$ Hz, 1 H), 2.08 (s, 1H, OH_a), 2.10 (s, 1H, OH_b), 2.54 (d, $^4J = 2.35$ Hz, 1H, C≡CH_b), 2.57 (d, $^4J = 2.34$ Hz, 1H, C≡CH_a), 4.52–4.91 (m, 16H, O$CH_2C_6H_5$), 7.24–7.44 (m, 40H, O$CH_2C_6H_5$). FAB MS (m/z): 537.2 [M$^+$ + H].

1a: ^{13}C-NMR (125 MHz, $CDCl_3$): δ 61.9 (C-3), 68.6 (C-7), 71.8, 73.2, 74.5, 74.6, 75.0 (O$CH_2C_6H_5$, C-1), 78.2, 79.1, 79.9 (C-4–C-6), 82.9 (C-2), 127.6–128.2 (O$CH_2C_6H_5$), 137.8, 138.0, 138.1, 138.2 (C-*ipso*).

1b: ^{13}C-NMR (125 MHz, $CDCl_3$): δ 62.8 (C-3), 68.6 (C-7), 71.8, 73.2, 74.1, 74.5, 75.0 (O$CH_2C_6H_5$, C-1), 78.2, 78.8, 79.9 (C-4–C-6), 82.9 (C-2), 127.2–128.1 (O$CH_2C_6H_5$), 137.8, 137.9, 138.0, 138.1 (C-*ipso*).

*4.3.1.3. 1,2-Dideoxy-3(R/S)-hydroxy-4,5,6,7-tetra-O-benzyl-D-ribono-hept-1-initol (**2a**/**b**).* Chromatographic separation gave 280 mg (5.3 mmol, 53%) of **2** as a mixture of isomers in the ratio **2a**:**b** = 4:1 as a colorless oil. IR (KBr): ν(C≡C) 3288 m, ν(≡CH) 2114 w, ν(OH) 3429 vs cm^{-1}; FABMS (m/z): 537.2 [M$^+$ + H].

2a: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.62 (s, 1H, OH), 2.48 (d, $^4J = 2.23$ Hz, 1H, H-1), 3.73 (dd, $^2J = 10.38$, $^3J = 5.27$ Hz, 1H, H-7), 3.79 (dd, $^2J = 10.38$, $^3J = 3.68$ Hz, H-7′), 3.20 (d, $^3J = 6.59$ Hz, 1H, H-4/H-5), 3.91 (pt, $^3J = 5.10$ Hz, 1H, H-4/H-5), 4.02 (m, 2H, H-6, H-3), 4.50–4.79 (m, 8H, O$CH_2C_6H_5$), 7.28–7.36 (m, 20H,

$OCH_2C_6H_5$); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 63.6 (C-3), 69.7 (C-7), 72.5, 73.2, 74.0, 73.5, 73.9 ($OCH_2C_6H_5$, C-1), 78.0, 79.5, 80.7 (C-4–C-6), 82.8 (C-2), 127.5–128.3 ($OCH_2C_6H_5$), 137.8, 137.9, 138.0, 138.1 (C-*ipso*).

2b: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.53 (s, 1H, OH), 2.52 (d, $^4J = 2.25$ Hz, 1H, H-1), 3.70 (m, 2 H) and 3.38 (d, $^{2/3}J = 9.85$ Hz, 1H, H-5, H-7, H-7′), 3.82 (dd, $^3J = 8.02$, $^3J = 3.00$ Hz, 1H, H-4), 4.01 (m, 1H, H-6), 4.08 (dd, $^4J = 2.25$, $^3J = 8.02$ Hz, 1H, H-3), 4.43–5.83 (m, 8H, $OCH_2C_6H_5$), 7.25–7.35 (m, 20H, $OCH_2C_6H_5$); ^{13}C-NMR (60 MHz, $CDCl_3$): δ 62.3 (C-3), 70.2 (C-7), 72.4, 73.3, 73.6, 73.8, 74.0 ($OCH_2C_6H_5$, C-1), 78.5, 79.1, 80.0 (C-4–C-6), 83.6 (C-2), 127.5–128.4 ($OCH_2C_6H_5$), 137.5, 137.5, 137.6, 138.4 (C-*ipso*).

*4.3.1.4. 7,8-Dideoxy-1,2:3,4-di-O-isopropylidene-6(R/S)-hydroxy-a-D-galacto-oct-7-inopyranose (**7**).* Chromatographic separation gave 190 mg (6.9 mmol, 69%) of **7** as a mixture of isomers in the ratio **7a**:**b** = 5:1 as a colorless solid. Anal. Found: C, 59.18; H, 7.71. $C_{14}H_{20}O_6$ (284.3); Calc.: C, 59.14; H, 7.09; IR (KBr): ν(C≡C) 3265 m, ν(≡CH) 2114 w, ν(OH) 3487 vs cm^{-1}.

7a: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.30 (s, 3H, $C(CH_3)_2$), 1.38 (s, 3H, $C(CH_3)_2$), 1.42 (s, 3H, $C(CH_3)_2$), 1.52 (s, 3H, $C(CH_3)_2$), 2.08 (s, 1H, OH), 2.53 (d, $^4J = 2.20$ Hz, 1H, C≡C*H*), 3.78 (dd, $^3J = 6.20$, $^3J = 0.7$ Hz, 1H, H-5), 4.31 (dd, $^3J = 5.00$, $^3J = 1.10$ Hz, 1H, H-2), 4.57 (dd, $^3J = 6.20$, $^4J = 2.20$ Hz, 1H, H-6), 4.62 (m, 2H, H-3, H-4), 5.58 (d, $^3J = 5.00$ Hz, 1H, H-1); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 24.2, 24.8, 25.7, 25.9 ($C(CH_3)_2$), 62.6 (C-6), 68.5, 70.3, 70.7, 71.2 (C-2–C-5), 74.2 ($^1J_{CH} = 251$ Hz, C≡*C*H), 82.2 (*C*≡CH), 96.5 (C-1), 108.8, 109.7 ($C(CH_3)_2$).

7b: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.27 (s, 3H, $C(CH_3)_2$), 1.30 (s, 3H, $C(CH_3)_2$), 1.41 (s, 3H, $C(CH_3)_2$), 1.51 (s, 3H, $C(CH_3)_2$), 2.51 (d, $^4J = 2.19$ Hz, 1H, CC*H*), 3.73 (dd, $^3J = 8.59$, $^3J = 1.69$ Hz, 1H, H-5), 4.31 (1H, H-2), 4.43 (dd, $^3J = 7.89$, $^3J = 1.60$ Hz, H-4), 4.54 (dd, $^3J = 8.70$, $^4J = 2.19$ Hz, 1H, H-6), 4.60 (1H, H-3), 5.52 (d, $^3J = 4.87$ Hz, 1H, H-1); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 24.2, 24.8, 25.8, 25.9 ($C(CH_3)_2$), 61.7 (C-6), 68.5, 70.6, 70.7, 71.4 (C-2–C-5), 74.2 (C≡*C*H), 80.2 (*C*≡CH), 96.2 (C-1), 109.0, 109.6 ($C(CH_3)_2$).

*4.3.1.5. 1,2:4,5-Di-O-isopropylidene-3-C-ethinyl-β-D-psicopyranose (**9**).* Chromatographic separation gave 230 mg (8.2 mmol, 82%) of **9** as a colorless solid. Anal. Found: C, 59.11; H, 7.25. $C_{14}H_{20}O_6$ (284.3) Calc.: C, 59.14; H, 7.09; IR (KBr): ν (C≡C) 3271 m, ν(≡CH) 2124 w, ν(OH) 34847 vs cm^{-1}; ^{1}H-NMR (500 MHz, C_6D_6): δ 1.51 (s, 3H, $C(CH_3)_2$), 1.51 (s, 3H, $C(CH_3)_2$), 1.52 (s, 3H, $C(CH_3)_2$), 1.55 (s, 3H, $C(CH_3)_2$), 2.08 (s, 1H, OH), 2.98 (s, 1H, C≡C*H*), 3.71 (m, 1H, H-5), 3.98 (m, 2H, H-6, H-6′), 4.38 (d, $^2J =$ 9.14 Hz, 1H, H-1), 4.43 (d, $^3J = 5.96$ Hz, H-4), 4.80 (d, $^2J = 9.14$ Hz, 1H, H-1); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 25.1, 25.7, 25.9, 26.5 ($C(CH_3)_2$), 69.0 (C-3), 70.7, 59.7 (C-6, C-1), 73.0 ($^1J_{CH} = 252$ Hz, C≡*C*H), 73.3, 76.1 (C-4, C-5), 82.6 ($^1J_{CH} = 59$ Hz, *C*≡CH), 105.2 (C-2), 109.5, 113.3 ($C(CH_3)_2$).

*4.3.2. Synthesis of complexes **3**–**6**, **8***

4.3.2.1. General procedure B. $M(CO)_6$ (5 mmol, M = Cr, W) was dissolved in 250 ml THF and irradiated for 5 h at −10°C. Under reduced pressure half of the solvent was removed and the mixture was added to a solution of 3 mmol of the alkynol in 10 ml methanol. The mixture was stirred for 48 h at r.t. The solvents were removed under reduced pressure and the crude product was purified by column chromatography.

*4.3.2.2. Pentacarbonyl[1-(1,2-dideoxy-3,4,5,6-tetra-O-benzyl-D-arabino-hex-1-(E)-enitolyl)(methoxy)carbene]-chromium(0) (**3**).* Chromatographic separation gave 22 mg (0.03 mmol, 1%) of **3** as a red oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.64 (dd, $^3J = 4.2$, $^2J = 10.5$ Hz, 1H, H-6a), 3.71–3.80 (m, 3H, H-4, H-5, H-6b), 4.30 (dd, $^3J = 6.6$, $^3J = 2.8$ Hz, 1H, H-3), 4.63 (s, 3H, OCH_3), 4.41–4.62 (m, 8H, $CH_2C_6H_5$), 6.31 (ddd, $^3J = 15.2$, $^3J = 6.6$, $^4J = 1$ Hz, 1H, =C*H*), 7.20–7.30 (m, 20H, $CH_2C_6H_5$), 7.45 (d, $^3J = 15.2$ Hz, 1H, =C*H*); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 68.1 (C-6), 68.4 (OCH_3), 71.1, 71.9, 73.3, 74.6 ($OCH_2C_6H_5$), 77.8, 78.5, 80.7 (C-3–C-5), 127.4–128.3 ($CH_2C_6H_5$), 137.7, 138.0, 138.1, 138.3 (C-*ipso*), 130.9, 143.7 (*C*=C), 216.5 (CO *cis*), 223.9 (CO *trans*), 335.9 (*C*=Cr); FABMS (*m*/*z*): 602 [$M^+ - 5CO$].

*4.3.2.3. Pentacarbonyl[1-(1,2-dideoxy-3,4,5,6-tetra-O-benzyl-D-arabino-hex-1-(E)-enitolyl)(methoxy)carbene]-tungsten(0) (**4**).* Chromatographic separation gave 1570 mg (1.8 mmol, 60%) of **4** as a red oil. Anal. Found: C, 46.56; H, 4.61. $C_{41}H_{38}O_{10}W$ (874.6) Calc.: C, 46.31; H, 4.38; IR (PE): $\nu(A_1)$ 2070 m, $\nu(E, A_1^2)$ 1946 vs cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.68 (dd, $^3J = 3.5$, $^2J = 10.5$ Hz, 1H, H-6a), 3.76–3.85 (m, 3H, H-4, H-5, H-6b), 4.23 (dd, $^3J = 6.4$, $^3J = 1$ Hz, 1H, H-3), 4.50 (s, 3H, OCH_3), 4.28–4.65 (m, 8H, $CH_2C_6H_5$), 6.31 (ddd, $^3J = 15.4$, $^3J = 6.4$, $^4J = 1$ Hz, 1H, =C*H*), 7.20–7.35 (m, 20H, $CH_2C_6H_5$), 7.45 (d, $^3J = 15.4$ Hz, 1H, =C*H*); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 68.4 (C-6), 69.1 (OCH_3), 74.6, 73.3, 72.0, 71.1 ($CH_2C_6H_5$), 77.8, 78.7, 80.5 (C-3–C-5), 127.5–128.4 ($CH_2C_6H_5$), 137.7, 138.0, 138.1, 138.3 (C-*ipso*), 134.6, 147.5 (*C*=C), 197.3 (CO *cis*), 203.6 (CO *trans*), 309.3 (*C*=W); FABMS (*m*/*z*): 874 [M^+], 790 [$M^+ - 3CO$].

*4.3.2.4. Pentacarbonyl[1-(1,2-dideoxy-3,4,5,6-tetra-O-benzyl-D-ribono-hex-1-(E)-enitolyl)(methoxy)carbene]-chromium(0) (**5**).* Chromatographic separation gave 66 mg (0.09 mmol, 3%) of **5** as a red oil. IR (PE): $\nu(A_1^1)$ 2060 m, $\nu(E, A_1^2)$ 1948 vs cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 3.56 (dd, $^3J = 4.2$, $^2J = 9.2$ Hz, 1H, H - 6a), 3.66 (m, 2H, H - 5, H - 6b), 3.84 (dd, $^3J = 6.8$, $^3J = 3.6$ Hz, 1H, H-4), 4.21 (ddd, $^3J = 6.5$, $^3J = 3.6$, $^4J = 1$ Hz, 1H, H - 3), 4.60 (s, 3H, OCH_3), 4.36–4.68 (m, 8H, $CH_2C_6H_5$), 6.02 (dd, $^3J = 15.3$, $^3J = 6.5$ Hz, =CH), 7.10–7.20 (m, 20H, $CH_2C_6H_5$), 7.41 (dd, $^3J = 15.3$, $^4J = 1$ Hz, 1H, =CH); ^{13}C - NMR (125 MHz, $CDCl_3$): δ 66.5 (OCH_3), 69.0 (C-6), 71.5, 72.0, 73.3, 74.0 ($OCH_2C_6H_5$), 77.6, 78.8, 80.6 (C - 3–C - 5), 127.5–128.4 ($CH_2C_6H_5$), 137.9 (br, C - *ipso*), 132.0, 144.3 (C=C), 216.5 (CO *cis*), 223.9 (CO *trans*), 336.1 (C=Cr); FABMS (*m*/*z*): 742 [M^+], 602 [$M^+ - 5CO$].

*4.3.2.5. Pentacarbonyl[1-(1,2-dideoxy-3,4,5,6-tetra-O-benzyl-D-ribono-hex-1-(E)-enitolyl)(methoxy)carbene]-tungsten(0) (**6**).* Chromatographic separation gave 530 mg (0.6 mmol, 20%) of **6** as a red oil. IR (PE): $\nu(A_1^1)$ 2070 m, $\nu(E, A_1^2)$ 1944 vs cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 3.67 (dd, $^3J = 5.1$, $^2J = 10.8$ Hz, 1H, H-6a), 3.73–3.83 (m, 2H, H - 5, H - 6b), 3.95 (dd, $^3J = 6.8$, $^3J = 3.6$ Hz, 1H, H - 4), 4.28 (ddd, $^3J = 6.4$, $^3J = 3.6$, $^4J = 1$ Hz, 1H, H - 3), 4.63 (s, 3H, OCH_3), 4.41–4.62 (m, 8H, $CH_2C_6H_5$), 6.40 (dd, $^3J = 15.3$, $^3J = 6.4$ Hz, =CH), 7.20–7.38 (m, 20H, $CH_2C_6H_5$), 7.42 (d, $^3J =$ 15.3 Hz, 1H, =CH); ^{13}C - NMR (100 MHz, $CDCl_3$): δ 69.0 (C-6), 69.1 (OCH_3), 71.5, 72.0, 73,3, 74.0 (OCH_2C_6-H_5), 77.6, 79.0, 80.4 (C - 3–C - 5), 127.5–128.4 (CH_2C_6-H_5), 137.5, 138.0, 138.1, 138.2 (C - *ipso*), 134.5, 147.9 (C=C), 197.3 (CO *cis*), 203.7 (CO *trans*), 309.6 (C=W); FABMS (*m*/*z*): 874 [M^+], 790 [$M^+ - 3CO$].

*4.3.2.6. Pentacarbonyl[7-(1,5-anhydro-6,7-dideoxy-1,2:3,4-di-O-isopropylidene-α-D-galacto-hept-6-(E)-eno-pyranosyl)(methoxy)carbene]tungsten(0) (**8**).* Chromatographic separation gave 560 mg (0.9 mmol, 30%) of **8** as a red solid. Anal. Found: C, 38.54; H, 3.53. $C_{20}H_{22}O_{11}W$ (622.0) Calc.: C, 38.61; H, 3.56. IR (PE): $\nu(A_1^1)$ 2070 m, ν(E) 1958 s, $\nu(A_1^2)$ 1944 vs cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.29 (s, 3H, $C(CH_3)_2$), 1.31 (s, 3H, $C(CH_3)_2$), 1.41 (s, 3H, $C(CH_3)_2$), 1.50 (s, 3H, $C(CH_3)_2$), 4.27 (dd, $^3J = 2.1$, $^3J = 7.7$ Hz, 1H, H - 4), 4.32 (*p*td, $^3J = 4.6$, $^4J = 1.7$, $^3J = 2.1$ Hz, 1H, H - 5), 4.35 (dd, $^3J = 2.5$, $^3J = 5.1$ Hz, 1H, H - 2), 4.56 (s, 3H, OCH_3), 4.64 (d, $^3J = 2.5$, $^3J = 7.7$ Hz, 1H, H - 3), 5.70 (d, $^3J = 5.1$ Hz, 1H, H - 1), 6.30 (dd, $^3J =$ 15.1, $^3J = 4.6$ Hz, 1H, =CH), 7.48 (dd, $^3J = 15.1$, $^4J =$ 1.8 Hz, 1H, =CH); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 24.5, 24.9, 25.9, 26.1 ($C(CH_3)_2$), 67.5 (C-5), 69.1 (OCH_3), 70.3 (C-2), 70.9 (C-3), 72.7 (C-4), 96.4 (C-1), 108.9, 109.9 ($C(CH_3)_2$), 131.2, 147.1 (C=C), 197.3 (CO *cis*), 204.0 (CO *trans*), 310.3 (C=W); EIMS (EI) (*m*/*z*): 622.0 [M^+], 607.0 [$M^+ - CH_3$], 566.0 [$M^+ - 2CO$], 538.0 [$M^+ - 3CO$], 510.0 [$M^+ - 4CO$].

*4.3.3. Synthesis of complexes **10** and **11***

4.3.3.1. General procedure C. The reaction was performed according to procedure B but the reaction was stopped after 24 h. Complexes **10** and **11** were separated by column chromatography. At r.t. in solution **10** was converted quantitatively into **11**. If the reaction was carried out in the absence of methanol complex **11** was formed directly. Chromatographic separation gave 300 mg (0.48 mmol, 16%) of **10** and 230 mg (0.42 mmol, 14%) of **11** as red oils. The reaction in the absence of methanol afforded 330 mg (0.6 mmol, 20%) of **11**.

*4.3.3.2. Pentacarbonyl[methoxy(1′-(Z)-(3-deoxy-1,2:4,5-di-O-isopropylidene-3-methylidene-α-D-psicopyranosyl))-carbene]tungsten(0) (**10**).* HRMS: $C_{20}H_{22}O_{11}{}^{182}W$: Found: 620.0641, Calc.: 620.0644; IR (PE): $\nu(A_1^1)$ 2072 m, $\nu(E, A_1^2)$ 1963 vs cm^{-1}; ^{1}H - NMR (500 MHz, C_6D_6): δ 1.08 (s, 3H, $C(CH_3)_2$), 1.21 (s, 3H, $C(CH_3)_2$), 1.21 (s, 3H, $C(CH_3)_2$), 1.39 (s, 3H, $C(CH_3)_2$), 2.62 (dd, $^3J = 1.5$, $^2J = 13.1$ Hz, 1H, H - 6a), 3.13 (s, 3H, OCH_3), 3.45 (d, $^3J = 8$ Hz, 1H, H - 5), 3.48 (d, $^2J =$ 13.1 Hz, 1H, H-6b), 3.98 (d, $^2J = 9.5$ Hz, 1H, H-1a), 4.08 (d, $^2J = 9.5$ Hz, 1H, H - 1b), 4.23 (d, $^3J = 8$ Hz, 1H, H - 4), 6.58 (s, 1H, =CH); ^{13}C - NMR (125 MHz, C_6D_6): δ 23.1, 24.1, 24.3, 25.1 ($C(CH_3)_2$), 48.7 (OCH_3), 61.9, 64.9, 69.4, 76.9 (C-1, C-4–C-6), 104.1 (C - 2), 111.4, 123.9 ($C(CH_3)_2$), 144.1, 152.5 (C=C), 197.4 (CO *cis*), 205.4 (CO *trans*), 295.2 (C=W); EIMS (*m*/*z*): 622.0 [M^+], 566.0 [$M^+ - 2CO$].

*4.3.3.3. Pentacarbonyl[4,5-dihydro-(4′,5′-di-O-isopropylidene-2′,3′-dideoxy-β-D-fructopyranoso)-[2′,3′-b]-1-oxacyclopent-3-(Z)-en-2-ylidene]tungsten(0) (**11**).* HRMS: $C_{15}H_{14}O_9{}^{184}W$ [$M^+ - CO$]: Found: 522.0135, Calc.: 522.0150; IR (PE): $\nu(A_1^1)$ 2073 m, $\nu(E, A_1^2)$ 1963 vs cm^{-1}; ^{1}H - NMR (500 MHz, C_6D_6): δ 1.02 (s, 3H, $C(CH_3)_2$), 1.32 (s, 3H, $C(CH_3)_2$), 2.54 (dd, $^3J = 0.8$, $^2J = 13.1$ Hz, 1H, H - 6′a), 3.35 (m, 1H, H - 5′), 3.41 (dd, $^2J = 13.1$, $^3J = 0.8$ Hz, 1H, H - 6′b), 3.75 (d, $^2J =$ 11.3 Hz, 1H, H - 1′a), 3.84 (d, $^2J = 11.3$ Hz, 1H, H - 1′b), 4.15 (d, $^3J = 8.1$ Hz, 1H, H - 4′), 6.52 (s, 1H, =CH); ^{13}C - NMR (125 MHz, C_6D_6): δ 23.1, 25.1 ($C(CH_3)_2$), 63.7, 65.1 (C - 1′, C - 6′), 69.3, 76.9 (C - 4′, C - 5′), 111.4, 124.7 (C - 2′, $C(CH_3)_2$), 144.4, 152.1 (C=C), 197.4 (CO *cis*), 205.3 (CO *trans*), 295.1 (C=W); FABMS (*m*/*z*): 550 [M^+], 522 [$M^+ - CO$], 494 [$M^+ - 2CO$], 466 [$M^+ - 3CO$], 226.1 [$M^+ - W(CO)_5$].

*4.3.4. Synthesis of complexes **13** and **14***

4.3.4.1. General procedure D. $W(CO)_6$ (2 mmol) was dissolved in 250 ml THF and irradiated for 5 h at −10°C. Under reduced pressure two thirds of the solvent were removed and the mixture was added to a mixture of 3 mmol of the corresponding alkynol and 1.8 g (7 mmol) of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose. The mixture was stirred for 48 h at r.t. The solvents were removed under reduced pressure and the crude was purified by column chromatography.

*4.3.4.2. Pentacarbonyl[7-(1,5-anhydro-6,7-dideoxy-1,2:3,4-di-O-isopropylidene-α-D-galacto-hept-6-(E)-enopyranosyl)(1,2:3,4-di-O-isopropylidene-α-D-galactopyranosylcarbene]tungsten(0) (**13**).* Chromatographic separation gave 127 mg (0.15 mmol, 15%) of **13** as a red oil. IR (PE): $\nu(A_1^1)$ 2070 m, ν(E) 1953 vs, $\nu(A_1^2)$ 1946 vs cm^{-1}; ^{1}H-NMR (500 MHz, C_6D_6): δ 1.04 (s, 3H, $C(CH_3)_2$), 1.05 (s, 3H, $C(CH_3)_2$), 1.14 (s, 3H, $C(CH_3)_2$), 1.16 (s, 3H, $C(CH_3)_2$), 1.38 (s, 3H, $C(CH_3)_2$), 1.47 (s, 3H, $C(CH_3)_2$), 1.51 (s, 3H, $C(CH_3)_2$), 1.52 (s, 3H, $C(CH_3)_2$), 3.77 (dd, $^3J = 7.85$, $^3J = 2.0$ Hz, 1H, H-4′), 4.02 (dd, $^3J = 7.85$, $^3J = 2.0$ Hz, H-4), 4.15 (dd, $^3J = 2.38$, $^3J = 5.06$ Hz, 1H, H-2′), 4.18 (dd, 1H, $^3J = 2.59$, $^3J = 5.01$ Hz, 1H, H-2), 4.38 (ddd, $^3J = 2.0$, $^3J = 7.8$, $^3J = 4.2$ Hz, H-5′), 4.41–4.44 (m, 2H, H-5, H-3′), 4.50 (dd, $^3J = 2.59$, $^3J = 7.85$ Hz, 1H, H-3), 4.89 (dd, $^2J = 10.8$, $^3J = 4.2$ Hz, 1H, H-6′a), 5.05 (dd, $^2J = 10.8$, $^3J = 7.8$ Hz, 1H, H-6′b), 5.48 (d, $^3J = 4.97$ Hz, 1H, H-1), 5.53 (d, $^3J = 5.07$ Hz, 1H, H-1′), 6.70 (dd, $^3J = 15.3$, $^3J = 4.50$ Hz, 1H, =C*H*), 7.71 (d, $^3J = 15.3$ Hz, 1H, =C*H*); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 24.4, 24.6, 24.8, 24.9, 25.8, 25.9, 26.0, 26.1 ($C(CH_3)_2$), 66.4 (C-5), 67.6 (C-5), 70.4, 70.4, 70.7, 70.8, 70.9 (C-4, C-3, C-3′, C-2, C-2′), 72.5 (C-4′), 80.6 (C-6′), 96.2 (C-1′), 96.4 (C-1), 108.7, 108.9, 109.8, 109.9 ($C(CH_3)_2$), 132.4, 147.2 (*C*=*C*), 197.6 (CO *cis*), 204.1 (CO *trans*), 309.2 (*C*=W); FABMS (*m*/*z*): 850.2 [M^+], 822.2 [$M^+ - CO$], 766.1 [$M^+ - 3CO$], 738.1 [$M^+ - 4CO$].

*4.3.4.3. Pentacarbonyl[1-(1,2-dideoxy-3,4,5,6-tetra-O-benzyl-D-arabino-hex-1-enitolyl)-(1,2:3,4-di-O-isopropylidene-α-D-galactopyranosylcarbene]tungsten(0) (**14**).* Chromatographic separation gave 230 mg (0.21 mmol, 21%) of **14** as a red oil and a 9:1 mixture of *E*:*Z* isomers.

E-Isomer (**14a**): IR (PE): $\nu(A_1^1)$ 2070 m, $\nu(E, A_1^2)$ 1944 vs cm^{-1}; ^{1}H-NMR (500 MHz, C_6D_6): δ 1.08 (s, 3H, $C(CH_3)_2$), 1.20 (s, 3H, $C(CH_3)_2$), 1.48 (s, 3H, $C(CH_3)_2$), 1.58 (s, 3H, $C(CH_3)_2$), 3.83 (dd, $^3J = 4.66$, $^2J = 10.33$ Hz, 1H, H-6a), 3.89 (dd, $^3J = 3.38$, $^2J = 10.33$ Hz, 1H, H-6b), 3.99–4.06 (m, 3H, H-4, H-4′, H-5), 4.19 (dd, $^3J = 2.50$, $^3J = 4.96$ Hz, 1H, H-2′), 4.36 (pt, $^3J = 5$ Hz, H-3), 4.39 (m, 1H, H-5′), 4.56 (dd, $^3J = 2.50$, $^3J = 7.75$ Hz, 1H, H-3′), 4.36–4.83 (m, 8H, $CH_2C_6H_5$), 4.82 (m, 1H, H-6′a), 5.27 (dd, $^2J = 10.93$, $^3J = 8.35$ Hz, 1H, H-6′b), 5.43 (d, $^3J = 4.96$ Hz, 1H, H-1′), 6.75 (dd, $^3J = 15.0$, $^3J = 6.2$ Hz, 1H, =C*H*), 7.15–7.48 (m, 20H, $CH_2C_6H_5$), 7.78 (d, $^3J = 15.0$ Hz, 1H, =C*H*); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 24.6, 24.8, 25.8, 26.0 ($C(CH_3)_2$), 66.4, 70.3, 70.7, 70.9 (C-2′, C-3′, C-4′, C-5′), 71.7, 72.0, 73.2, 74.8 ($CH_2C_6H_5$), 77.8, 78.5, 80.6 (C-3-C-5), 80.8 (C-6′), 96.2 (C-1′), 110.0, 108.8 ($C(CH_3)_2$), 127.5–128.4 ($CH_2C_6H_5$), 137.8, 138.0, 138.2, 138.3 (C-*ipso*), 135.2, 147.6 (*C*=*C*), 197.1 (CO *cis*), 203.8 (CO *trans*), 307.7 (*C*=W).

Z-Isomer (**14b**): ^{1}H-NMR (500 MHz, C_6D_6): δ 7.01 (dd, $^3J = 5.50$, $^3J = 3.18$ Hz, 1H, =C*H*).

4.3.5. Diels–Alder reactions

*4.3.5.1. Pentacarbonyl[2-(3-(D-arabino-1′,2′,3′,4′-tetra-O-benzylbutyl)bicyclo-[2.2.1]hept-5-enyl)-(methoxy)carbene]tungsten(0) (**15**).* Complex **4** (0.2 g, 0.23 mmol) was dissolved in 4 ml of freshly distilled cyclopentadiene. The oxygen was removed by three cycles of 'freeze, pump and thaw'. The mixture was stirred for 5 h at r.t. while the deep-red color lightened to yellow. The diene was removed under reduced pressure and the crude product was purified by column chromatography which gave 180 mg (0.2 mmol, 87%) of **15** as a yellow oil containing a mixture of four isomers in the ratio **16a**:**b**:**c**:**d** = 10:9:1.5:1. The isomers could be separated by HPLC.

endo-Isomer **15a**: IR (PE): $\nu(A_1^1)$ 2068 m, $\nu(E, A_1^2)$ 1948 vs cm^{-1}; ^{1}H-NMR (500 MHz, C_6D_6): δ 1.31 (dd, $^3J = 1.5$, $^2J = 8.22$ Hz, 1H, H-7a), 1.95 (d, $^2J = 8.22$ Hz, 1H, H-7b), 2.37 (ddd, $^3J = 5.2$, $^3J = 7.10$, $^3J = 1.37$ Hz, 1H, H-3), 2.95 (br, 1H, H-1/H-4), 3.62 (br, 1H, H-1/H-4), 3.76 (dd, $^3J = 4.38$, $^3J = 7.10$ Hz, 1H, H-1′), 3.78–3.34 (m, 2H, H-3′, H-4′a), 3.87 (pt, $^3J = 5.1$ Hz, 1H, H-2′), 3.98 (dd, $^2J = 9.48$, $^3J = 2.5$ Hz, 1H, H-4′b), 4.51 (s, 3H, OCH_3), 4.67 (m, $^3J = 3.13$ Hz, H-2), 4.50–4.80 (m, 8H, $CH_2C_6H_5$), 5.74 (dd, $^3J = 2.60$, $^3J = 5.70$ Hz, 1H, =C*H*), 6.18 (dd, $^3J = 3.20$, $^3J = 5.70$ Hz, 1H, =C*H*), 7.20–7.40 (m, 20H, $CH_2C_6H_5$); ^{13}C-NMR (100 MHz, $(CD_3)_2CO$)): δ 47.8 (C-7), 46.1, 48.6, 51.8 (C-1, C-3, C-4), 70.7 (C-4′), 71.9 (OCH_3), 72.8, 73.7, 73.8, 75.1 ($CH_2C_6H_5$), 78.4, 80.6, 82.1, 82.2 (C-1′-C-3′, C-2), 128.0–129.9 ($CH_2C_6H_5$, =C*H*), 132.9 (=C*H*), 139.8–140.1 (C-*ipso*), 198.5 (CO *cis*), 203.7 (CO *trans*), 335.3 (*C*=W); FABMS (*m*/*z*): 940.2 [M^+], 856.2 [$M^+ - 3CO$], 825.2 [$M^+ - 4CO$].

endo-Isomer **15b**: IR (PE): $\nu(A_1^1)$ 2067.6 m, $\nu(E, A_1^2)$ 1946.1 vs cm^{-1}; ^{1}H-NMR (500 MHz, C_6D_6): δ 1.28 (dd, $^3J = 1.69$, $^2J = 8.3$ Hz, 1H, H-7a), 1.95 (d, $^2J = 8.3$ Hz, 1H, H-7b), 3.23 (ddd, $^3J = 1.80$, $^3J = 5.15$, $^3J = 7.10$ Hz, 1H, H-3), 3.02 (br, 1H, H-1/H-4), 3.53 (br, 1H, H-1/H-4), 3.73 (dd, $^2J = 11.37$, $^3J = 6.10$ Hz, 1H, H-4′a), 3.81 (dd, $^3J = 4.38$, $^3J = 7.10$ Hz, 1H, H-1′), 3.85 (pt, $^3J = 4.5$ Hz, 1H, H-2′), 3.91–3.95 (m, 2H, H-3′,

H-4′), 4.38 (s, 3H, OCH_3), 4.57 (dd, $^3J = 3.1$, $^3J = 5.15$ Hz, H-2), 4.52–4.84 (m, 8H, CH_2C$_6$H$_5$), 5.74 (dd, $^3J =$ 2.78, $^3J = 5.70$ Hz, 1H, =C*H*), 6.23 (dd, $^3J = 3.20$, $^3J =$ 5.70 Hz, 1H, =C*H*), 7.20–7.42 (m, 20H, CH$_2$C$_6$*H*$_5$); ^{13}C-NMR (100 MHz, (CD$_3$)$_2$CO)): δ 48.0 (C-7), 46.7, 46.9, 52.0 (C-1, C-3, C-4), 71.0 (C-4′), 71.9 (O*C*H$_3$), 72.6, 74.1, 74.7, 75.2 (*C*H$_2$C$_6$H$_5$), 79.4, 80.2, 82.4, 82.5 (C-1′-C-3′, C-2), 128.3–129.4 (CH$_2$*C*$_6$H$_5$, =*C*H), 134.1 (=*C*H), 140.3–140.4 (C-*ipso*), 198.7 (CO *cis*), 204.1 (CO *trans*), 335.5 (*C*=W); FABMS (*m*/*z*): 941.2 [M$^+$ + H], 824.2 [M$^+$ − 4CO], 643.0 [M$^+$ − W(CO)$_5$ + H].

exo-Isomer **15c**: IR (PE): ν(A$_1^1$) 2067.6 m, ν(E, A$_1^2$) 1944.2 vs cm^{-1}; ^{13}C-NMR (100 MHz, C$_6$D$_6$): δ 45.1, 45.5, 45.6, 50.5 (C-1, C-3, C-4, C-7), 70.2, 70.3 (C-4′, O*C*H$_3$), 72.0, 72.6, 73.3, 73.5 (*C*H$_2$C$_6$H$_5$), 77.5, 78.6, 80.3, 82.8 (C-1′-C-3′, C-2), 128.3–129.4 (CH$_2$*C*$_6$H$_5$), 126.6, 136.6 (*C*=*C*), 139.2, 139.4, 139.5, 139.8 (C-*ipso*), 199.7 (CO *cis*), 202.2 (CO *trans*), n.o. (*C*=W); FABMS (*m*/*z*): 940.1 [M$^+$], 856.1 [M$^+$ − 3CO], 824.2 [M$^+$ − 4CO].

exo-Isomer **15d**: ^{13}C-NMR (100 MHz, (CD$_3$)$_2$CO)): δ 46.3, 46.3, 50.5, 55.1 (C-1, C-3, C-4, C-7), 71.2, 71.6 (C-4′, O*C*H$_3$), 72.5, 73.0, 74.0, 74.5 (*C*H$_2$C$_6$H$_5$), 79.9, 79.9, 80.4, 82.3 (C-1′-C-3′, C-2), 128.3–129.4 (CH$_2$*C*$_6$H$_5$ =*C*H), 137.5, 137.6, 140.0, 140.7 (C-*ipso*), n.o. (CO *cis*, CO *trans*), 335.9 (*C*=W); FABMS (*m*/*z*): 940.1 [M$^+$], 856.1 [M$^+$ − 3CO], 824.2 [M$^+$ − 4CO + H].

*4.3.5.2. Pentacarbonyl[2-(3-(1′,5′-anhydro-1′,2′:3′,4′-di-O-isopropylidene-α-D-galacto-pentopyranosyl))bicyclo-[2.2.1]hept-5-enyl)(methoxy)carbene]tungsten(0) **(16)**.* Complex **8** (0.27 g, 0.27 mmol) was dissolved in 4 ml of freshly distilled cyclopentadiene. The oxygen was removed by three cycles of 'freeze, pump and thaw'. The mixture was stirred for 0.5 h at r.t. while the deep-red color lightened to yellow. The diene was removed under reduced pressure and the crude was purified by column chromatography which gave 270 mg (0.4 mmol, 91%) of **16** as yellow solid and a 3:1 mixture of *endo*/*exo* isomers. The isomers could be separated by HPLC. Anal. Found: C, 44.04; H, 3.92. $C_{25}H_{28}O_{11}W$ (688.3): Calc.: C, 43.62; H, 4.10.

endo-Isomer **16a**: IR (PE): ν(A$_1^1$) 2068 m, ν(E) 1949.9 s, ν(A$_1^2$) 1936 vs cm^{-1}; ^{1}H-NMR (500 MHz, C$_6$D$_6$): δ 1.22 (s, 3H, C(CH_3)$_2$), 1.40 (s, 3H, C(CH_3)$_2$), 1.41 (s, 3H, C(CH_3)$_2$), 1.62 (s, 3H, C(CH_3)$_2$), 1.21–1.42 (m, 2H, H-7a, H-7b), 2.27 (ddd, $^3J = 10.0$, $^3J = 5.16$, $^3J = 1.75$ Hz, 1H, H-3), 3.21 (br, 1H, H-1/H-4), 3.51 (br, 1H, H-1/H-4), 3.76 (s, 3H, OCH_3), 3.62 (dd, $^3J = 2.0$, $^3J =$ 10.0 Hz, H-5′), 4.60 (dd, $^3J = 5.16$, $^3J = 2.56$ Hz, 1H, H-2′), 4.32 (dd, $^3J = 7.84$, $^3J = 2.00$ Hz, 1H, H-4′), 4.34 (dd, $^3J = 3.18$, $^3J = 5.16$ Hz, 1H, H-2), 4.60 (dd, $^3J =$ 2.56, $^3J = 7.84$ Hz, 1H, H-3′), 5.42 (dd, $^3J = 2.82$, $^3J =$ 5.54 Hz, 1H, =C*H*), 5.51 (d, $^3J = 5.16$ Hz, 1H, H-1′), 6.08 (dd, $^3J = 2.28$, $^3J = 5.54$ Hz, 1H, =C*H*); ^{13}C-NMR (100 MHz, CDCl$_3$): δ 24.1, 24.9, 25.9, 26.1 (C(*C*H$_3$)$_2$), 44.5 (C-3), 49.9, 46.1 (C-1, C-4), 47.4 (C-7), 70.2 (C-2′), 70.8, 70.8 (C-3′, C-5′), 74.9, 71.7 (C-2, C-4′), 79.9 (O*C*H$_3$), 96.4 (C-1′), 108.5, 109.0 (*C*(CH$_3$)$_2$), 131.0, 138.8 (*C*=*C*), 197.7 (CO *cis*), 202.3 (CO *trans*), 332.6 (*C*=W); FABMS (*m*/*z*): 688.1 [M$^+$], 660.1 [M$^+$ − CO], 604.1 [M$^+$ − 3CO].

exo-Isomer **16b**: IR (PE): ν(A$_1^1$) 2067.6 m, ν(E) 1949.9 s, ν(A$_1^2$) 1936.4 vs cm^{-1}; ^{1}H-NMR (500 MHz, (CD$_3$)$_2$CO): δ 1.24 (s, 3H, C(CH_3)$_2$), 1.30 (s, 3H, C(CH_3)$_2$), 1.37 (s, 3H, C(CH_3)$_2$), 1.49 (s, 3H, C(CH_3)$_2$), 1.30 (ü, 2H, H-7a, H-7b), 2.74 (ddd, $^3J = 3.26$, $^3J =$ 5.26, $^3J = 10.48$ Hz, 1H, H-3), 2.98 (br, 1H, H-1/H-4), 3.05 (dd, $^3J = 1.99$, $^3J = 10.48$ Hz, H-5′), 3.11 (br, 1H, H-1/H-4), 3.52 (d, $^3J = 5.26$ Hz, 1H, H-2), 4.05 (dd, $^3J = 7.95$, $^3J = 1.99$ Hz, 1H, H-4′), 4.23 (dd, 1H, $^3J =$ 2.38, $^3J = 5.07$ Hz, 1H, H-2′), 4.49 (dd, $^3J = 2.38$, $^3J =$ 7.95 Hz, 1H, H-3′), 4.63 (s, 3H, OCH_3), 5.48 (d, $^3J = 5.07$ Hz, 1H, H-1′), 6.20 (dd, $^3J = 2.88$, $^3J = 5.50$ Hz, 1H, =C*H*), 6.35 (dd, $^3J = 3.28$, $^3J = 5.50$ Hz, 1H, =C*H*); ^{13}C-NMR (100 MHz, (CD$_3$)$_2$CO)): δ 24.1 24.9, 25.9, 25.9 (C(*C*H$_3$)$_2$), 44.0, 44.0, 49.7 (C-1, C-3, C-4), 44.5 (C-7), 70.2 (O*C*H$_3$), 70.5 (C-2′), 70.6, 70.7 (C-3′, C-5′), 71.8, 75.8 (C-2, C-4′), 96.2 (C-1′), 108.3, 108.9 (*C*(CH$_3$)$_2$), 136.5, 173.2 (*C*=*C*), 197.7 (CO *cis*), 202.5 (CO *trans*), 333.9 (*C*=W); FABMS (*m*/*z*): 688.1 [M$^+$], 604.1 [M$^+$ − 3CO].

*4.3.5.3. Pentacarbonyl[5-(1,2-dimethyl-4-(D-arabino-1′,2′,3′,4′-tetra-O-benzylbutyl)-cyclohex-1-enyl)(methoxy)carbene]tungsten(0) **(17)**.* Complex **4** (280 g, 0.32 mmol) was dissolved in 4 ml of freshly distilled 2,3-dimethylbutadiene. The oxygen was removed by three cycles of 'freeze, pump and thaw'. The mixture was stirred for 72 h at r.t. while the deep-red color lightened to yellow. The diene was removed under reduced pressure and the crude was purified by column chromatography which gave 160 mg (0.17 mmol, 53%) of **17** as a yellow oil and a 7:1 mixture of isomers **17a**:**b**. Anal. Found: C, 59.55; H, 5.42. $C_{47}H_{48}O_{10}W$ (956.7) Calc.: C, 59.00; H, 5.06. IR (PE): ν(A$_1^1$) 2069.5m, ν(E, A$_1^2$) 1942 vs. cm^{-1}; FABMS (*m*/*z*): 900.2 [M$^+$ − 2CO], 872.3 [M$^+$ − 3CO].

17a: ^{1}H-NMR (500 MHz, (CD$_3$)$_2$CO)): δ 1.44 (s, 3H, CH_3), 1.61 (s, 3H, CH_3), 1.72–1.90 (m, 3H, H-6a, H-3, H-3a), 2.28 (dd, 1H, $^3J = 4$, $^2J = 16.8$ Hz, H-6b), 2.42 (dptpt, 1H, $^3J = 5.5$, $^3J = 9.5$ Hz, H-4), 3.79, 3.60 (dd, 2H, $^3J = 6.5$, $^3J = 4.5$, $^3J = 6.5$, $^3J = 4.5$ Hz, H-2′, H-3′), 3.86 (dd, 1H, $^2J = 10.2$, $^3J = 4.7$ Hz, H-4′a), 3.94 (dd, 1H, $^3J = 4.4$, $^3J = 9$ Hz, H-1′), 4.02 (dd, 1H, $^2J = 10.2$, $^3J = 3.9$ Hz, H-4′b), 4.28 (dpt, 1H,, $^3J = 9.5$, $^3J = 4$ Hz, H-5), 4.64 (s, 3H, OCH_3), 4.59–4.92 (m, 8H, CH_2C$_6$H$_5$), 7.20–7.50 (m, 20H, CH$_2$C$_6$*H*$_5$); ^{13}C-NMR (100 MHz, (CD$_3$)$_2$CO)): δ 18.6 (2C, CH$_3$), 36.1, 36.7, 40.5 (C-3, C-4, C-6), 69.8, 70.9, 71.1 (O*C*H$_3$, C-5, C-4′), 72.3, 73.7, 74.4, 74.9 (*C*H$_2$C$_6$H$_5$), 80.0, 81.3, 83.3 (C-1′–C-3′), 128.1–129.0 (CH$_2$*C*$_6$H$_5$), 123.5, 125.5 (=*C*H),

137.8, 139.8, 139.9 (C-*ipso*), 198.2 (CO *cis*), 204.0 (CO *trans*), 342.4 (*C*=W).

17b: ^{13}C-NMR (100 MHz, $(CD_3)_2CO$)): δ 36.1, 37.7, 40.2 (C-3, C-4, C-6), 72.4, 73.7, 74.3, 75.1 ($CH_2C_6H_5$), 79.9, 81.2, 83.2 (C-1′–C-3′), 123.5, 125.8 (=*C*H).

*4.3.5.4. Pentacarbonyl[5-(4-(5′-(1′,5′-anhydro-1′,2′:3′, 4′-di-O-isopropylidene-α-D-galacto-pento-pyranosyl))-1,2-dimethylcylohex-1-enyl)(methoxy)carbene]tungsten(0) (**18**).* Complex **8** (120 mg, 0.2 mmol) was dissolved in 3 ml of 2,3-dimethylbutadiene. The oxygen was removed by three cycles of 'freeze, pump and thaw'. The mixture was stirred for 12 h at r.t. while the deep-red color lightened to yellow. The diene was removed under reduced pressure and the crude was purified by column chromatography which gave 130 mg (0.18 mmol, 91%) of **18** as a yellow solid and a 2.5:1 mixture of isomers **18a**:**b** which were separated by a second column chromatography. HRMS $C_{25}H_{32}O_{10}^{182}W$, $M^+ - CO$: Found: 674.1474, Calc.: 674.1470; EIMS (*m*/*z*): 704.2 [M^+], 689.2 [$M^+ - CH_3$], 676.3 [$M^+ - CO$], 648.2 [$M^+ - 2CO$], 620.2 [$M^+ - 3CO$], 592.2 [$M^+ - 4CO$].

18a: IR (PE): $\nu(A_1^1)$ 2070 m, $\nu(A_1^2)$ 1956 m, ν(E) 1940 vs cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.28, 1.31 (s, 6H, CH_3), 1.43, 1.43, 1.59, 1.59 (s, 12H, C(CH_3)), 1.70, 1.82, 2.06, 2.24 (m, 4H, H-3, H-4, H-3a, H-6a, H-6b), 3.54 (dd, 1H, $^3J = 1.3$, $^3J = 9.8$ Hz, H-5′), 4.02 (m, 1H, H-5), 4.03 (dd, 1H, $^3J = 1.3$, $^3J = 8.1$ Hz, H-4′), 4.21 (dd, 1H, $^3J = 2.2$, $^3J = 5.1$ Hz, H-2′), 4.51 (dd, 1H, $^3J = 2.2$, $^3J = 8.1$ Hz, H-3′), 4.58 (s, 3H, OCH_3), 5.49 (d, 1H, $^3J = 5.1$ Hz, H-1′); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 18.5, 18.7 (*C*H_3), 24.1, 24.9, 25.7, 26.0 (*C*$(CH_3)_2$), 34.7, 34.8, 37.1 (C-3, C-4, C-6), 70.1, 70.4, 70.5, 70.7, 70.9, 72.5 (C-2′–C-5′, OCH_3, C-5), 96.7 (C-1′), 108.5, 108.7 (*C*$(CH_3)_2$), 122.1, 125.1 (*C*=*C*), 197.3 (CO *cis*), 202.5 (CO *trans*), 338.9 (*C*=W).

18b: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.25, 1.33 (s, 6H, CH_3), 1.41, 1.41, 1.57, 1.57 (s, 12H, C(CH_3)), 1.76–1.88 (m, 2H, CH_2), 2.06 (m, 1H, CH_2), 2.24 (m, 1H, CH_2), 2.66 (dpq, 1H, $^3J = 5.8$, $^3J = 10.1$ Hz, H-4), 3.38 (dd, 1H, $^3J = 2.2$, $^3J = 10.1$ Hz, H-5′), 3.95 (dpt, 1H, $^3J = 4.9$, $^3J = 10.1$ Hz, H-5), 4.19 (dd, 1H, $^3J = 7.6$, $^3J = 2.2$ Hz, H-4′), 4.25 (dd, 1H, $^3J = 2.6$, $^3J = 5.3$ Hz, H-2′), 4.50 (dd, 1H, $^3J = 2.6$, $^3J = 7.7$ Hz, H-3′), 4.51 (s, 3H, OCH_3), 5.46 (d, 1H, $^3J = 5.4$ Hz, H-1′); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 18.5, 18.6 (*C*H_3), 24.7, 25.2, 25.5, 26.2 (*C*$(CH_3)_2$), 34.1, 34.5, 38.8 (C-3, C-4, C-6), 69.5, 69.6, 69.9, 71.1, 71.2, 71.5 (C-2′–C-5′, OCH_3, C-5), 96.9 (C-1′), 108.5, 109.1 (*C*$(CH_3)_2$), 123.4, 124.0 (*C*=*C*), 198.0 (CO *cis*), 203.6 (CO *trans*), 339.5 (*C*=W).

4.3.6. Michael-type addition reaction

*4.3.6.1. Pentacarbonyl[1-(2(R,S)-C-cyclohexan-2′-one-1,2-dideoxy-1,2:3,4-tetra-O-benzyl-D-glucitolyl)(methoxy)carbene]tungsten(0) (**19a**/**b**).* 1-Trimethylsilyloxycyclohexene (0.17 ml, 0.91 mmol) was dissolved in 5 ml THF. At 0°C, 1.09 mmol *n*-BuLi (0.47 ml of a 0.35 M solution in *n*-hexan) was added. The mixture was stirred for 1 h at this temperature. Complex **4** (0.67 g, 0.76 mmol) was dissolved in 6 ml THF. The first solution was added to this mixture at −78°C. During a period of 2 h the temperature was allowed to warm to −50°C while the deep-red color of the starting material disappeared. At −78°C, 2 ml methanol were added. The solvents were removed under reduced pressure. Chromatographic separation gave 330 mg (0.34 mmol, 44%) of **19a** and 110 mg (0.11 mmol, 15%) of **19b** as yellow oils.

19a (major diastereomer): IR (PE): $\nu(A_1^1)$ 2070 m, $\nu(E, A_1^2)$ 1942 vs cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): Cyclohexanone: δ 0.96 (ddd, $^3J = 3.0$, $^3J = 12.8$, $^2J = 26.2$ Hz, 1H), 1.26 (m, 1 H), 1.43 (ptdd, $^3J = 4.5$, $^3J = 13.0$, $^2J = 26.5$ Hz, 1 H), 1.66 (m, 2 H), 1.78 (dpt, $^3J = 6.0$, $^3J = 13.0$ Hz, 1 H), 1.86 (m, 1 H), 2.13 (m, 2 H), sugar chain: $\delta = 2.88$ (psep, $^3J_{2,3} = 3.7$, $^3J_{2,1'} = 3.7$, $^3J_{2,1a} = 7.9$, $^3J_{2,1b} = 7.9$ Hz, 1H, H-2), 3.03 (dd, $^2J = 18.7$, $^3J = 3.8$ Hz, 1H, H-1a), 3.43 (dd, $^3J = 3.7$, $^3J = 5.9$ Hz, H-3), 3.51 (dd, 1H, $^2J = 18.7$, $^3J = 7.9$ Hz, H-1b), 3.71 (dd, $^3J = 4.67$, $^3J = 5.9$ Hz, 1H, H-4), 3.76–3.83 (m, 2H, $^3J = 5.9$ Hz, H-6a, H-5), 3.89 (dd, $^2J = 9.7$, $^3J = 1.4$ Hz, H-6b), 4.22 (s, 3H, OCH_3), 4.29 (d, $^2J = 12$ Hz, 1H, C$H_2C_6H_5$), 5.53 (s, 2H, C$H_2C_6H_5$), 4.57 (d, $^2J = 12$ Hz, 1H, C$H_2C_6H_5$), 4.64 (d, $^2J = 12$ Hz, 1H, C$H_2C_6H_5$), 4.68 (d, $^2J = 12$ Hz, 1H, C$H_2C_6H_5$), 4.73 (d, $^2J = 3.7$ Hz, 1H, C$H_2C_6H_5$), 4.75 (d, $^2J = 3.7$ Hz, 1H, C$H_2C_6H_5$), 7.11–7.32 (m, 20H, $CH_2C_6H_5$); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 25.3, 28.0, 32.1 (C-4′, C-5′, C-6′), 36.8 (C-2), 42.3 (C-3′), 52.6 (C-1′), 64.5 (C-1), 69.9 (C-6), 70.2 (O*C*H_3), 71.7, 73.3, 74.2, 74.4 (*C*$H_2C_6H_5$), 79.2, 80.2. 81.4 (C-3–C-5), 127.5–128.4 ($CH_2C_6H_5$), 138.4, 138.5, 138.7, 138.9 (C-*ipso*), 197.4 (CO *cis*), 202.9 (CO *trans*), 212.4 (C ketone), 332.0 (*C*=W); FABMS (*m*/*z*): 888.4 [$M^+ - 3CO$], 859.3 [$M^+ - 4CO$]; Anal. Found: C, 58.43; H, 5.31. $C_{47}H_{47}O_{11}W$ (874.6) Calc.: C, 58.09; H 4.87.

19b (minor diastereomer): IR (PE): $\nu(A_1^1)$ 2069.5 m, $\nu(E, A_1^2)$ 1942.2 vs cm^{-1}; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 25.3, 28.0, 32.4 (C-4′, C-5′, C-6′), 38.7 (C-2), 42.7 (C-3′), 52.6 (C-1′), 65.2 (C-1), 70.0 (C-6), 70.2 (O*C*H_3), 72.2, 73.3, 73.7, 73.9, (*C*$H_2C_6H_5$), 78.0, 79.6, 80.8 (C-3–C-5), 127.4–128.5 ($CH_2C_6H_5$), 138.2–139.4 (C-*ipso*), 197.5 (CO *cis*), 203.2 (CO *trans*), 212.8 (CO–ketone), 333.7 (*C*=W); FABMS (*m*/*z*): 973.3 [M^+], 888.4 [$M^+ - 3CO$], 859.3 [$M^+ - 4CO$].

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