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Organotransition metal modified sugars Part 27. Stereoselective radical spiro-cycloaddition reactions of Fischer carbene complexes☆

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Abstract

Carbohydrate-functionalised heterocyclic spiro compounds of potential biological relevance are accessible using an organometallic route based on the radical addition of 1,1-dichlorovinylcyclopropane to sugar-derived *exo*-methylene chromium oxacyclopentylidenes.

Keywords: Carbene complexes; Chromium complexes; Organometallic monosaccharides; Spirocycloaddition; Radicals

1. Introduction

Spirocyclic compounds are of particular significance as natural products. Their principle structural feature frequently occurs as a subunit in biologically active natural products such as polyether antibiotics and sex pheromones. Spiro-compounds are also found as metabolites from microbes, fungi, insects and marine organisms [2].

Homogynolide A and B (Scheme 1), isolated from *Homogyne alpina*, are sesquiterpenes which contain a α-spiro-β-methylene-γ-butyrolactone moiety. These terpenes possess antifeedant activity against certain types of beetle adults and larvae. They were synthesised by Srikrishna [3] et al. using a radical cyclisation methodology.

The pharmacological importance of spiro-compounds [4] has triggered intensive research efforts; in this context, we concentrated on carbohydrate-derived spiro-compounds [5]. As part of our investigations aiming at the synthetic potential of radical Fischer-carbene intermediates [6], we have developed a diastereoselective route to spirobicyclic metal carbenes.

2. Results and discussion

Fischer carbene complexes have been successfully applied to stereoselective syntheses [7]. The isolobal analogy [8] correlates the $M(CO)_5$-fragment (M = Cr, W, Mo) with an oxygen atom and, thus, rationalises the relationship between α,β-unsaturated Fischer carbene complexes and carboxylic esters. In addition, the electronic feature of the metal carbonyl fragment enhances the electrophilicity of the α,β-unsaturated C=C bond.

Aiming at organometallic carbohydrate-derived oxaspirocycles we have reacted monosaccharide-substituted *exo*-methylene 2-oxacyclopentylidene chromium complexes with dichlorovinylcyclopropane [9] under radical reaction conditions [10] (Scheme 2). In the course of the reaction, the dichlorocyclopropane derivative is converted in situ into the corresponding dehalogenated vinylcyclopropane suggesting a photochemically induced halogen transfer to the solvent (toluene) according to Scheme 2, Eq. (1), generating vinylcyclopropane.

The carbohydrate-substituted α,β-unsaturated Fischer carbene complexes **5a**–**d** were synthesised from

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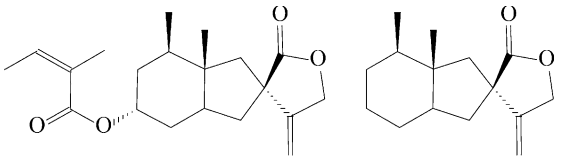
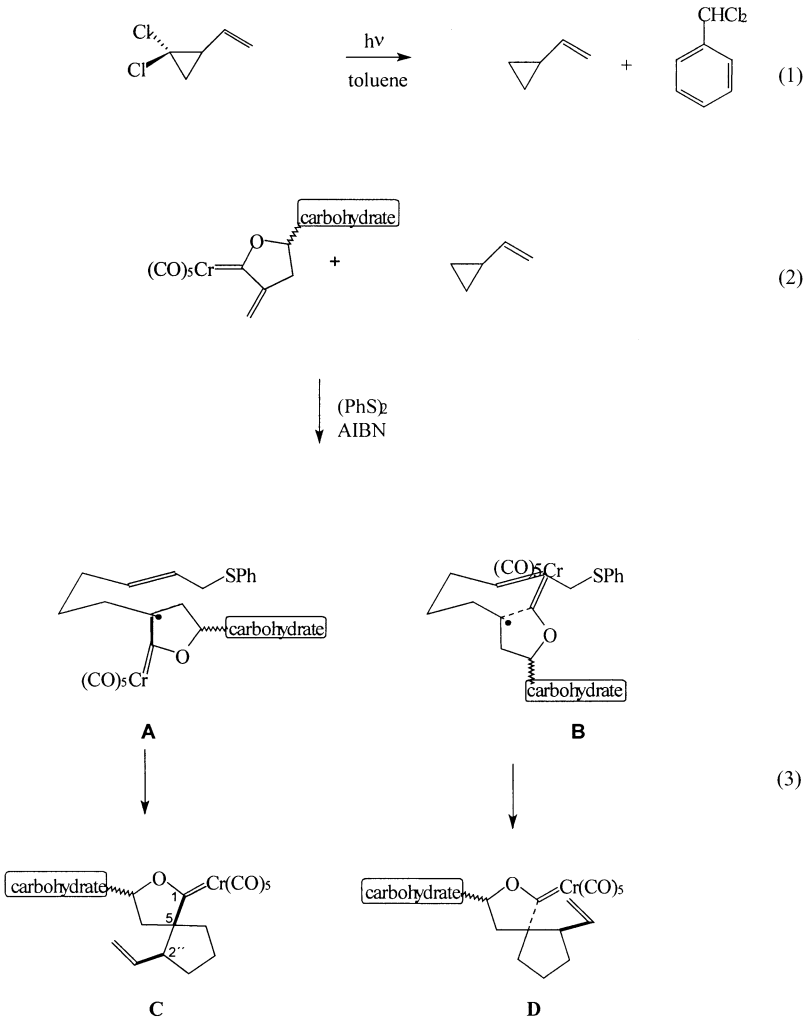


Homogynolide A Homogynolide B

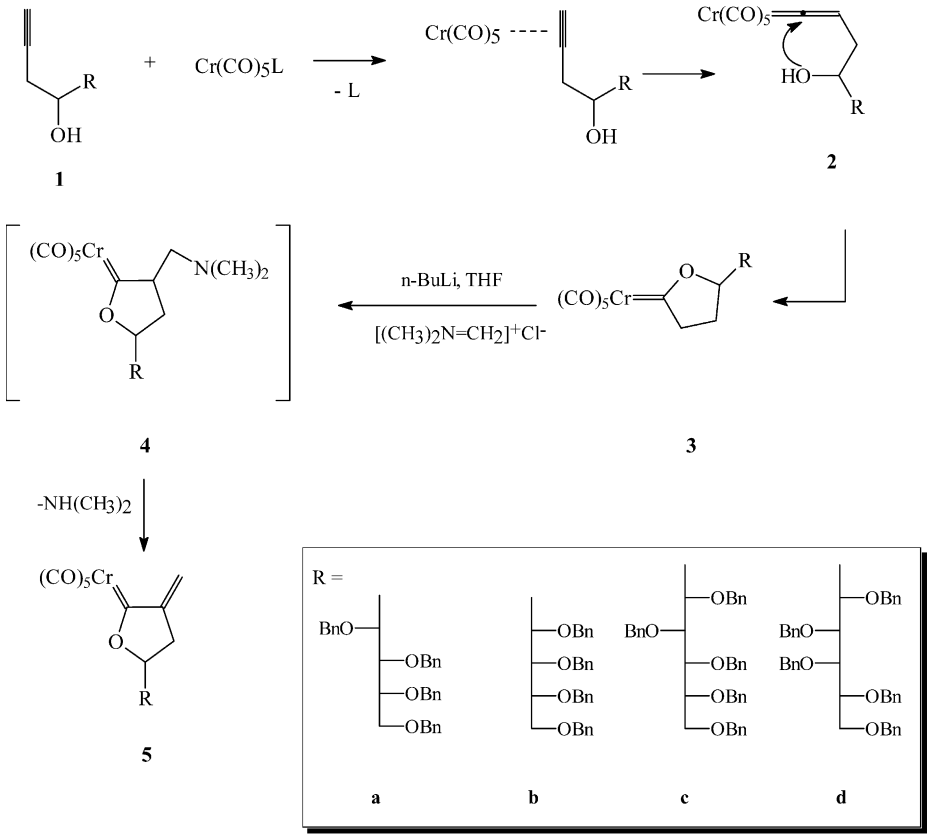
Scheme 1. Prominent spirocyclic natural products.

complex **3** in analogy to a procedure previously described in the literature [12]. Starting from racemic alkynols two diastereomeric oxacyclopentylidene complexes were obtained which could be separated by flash chromatography. The diastereomeric ratio seems to depend on the configuration of C-1′: whereas the pair of *arabino*-complexes is formed in comparable yields, the ratio distinctly increases for the *ribo*-complexes. The major diastereomers **5a**–**d** characterised as 3-(*R*)-isomers by NMR spectroscopy [13] were used for the radical spirocycloaddition reactions. Scheme 3 summarises the synthesis of oxacyclopentylidene complexes **5a**–**d** from the corresponding carbohydrate-substituted alkynols **1a**–**d**; it is based on a sequential coordination of the C≡C triple bond to the metal center, rearrangement to vinylidene complexes **2a**–**d**, cycloisomerisation to oxacyclopentylidene complexes **3a**–**d** and final *exo*-methylene functionalisation with the electrophilic C_1-source *N*,*N*-dimethylmethylene–iminium chloride to give complexes **5a**–**d**.

Feldman has described the formation of a dichloro spiro-compound via a radical-catalysed [3+2] cycloaddition of dichlorovinylcyclopropane to α-methylene–butyrolactone [10,11]. Applying this reaction to carbohydrate α,β-unsaturated Fischer carbene-complexes **5a**–**d** under more rigorous reaction conditions we observed the formation of the dechlorinated products **6a**–**d** (Table 1). The analogous reaction of the parent oxacyclopentylidene complexes **7a**,**b** (Table 2) also led to the chlorine-free spiro-compounds **8a**,**b**. The reactions are regio- and diastereoselective as indicated by NMR-spectroscopy. Of the two possible isomers, the 1,2″-*cis*-



Scheme 2. Photo-induced formal [3+2] cycloaddition of *exo*-methylene oxacyclopentylidene complexes with vinylcyclopropane.



Scheme 3. Synthesis of carbohydrate-substituted α,β-unsaturated Fischer carbene complexes **5a**–**d**.

substituted (**C**) and 1,2″-*trans*-substituted–spiro-compounds (**D**) (Scheme 2) we generally obtained the 1,2″-substituted *cis*-diastereomers (**C**); only for the glucose derivative also traces of the *trans*-diastereomer (**D**) were observed.

The preference for diastereomer **C** can be rationalised in terms of a minimisation of steric interactions between the pentacarbonyl chromium fragment and the vinyl fragment; in contrast, isomer **D** is expected to suffer from considerable steric strain. The pentose derivatives were obtained after 6 hours of irradiation in toluene under reflux affording 30% of *arabino*se derivative **6a** and 65% of *ribo*se derivative **6b**. In the hexose series, the glucose and galactose derivatives **6c** and **6d** were isolated in 68 and 5% yield, respectively. The yield of the galactose derivative could not be improved by longer irradiation or by adding the substrate in excess. The parent spiro-compounds **8a**,**b** missing the sugar functionality were obtained in 53 and 31% yield, respectively.

The dechlorination may be rationalised in terms of a radical chain reaction involving the solvent toluene which may act as chlorine acceptor and undergo side chain chlorination.

In conclusion, we have demonstrated that the radical cycloaddition of vinylcyclopropanes with unsaturated sugar carbene complexes provides a diastereoselective access to oxaspirocycles bearing a metal carbene label which may be utilised for further subsequent functionalisation.

3. Experimental

All operations involving organometallic compounds were performed in an inert gas atmosphere under rigorous exclusion of air and water. The solvents were dried using standard methods and distilled under argon (toluene, methylene chloride and petroleum ether (40–60 °C) over calcium hydride, diethyl ether over sodium hydride). Photochemical reactions were run using a 500-W sunlamp.

Column chromatography of organometallic compounds was performed using silica gel (Merck 60, 0.063–0.200 mm) which was dried in vacuo and stored under argon. Thin layer chromatography was performed using foils from Merck (Typ 60, F254) with UV-detection; carbohydrates were detected by a spray containing sulfuric acid (20%), acetic acid (50%), and ethanol (30%). FT-IR: Nicolet Magna. EI-MS: Kratos MS 50. NMR: Bruker AM-250; Bruker AM-400; Bruker DRX 500. The D-*arabino*- and D-*ribono*-complexes **5a** and **5b** have been prepared as previously described [13].

Table 1
Sugar *exo*-methylene oxacyclopentylidene complexes **5a**–**d** and oxaspirobicycles **6a-d** obtained therefrom

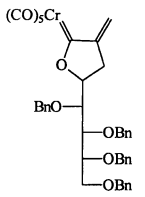
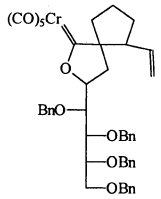
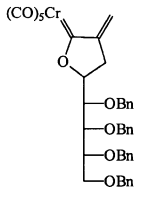
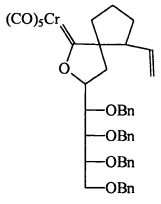
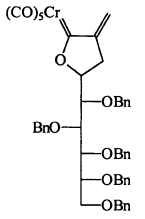
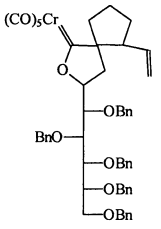
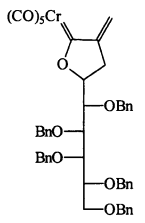
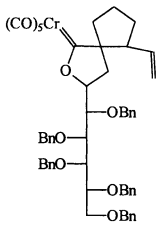
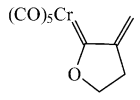
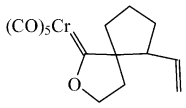
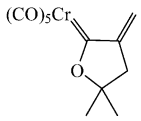
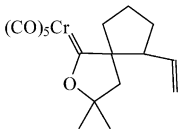
Educt	Product	yield
 **5a**	 **6a**	30%
 **5b**	 **6b**	65%
 **5c**	 **6c**	68%
 **5d**	 **6d**	5%

Table 2
Oxacyclopentylidene complexes **7a**,**b** and spiro-derivatives **8a**,**b**

Educt	Product	Yield
 **7a**	 **8a**	53%
 **7b**	 **8b**	31%

3.1. General procedure for the preparation of **5c** and **5d**

n-Butyl lithium (1.6 M in *n*-hexane) (0.3 ml, 0.5 mmol) was added to a solution of 0.47 mmol of oxacyclopentylidene complex **3c**,**d** in 15 ml tetrahydrofuran under argon at −78 °C . After stirring for 30 min. *N*,*N*-dimethylmethylene–iminium chloride (0.083 g, 0.94 mmol) was added to the stirred solution at −20 °C. The solution turned orange; after 30 min silica gel was added at −40 °C, and the solution was dried in vacuo. Column chromatography over silica gel (petroleum ether–diethyl ether, 2:1) at 0 °C afforded **5c** (0.33 mmol, 71%) and **5d** (0.32 mmol, 69%) as red oils.

3.1.1. Pentacarbonyl[5-exo-methylene-[3-(R)-(1′(R),2′,3′,4′,5′-penta-O-benzyl-D-arabinitolyl)-2-oxacyclopentylidene]chromium (**5c**)

IR (PE): 2059 (m), 1984 (w), 1945 (vs) cm^{-1}; ^{1}H-NMR (400 MHz/$CDCl_3$): 0.91 (dd, 1H, $J = 4.45$, $J =$ 3.72 Hz, H-4b), 1.51 (m, 1H, H-4a), 3.71 (t, 1H, $J =$ 3.02, 4.36 Hz, H-5′b), 3.86 (m, 2H, H-4′, H-5′a), 4.00 (dd, 1H, $J = 4.17$, 3.79 Hz, H-3′), 4.10 (t, 1H, $J = 3.79$, $J = 4.59$ Hz, H-2′), 4.25 (dd, 1H, $J = 3.79$, $J = 3.05$ Hz, H-1′), 4.52 (m, 1H, H-3), 4.88–4.65 (m, 10H, CH_2Ph), 5.96 (s, 1H, H-1″a), 6.52 (s, 1H, H-1″b), 7.25–7.42 (m, 25H, Ph) ppm; ^{13}C-NMR (125 MHz/$CDCl_3$): 29.4 (C-4), 69.6 (C-5′), 72.7–76.9 (CH_2Ph), 79.1 (C-4′), 79.7 (C-3′), 79.7 (C-2′), 80.7 (C-1′), 96.8 (C-3), 127.6–128.8 (C–Ph), 131.3 (C-1″), 137.6, 137.9, 138.0, 138.1, 138.2 (*ipso*-C), 158.9 (C-5), 212.5 (*cis*-CO), 224.5 (*trans*-CO), 323.5 (Cr=*C*) ppm; FABMS: *m*/*z*: 874.2 [M^+], 790.2 [$M - 3CO]^+$, 762.2 [$M - 4CO]^+$, 734.3 [$M - 5CO]^+$.

3.1.2. Pentacarbonyl[5-exo-methylene-[3-(R)-(1′,2′,3′,4′,5′-penta-O-benzyl-D-lyxitolyl)-2-oxacyclopentylidene]chromium (**5d**)

IR (PE): 2059 (m), 1983 (w), 1943 (vs) cm^{-1}; ^{1}H-NMR (250 MHz/$CDCl_3$): 0.91 (dd, 1H, $J = 6.42$, $J =$ 3.38 Hz, H-4b), 1.31 (t, $J = 3.91$, 3.69 Hz, H-4a), 3.69 (dd, 1H, $J = 3.91$, 3.69 Hz, H-5b′), 3.95 (t, 1H, $J = 3.92$; $J = 1.03$ Hz, H-5a′), 4.16 (m, 3H, H-2′, H-3′, H-4′), 4.30 (, 1H, $J = 4.32$, $J = 5.21$ Hz, H-1′), 4.52-4.69 (m, CH_2Ph), 4.86 (dd, 1H, $J = 4.36$, $J = 3.62$ Hz, H-3), 6.11 (s, 1H, H-1″a), 6.62 (s, 1H, H-1″b), 7.31–7.50 (m,

25H, Ph) ppm; ^{13}C-NMR (125 MHz/$CDCl_3$): 29.1 (C-4), 70.5 (C-5′), 73.1–76.5 (CH_2Ph), 78.2 (C-4′), 79.2 (C-3′), 79.5 (C-2′), 79.8 (C-1′), 96.1 (C-3), 127.3–128.4 (C–Ph), 131.8 (C-1″), 137.7, 137.9, 138.0, 138.2, 138.4 (*ipso*-C); 158.7 (C-5), 217.3 (*cis*-CO), 224.3 (*trans*-CO), 323.7 (Cr=C) ppm; FABMS: *m*/*z*: 874.2 [M^+], 790.2 [$M-3CO]^+$, 762.2 [$M-4CO]^+$, 734.3 [$M-5CO]^+$.

3.2. General procedure for the preparation of **6a–d** and **8a,b**

3,3-Dichlorovinylcyclopropane (0.33 mmol, one equivalent), 0.4 equivalents (for the *ribono*-compound) or 0.3 equivalents (for the gluco-compound) of diphenyldisulfide and 0.15 equivalents of AIBN were added to a solution of 0.66 mmol (two equivalents) of *exo*-methylene-oxacyclopentylidene complex **5a–d** in 20 ml toluene under argon. The solution was irradiated with the sunlamp under reflux for 3 h while the reaction was monitored by IR. Then, another 0.15 equivalents of AIBN were added to the solution, and the irradiation was continued for additional 3 h. The colour the solution changed during the irradiation from red to orange. After removal of the solvent the product was purified by chromatography over silica gel (petroleum ether–diethylether, 2:1) to give **6a** (30%), **6b** (65%), **6c** (68%) and **6d** (5%), respectively, as orange oils. **8a** and **8b** were purified by chromatography (petroleum ether–dichloromethane 2:1) and obtained as orange oils in yields of 53 and 31%, respectively.

3.2.1. Pentacarbonyl[2″-ethenyl-3-(D-arabino-1′,2,′3′,4′-penta-O-benzylbutyl)-(2-oxacyclopent-5,1″-spirocyclopent)ylidene]chromium (**6a**)

IR (PE): 2063 (m), 1949 (vs), 1932 (vs)cm − 1; ^{1}H-NMR (250 MHz/$CDCl_3$): 0.96 (dd, 1H, $J=0.89$, $J=4.66$ Hz, H-4b), 1.22–1.60 (m, 3H, H-2″, H-4″), 1.95 (m, 2H, H-3″), 3.04. (dd, $J=4.53$, $J=2.21$ Hz, H-5″), 3.61 (dd, 1H, $J=2.69$, $J=4.58$ Hz, H-4a), 3.81-3.47 (m, 4H, H-2′, H-3′, H-4′), 4.50–4.76 (m, 8H, CH_2Ph), 5.12 (t, 1H, $J=2.29$, $J=5.51$ Hz, H-3), 5.24 (t, 1H, $J=2.16$, $J=11.0$ Hz, H-1′), 6.19 (bs, 1H, H-6″), 6.21 (s, 1H, H-7″a), 6.34 (t, 1H, $J=2.78$, $J=2.88$ Hz, H-7″b), 7.35–7.26 (m, 20H, Ph) ppm; ^{13}C-NMR (125MHz/$CDCl_3$): 24.6 (C-3″), 28.0 (C-4″), 31.9 (C-2″), 39.78 (C-4), 43.9 (C-5″), 68.5 (C-4′), 69.5 (C-3′), 71.9 (C-5), 76.3 (C-2′), 79.3 (C-1′), 100.7 (C-3), 125.8 (C-6″), 128.9–127.0 (C–Ph), 138.7–137.3 (*ipso*-C), 144.9 (C-7″), 216.4 (*cis*-CO), 222.5 (*trans*-CO), 344.6 (Cr=C) ppm; FABMS: *m*/*z*: 823.2 [M^+], 739.2 [$M-3CO]^+$, 683.2 [$M-5CO]^+$.

3.2.2. Pentacarbonyl[2″-ethenyl-3-(D-ribono-1′,2,′3′,4′-penta-O-benzylbutyl)-(2-oxacyclopent-5,1″-spirocyclopent)ylidene]chromium (**6b**)

IR (PE): 2063 (m), 1950 (vs), 1932 (s) cm^{-1}; ^{1}H-NMR (500 MHz/$CDCl_3$): 1.25 (t, 1H, $J=4.56$, 2.49 Hz, H-4b), 1.32–1.51 (m, 2H, H-2″), 1.7 (m, 1H, H-4″), 1.92 (ddd, 1H, $J=11.0$, $J=8.94$, $J=9.14$ Hz, H-3a″), 2.00 (ddd, $J=11.0$, $J=4.17$, $J=10.28$ Hz, H-3″b), 2.93 (dd, $J=2.09$, $J=14.10$ Hz, H-5″), 3.11 (m, 1H, H-5″), 3.14 (dd, 1H, $J=2.89$, $J=1.79$, Hz, H-4a), 3.86 (dd, 1H, $J=1.39$, $J=4.18$ Hz, H-2′), 3.81 (dd, 1H, $J=3.88$, $J=4.18$ Hz, H-3′), 3.75 (dd, 1H, $J=5.56$, $J=14.1$ Hz, H-4a′), 3.70 (dd, 1H, $J=4.17$, $J=5.87$ Hz, H-4b′), 5.29 (dd, 1H, $J=6.06$, $J=1.69$ Hz, H-1′), 4.45–4.71 (m, 10H, CH_2Ph), 5.29 (td, 1H, $J=1.79$, $J=1.79$ Hz, H-3), 6.40 (bs, 1H, H-6″), 6.42 (s, 1H, H-7″a), 6.82 (t, 1H, $J=2.78$, $J=2.88$, H-7″b), 7.31–7.50 (m, 20H, Ph) ppm; ^{13}C-NMR (125 MHz/$CDCl_3$): 26.8 (1C, C-3″), 28.6 (C-4″), 31.3 (C-2″), 43.0 (C-4), 44.0 (C-5″), 69.0 (C-4′), 69.2 (C-3′), 70.0 (1C, C-5), 72.3, 73.4, 73.7, 73.8 (4C, Ch_2Ph), 77.4 (C-2′), 78.0 (C-1′), 100.8 (C-3), 124.4 (C-6″), 128.5–127.8 (C–Ph), 138.0-137.4 (*ipso*-C), 147.9 (C-7″), 216.5 (*cis*-CO), 222.6 (*trans*-CO), 344.9 (Cr=C) ppm; FABMS: *m*/*z*: 823.2 [M^+], 739.2 [$M-3CO]^+$, 683.2 [$M-5CO]^+$.

3.2.3. Pentacarbonyl[2″-ethenyl-3-(D-gluco-1′,2,′3′,4′-hexa-O-benzylpentyl)-(2-oxacyclopent-5,1″-spirocyclopent)ylidene]chromium (**6c**)

IR (PE): 2062 (m), 1948 (vs), 1930 (s) cm^{-1}; ^{1}H-NMR (400 MHz/$CDCl_3$): 1.21 (t, 1H, $J=3.11$, $J=2.32$ Hz, H-4b), 1.34.–1.90 (m, 5H, H-2″, H-4″, H-3a″), 2.09 (m, 1H, H-3b″), 2.85 (dd, $J=1.57$, $J=1.57$ Hz, H-5″), 3.49 (m, 1H, H-5a′), 3.63 (dd, 1H, $J=3.52$, $J=8.21$ Hz, H-4a), 3.73 (t, 1H, $J=5.71$, $J=9.00$ Hz, H-5b′), 3.80 (dd, 1H, $J=5.87$, $J=11.54$ Hz, H-4′), 4.45–4.73 (m, 10H, CH_2Ph), 4.78 (t, 1H, $J=10.57$, $J=8.21$ Hz, H-1′), 3.97 (m, 2H, H-2′, H-3′), 5.13 (td, 1H, $J=8.00$, $J=2.35$ Hz, H-3), 6.35 (bs, 1H, H-6″), 6.45 (s, 1H, H-7″a), 6.82 (s, H-7″b), 7.36-7.26 (m, 25H, Ph) ppm; ^{13}C-NMR (125 MHz/$CDCl_3$): 26.2 (C-3″), 28.8 (C-4″), 31.0 (C-2″), 39.2 (C-4), 43.8 (C-5″), 65.7 (C-5′), 68.1 (C-4′), 69.0 (C-3′), 69.3 (C-5), 72.5, 72.9, 73.3, 74.9, 75.3 (Ch_2Ph), 78.7 (C-2′), 79.2 (C-1′), 100.4 (C-3), 121.3 (C-6″), 127.0-129.4 (C–Ph), 137.5–138.1 (*ipso*-C), 147.9 (C-7″), 216.4 (*cis*-CO), 222.5 (*trans*-CO), 344.0 (Cr=C) ppm; FABMS: *m*/*z*: 942.5 [M^+], 858.5 [$M-3CO]^+$, 802.5 [$M-5CO]^+$.

3.2.4. Pentacarbonyl[2″-ethenyl-3-(D-galacto-1′,2,′3′,4′-hexa-O-benzylpentyl)-(2-oxacyclopent-5,1″-spirocyclopent)ylidene]chromium (**6d**)

IR (PE): 2063 (m), 1950 (vs), 1931 (vs); ^{13}C-NMR (125 MHz/$CDCl_3$): 26.1 (C-3″), 28.2 (C-4″), 31.0 (C-2″), 39.2 (C-4), 43.2 (C-5″), 64.7 (C-5′), 68.5 (C-4′), 70.0 (C-3′), 69.5 (C-5), 72.7, 72.9, 74.0, 74.5, 76.3 (CH_2Ph), 78.7 (C-2′), 80.2 (C-1′), 101.1 (C-3), 122.1 (C-6″), 127.0–130.0 (C–Ph), 137.0–138.1 (*ipso*-C), 149.0 (C-7″), 216.5 (*cis*-CO), 222.3 (*trans*-CO), 343.9 (Cr=C) ppm; FABMS: 942.5 [M^+], 858.5 [$M-3CO]^+$, 802.5 [$M-5CO]^+$.

*3.2.5. Pentacarbonyl[2″-ethenyl-(2-oxacyclopent-5,1″-spirocyclopent)ylidene]-chromium (**8a**)*

IR (PE): 2065 (m), 1967 (vs), 1954 (s) cm^{-1}; ^{1}H-NMR (400 MHz/$CDCl_3$): 1.14–1.44 (m, 2H, H-2′, H-4b), 2.15 (dd, 1H, $J = 4.56$, $J = 1.32$ Hz, H-3a), 2.33 (m, 3H, H-3′, H-4a), 3.00 (dd, 1H, $J = 2.35$, $J = 5.02$ Hz, H-5′), 3.46 (m, 1H, H-4a′), 3.95 (dd, 1H, $J = 4.56$, $J = 9.02$ Hz, H-3b), 5.13 (m, 1H, H-6′), 6.16 (s, 1H, H-7′a), 6.41 (t, 1H, H-7′b) ppm; ^{13}C-NMR (125 MHz/$CDCl_3$): 23.2 (C-3′), 26.0 (C-2′), 29.7 (C-4′), 31.6 (C-4), 65.9 (C-5′), 70.0 (C-5), 84.1 (C-3), 139.2 (C-7′), 143.3 (C-6′), 213.9 (*cis*-CO), 216.4 (*trans*-CO), 347.5 (Cr=C) ppm; EIMS: *m*/*z*: 344.0 $[M^+]$, 288.0 $[M-2CO]^+$, 260.0 $[M-3CO]^+$, 232.0 $[M-4CO]^+$, 204.0 $[M-5CO]^+$.

*3.2.6. Pentacarbonyl[2″-ethenyl-3,3-dimethyl-(2-oxacyclopent-5,1″-spirocyclopent)-ylidene]chromium (**8b**)*

IR (PE): 2064 (m), 1963 (vs), 1953 (s) cm^{-1}; ^{1}H-NMR (400 MHz/$CDCl_3$): 1.41–1.31 (m, 2H, H-4b, H-2′), 1.37 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 2.02 (m, 2H, H-4a), 2.51 (m, 2H, H-3′), 3.00 (d, 1H, $J = 14.5$ Hz, H-5′), 3.75 (t, 1H, $J = 9.00$, $J = 4.34$ Hz, H-4a′), 4.43 (dd, 1H, $J = 9.85$, $J = 9.02$ Hz, H-4b′), 5.05 (m, 1H, H-6′), 6.05 (s, 1H, H-7′a), 6.35 (t, 1H, H-7′b) ppm; ^{13}C-NMR (125 MHz/$CDCl_3$): 23.4 (C-3′), 24.1 (CH_3), 25.1 (CH_3), 25.6 (C-2′), 29.3 (C-4′), 30.8 (C-4), 68.5 (C-5′), 79.3 (C-5), 84.5 (C-3), 139.6 (C-7′), 143.7 (C-6′), 214.3 (*cis*-CO), 216.8 (*trans*-CO), 347.9 (Cr=C) ppm; EI-MS: *m*/*z*: 371.0 $[M^+]$, 315.0 $[M-2CO]^+$, 259.0 $[M-4CO]^+$, 231.0 $[M-5CO]^+$.

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