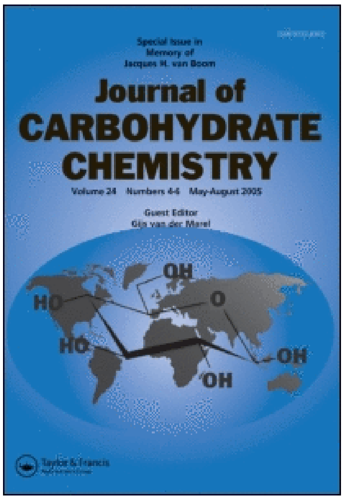

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Sugar Acyl Iron Complexes: Synthesis and Conformational Studies in Solution and in the Solid State

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SUGAR ACYL IRON COMPLEXES: SYNTHESIS AND CONFORMATIONAL STUDIES IN SOLUTION AND IN THE SOLID STATE[1]

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Dedicated to Professor Dr. Peter Welzel on the occasion of his 60th birthday

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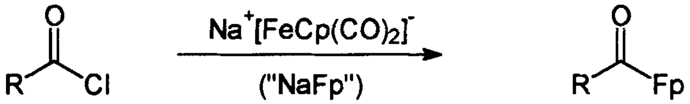
ABSTRACT

A synthetic strategy based on a combination of a sugar electrophile and a transition metal nucleophile allows a metal acyl functionalization at the C-1 carbon atom of acyclic carbohydrates. Following this methodology the per-*O*-acetylated acyl iron complexes dicarbonylcyclopentadienyl[2,3,4,5,6-penta-*O*-acetyl-D-galactonyl]iron(II) (**6**), dicarbonyl cyclopentadienyl[2,3,4,5,6-penta-*O*-acetyl-D-gluconyl]iron(II) (**7**), dicarbonylcyclopentadienyl[2,3,4,5-tetra-*O*-acetyl-L-arabinonyl]iron(II) (**8**), and dicarbonylcyclopentadienyl-[2,3,4,5-tetra-*O*-acetyl-D-ribonyl]iron(II) (**9**) are accessible in high yields. ^{1}H NMR studies indicate that in solution the *galacto* and *arabino* (**6**, **8**) complexes adopt planar zigzag conformations, whereas the *gluco* and *ribo* (**7**, **9**) analogs prefer non-extended ("sickle") conformations. A similar conformational preference is observed for the solid state as established by X-ray studies on the *galacto* and *gluco* derivatives **6** and **7**, underlining the strong impact of *syn*-1,3-interactions of the protecting groups on the conformation adopted.



Scheme 1. Synthesis of acyl iron complexes.

INTRODUCTION

Transition metals are widely used in stereoselective organic synthesis.[2] However, they have only a minor impact on the modification of carbohydrates so far, and examples of transition metal functionalized sugars are still very limited.[3] Glycosyl complexes of manganese[4] and iron[5] have been prepared and used in the functionalization of carbohydrates. The manganese compounds have been applied to the synthesis of C-glycosides under high pressure conditions. Recently, we reported the synthesis of group VIb and VIIIb metal carbene C-1 functionalized D-*galacto* sugars combining a galactonic acid chloride electrophile and carbonyl metalate nucleophiles.[6] The addition of the powerful nucleophile sodium dicarbonylcyclopentadienylferrate ("NaFp") to aliphatic or aromatic acid chlorides is known to generate acyl iron compounds (Scheme 1) which generally undergo alkylation by hard electrophiles to give cationic alkoxy iron carbenes.[7]

During the synthesis of the sugar acyl iron complexes we became interested whether the incorporation of the bulky organometallic fragment at the C-1 terminus might have an impact on the conformation along the carbohydrate skeleton. Generally, acyclic sugars prefer a planar zigzag conformation P unless severe *syn*-1,3-interactions enforce rotation around one or more C-C bonds to generate bent "sickle" conformations G[8] (for the G, P-terminology, see ref. 9). We now present a comparative conformational study on peracetylated galactose, glucose, arabinose and ribose derived acyl iron complexes **6** - **9** based on ^{1}H NMR studies in solution and X-ray analyses in the solid state.

RESULTS AND DISCUSSION

Synthesis of Acyl Iron Sugars. The synthesis of acyl iron complexes, outlined in Scheme 1, can be extended to peracetylated aldonic acid chlorides. The reaction of 2,3,4,5,6-penta-*O*-acetyl-D-galactonyl chloride (**1**), 2,3,4,5,6-penta-*O*-acetyl-D-gluconyl chloride (**2**), 2,3,4,5-tetra-*O*-acetyl-L-arabinonyl chloride (**3**) and 2,3,4,5-tetra-*O*-acetyl-D-ribonyl chloride (**4**) with sodium dicarbonylcyclopentadienylferrate (**5**) afforded the acyl iron modified sugars **6** - **9** in good to excellent yields (Table 1). Their ^{13}C NMR data (Table 2) reveal a tremendous downfield shift for the C1 carbon atom as a consequence of the coordination to the iron center. This deshielding influence also affects the adjacent carbon atom C-2.

Conformational Studies in Solution. The conformation along the carbohydrate skeleton of sugar acyl iron complexes **6** - **9** has been studied by temperature dependent ^{1}H NMR spectroscopy. We assume that vicinal coupling constants $^3J_{HH}$ of ~3 Hz indicate a gauche (synclinal) orientation whereas *trans*-periplanar hydrogen atoms give rise to coupling constants of ~9 Hz.[10]

For the galactose derivative **6** an alternating small-large-small sequence is observed for the coupling constants $J_{2,3}$, $J_{3,4}$ and $J_{4,5}$ which is in agreement with a *cis-trans-cis* relationship of the hydrogen atoms H-2, H-3, H-4 and H-5 (Table 3). In contrast, the medium-sized vicinal coupling constants $J_{5,6}$ and $J_{5,6'}$ indicate also a population of other rotamers about the C5-C6 bond than illustrated in Figure 1.

The coupling constants do not change significantly if the temperature is lowered from ambient temperature to -50 °C; only a minor decrease of the small coupling constants is accompanied by a slight increase of the large coupling constants, implying conformational homogeneity even at room temperature.

The configuration of the diastereomeric glucose derived complex **7** differs at C-4 from that of the galactose compound **6**. A *cis*-1,3-interaction of the acetoxy groups attached to C-2 and C-4 effective in the zigzag conformation P (Figure 2) can be avoided by rotation either around the C2-C3 (leading to $_2G^+$) or the C3-C4 bond (generating $_3G^+$). The coupling constants, especially $J_{3,4}$ and $J_{4,5}$, observed at room temperature are medium-sized indicating conformational flexibility. They may be interpreted in terms of a major contribution of the rotamers $_3G^+$, $_4G^+$ arising from counter-clockwise rotations around the C3-C4 and C4-C5 bonds, as illustrated in Figure 2. Taking all coupling constants in account, **7** adopts a conformational equilibrum between the P and G forms. Comparable results have been obtained previously for pentaacetylgluconic acid.[8d]

When the temperature is lowered to -60 °C, we notice a significant decrease of $J_{2,3}$ which is accompanied by an exchange in the values of $J_{3,4}$ and $J_{4,5}$. Though $J_{3,4}$ and J_{45} are

Table 1. Characterization of acyl iron sugars **6** - **9**.

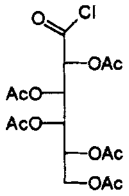
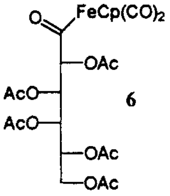
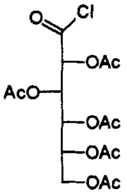
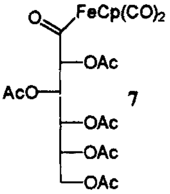
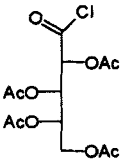
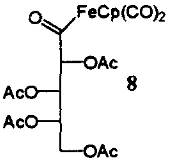
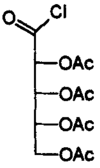
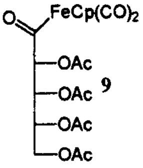
aldonic acid chloride	iron acyl complex	IR ν (cm^{-1}) CH_2Cl_2	isolated yield %
 1	 6	2027, 1967 1751, 1651	90 yellow solid
 2	 7	2027, 1967 1749, 1653	62 yellow solid
 3	 8	2027, 1969 1747, 1651	84 yellow oil
 4	 9	2029, 1971 1746, 1645	60 yellow oil

Table 2. Selected ^{13}C NMR data ($CDCl_3$)

compound	C-1	C-CO	C-Cp	C-2
6	253.8	213.8; 213.6	86.9	85.5
7	253.5	213.8 (2 C)	87.0	86.6
8	254.0	213.9; 213.3	86.9	85.7
9	250.8	213.4; 213.1	88.1	86.9

Table 3. Vicinal coupling constants of **6** - **9** at variable temperature (acetone-D_6).

compound	T [K]	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{4,5'}$	$J_{5,6}$	$J_{5,6'}$
6	298	1.6	9.7	2.1	-	5.2	7.2
	223	1.4	10.1	1.7	-	4.7	7.8
7	298	3.5	5.4	6.0	-	3.2	6.3
	213	1.6	6.5	5.1	-	2.2	7.2
8[a]	298	1.8	8.7	2.6	4.9	-	-
9	298	2.8	7.7	2.6	5.2	-	-
	213	1.7	9.7	2.2	3.5	-	-

a. Complex **8** was measured in $CDCl_3$.

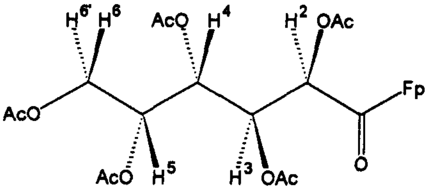


Figure 1. Conformation P of D-*galacto* complex **6** in solution.

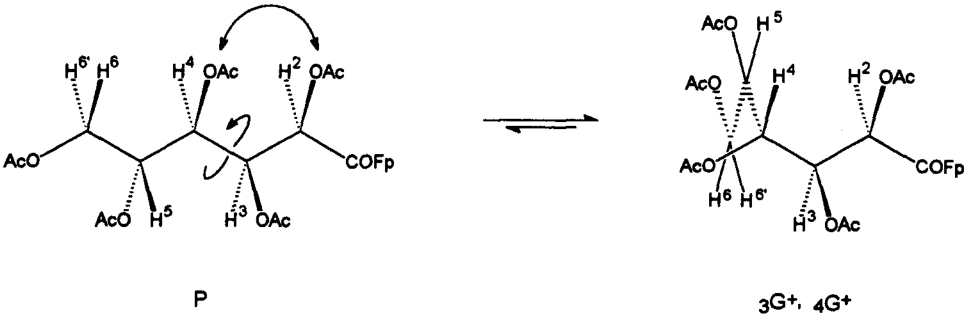


Figure 2. Conformational states of D-*gluco* complex **7**.

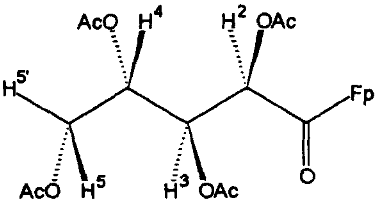


Figure 3. Conformation of L-*arabino* complex **8**.

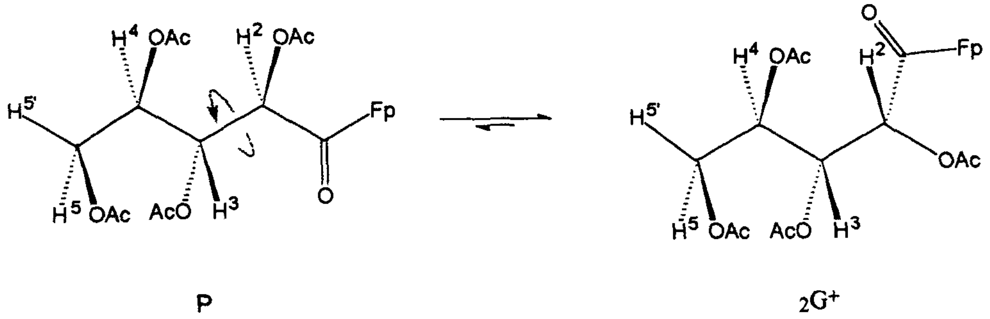
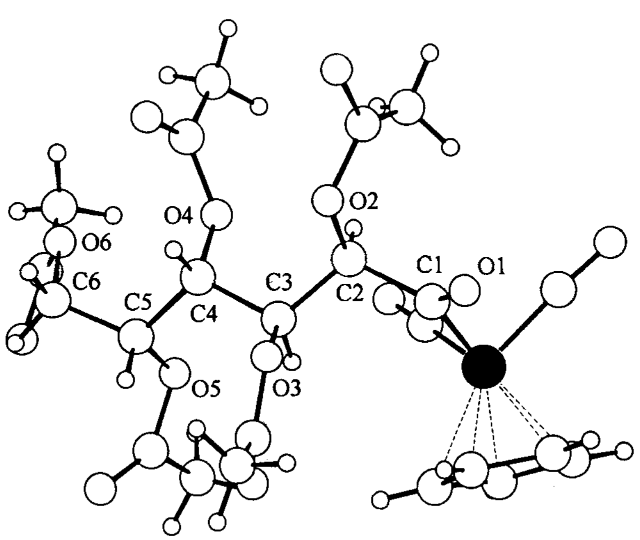


Figure 4. Conformations of D-*ribo* compound **9**.

still of intermediate magnitude, we assume that complex 7 prefers the less strained conformation ${}_3G^+$, ${}_4G^+$ at lower temperatures.

Similar considerations can be applied to the tetraacetylated pentose diastereomers, the L-*arabino* and D-*ribo* complexes **8** and **9**. At ambient temperature the *arabino* derivative **8** exhibits a distinct small-large sequence of coupling constants $J_{2,3}$ and $J_{3,4}$ (Table 3) which is consistent with a gauche and a *trans*-periplanar orientation of H2-H3 and H3-H4 (Figure 3).

A similar alternation of coupling constants - though less pronounced - is also observed for the ribose diastereomer. As discussed above for the glucose complex 7 a planar zigzag conformation of the ribose derivative **9** suffers from an unfavourable 1,3-interaction of the acetoxy groups attached to C2 and C4. It is obvious from the spin coupling constants that strain can be released by a counter-clockwise rotation around the C2-C3 bond generating a ${}_2G^+$ conformation as shown in Figure 4. The $J_{3,4}$ value at room temperature also indicates a minor contribution of a conformer arising from an additional

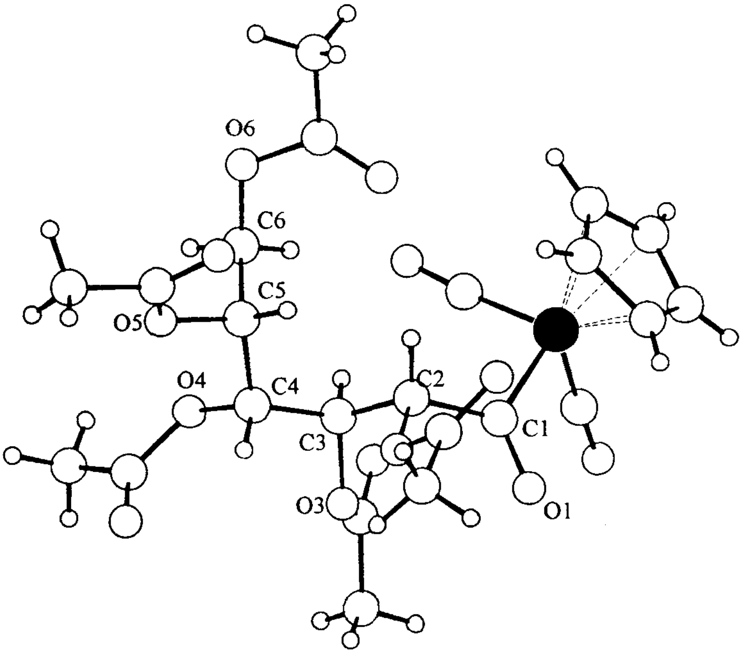


O1-C1-C2-C-3	-112.4 (4)	O1-C1-C2-O2	8.6 (5)
C1-C2-C3-C4	-175.1 (3)	O2-C2-C3-O3	57.2 (4)
C2-C3-C4-C5	159.7 (3)	O3-C3-C4-O4	158.6 (3)
C3-C4-C5-C6	178.7 (4)	O4-C4-C5-O5	60.7 (4)
C4-C5-C6-O6	65.7 (5)	O5-C5-C6-O6	-55.1 (5)

Figure 5. Solid state structure of **6**[12] and selected torsion angles [°].

rotation along the C3-C4 bond. A moderate decrease of the small and increase of the large vicinal coupling constants occur when the temperature is lowered to -60 °C which indicates the conformational flexibility of the sugar skeleton, but also give rise to the assumption that complex **9** exclusively adopts the ${}_2G^+$ sickle conformation at lower temperatures.

Conformational studies in the solid state. To compare the conformations in solution and in the solid state, the molecular structures of the hexose derived complexes **6** and **7** have been established by X-ray analysis. As depicted in Figure 5 the galactose modified complex **6** adopts the planar zigzag conformation also in the solid state. The torsion angles C2-C3-C4-C5 and O3-C3-C4-O4 indicate that the sugar backbone is slightly bent along the C3-C4 axis which might be a consequence of the interaction of the acetoxy group attached to C3 and the bulky Fp-substituent. Another deviation from the



O1-C1-C2-C3	-94.4 (5)	O1-C1-C2-O2	23.7 (5)
C1-C2-C3-C4	174.6 (3)	O2-C2-C3-O3	-67.2 (4)
C2-C3-C4-C5	53.2 (5)	O3-C3-C4-O4	-67.2 (4)
C3-C4-C5-C6	65.9 (5)	O4-C4-C5-O5	67.7 (4)
C4-C5-C6-O6	-171.7 (4)	O5-C5-C6-O6	70.1 (5)

Figure 6. Solid state structure of 7[12] and selected torsion angles [°].

ideal zigzag conformation refers to the C5-C6 axis along which a torsion angle O5-C5-C6-O6 of 55° imposes an unfavourable 1,3-interaction of protecting groups. Similar observations have been published for acetylated alditols.[11]

As deduced from ^{1}H NMR spectra in solution the glucose derived complex 7 prefers a bent sickle conformation also in the solid state (Figure 6). The carbon backbone of the sugar chain occupies two planes which are defined by C1-C4-O4 and C4-C6-O6 and include an angle of 88°. A similar conformation - along with a planar zigzag orientation - has been reported for the unprotected potassium-D-gluconate.[13]

Summary: Studies on the structure of sugar derived acyl iron complexes **6** - **9** - both by temperature-dependent ^{1}H NMR experiments in solution and by X-ray analyses in the solid state - indicate that the bulky organometallic Fp-fragment does not alter significantly the conformation along the carbohydrate skeleton. Thus a planar zigzag conformation is preferred for D-galactose and L-arabinose complexes **6** and **8** whereas *syn*-1,3-interactions between acetyl protecting groups impose major contributions of bent sickle conformations as demonstrated for D-glucose and D-ribose complexes **7** and **9**.

EXPERIMENTAL

General Methods. All organometallic transformations were performed under argon; solvents were dried by standard procedures. The chromatographic separations were carried out at 0 °C on silica gel 60 (0.063-0.200, E. Merck) using dried solvents. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-250, AM-400 or DRX-500 spectrometer. Chemical shifts refer to those of residual solvent signals based on δ_{TMS} = 0.00 ppm. FT IR: Nicolet Magna 505. FABMS: Kratos Concept 1H (matrix: *m*-nitrobenzylalcohol). Elemental analyses: Elementar Analysensysteme GmbH Vario EL. X-ray analyses, see Table 4. Aldonic acid chlorides **1** - **4**[14] and sodium dicarbonylcyclopentadienylferrate **5**[15] were prepared according to literature procedures. **5** was used as a 0.067 M solution in tetrahydrofuran.

General Procedure. 1 mmol of a sugar acid chloride (**1** - **4**) is added to 1.1 mmol of **5** at -78 °C. The reaction mixture is stirred for 1 h at the same temperature, adsorbed on silica gel and concentrated to dryness. The residue is chromatographed on silica gel using dried solvents (0 °C, petroleum ether/diethyl ether/dichloromethane v/v/v 1:1:1) yielding the acyl complexes **6** - **9** as yellow solids or oils.

Dicarbonylcyclopentadienyl[2,3,4,5,6-penta-*O*-acetyl-D-galactonyl]iron (6). 2.48 g (6.0 mmol) **1** yield 3.06 g (5.4 mmol, 90 %) of **6**. Single crystals were obtained by crystallization at -30°C from petroleum ether/dichloromethane (v/v 6:1). R_f (petroleum ether/diethyl ether/dichloromethane v/v/v 1:1:1): 0.37. ^{1}H NMR (500 MHz, acetone-D$_6$, 298 K) δ 5.86 (dd, $J_{3,4}$ = 9.7 Hz, $J_{2,3}$ = 1.6 Hz, 1H, H-3), 5.39 (dd, $J_{3,4}$ = 9.7 Hz, $J_{4,5}$ = 2.1 Hz, 1H, H-4), 5.27 (ddd, $J_{5,6'}$ = 7.2 Hz, $J_{5,6}$ = 5.2 Hz, $J_{4,5}$ = 2.1 Hz, 1H, H-5), 4.97 (d,

Table 4. Crystallographic data and summary of data collection and refinement.

	6	7
crystal data		
formula	$C_{23}H_{26}O_{13}Fe$	$C_{23}H_{26}O_{13}Fe$
M	566.3	566.3
color	yellow	yellow
dimension [mm]	0.20 x 0.25 x 0.50	0.10 x 0.30 x 0.45
crystal system	orthorhombic	triclinic
space group	$P2_12_12_1$ (No. 19)	P1 (No. 1)
a [Å]	10.883(7)	8.072(4)
b [Å]	12.493(8)	9.375(4)
c [Å]	19.937(11)	10.219(5)
α	90	106.54(4)
β	90	95.98(4)
γ	90	113.33(4)
V [$Å^3$]	2711(3)	659.7(5)
Z	4	1
$\rho_{calc.}$ [g cm^{-3}]	1.39	1.43
μ [mm]	0.62	0.64
F (000)	1176	294
structure solution and refinement		
full-matrix least-squares refinement on	F^2	F^2
parameter/restraints	334/0	334/3
measured reflection	6388	4994
unique reflection used in refinement	4785	4704
w R2	0.122	0.111
R_1 [for I>2 σ (I)]	0.047	0.045
Flack's x-parameter largest diff.	-0.01(2)	0.00(2)
peak and hole [e$Å^{-3}$]	0.38/-0.27	0.38/-0.25
data collection parameter		
diffractometer	Nicolet R3m	Nicolet R3m
radiation	MoKα	MoKα
[Å]	0.71073	0.71073
T [K]	293	293
2 $\theta_{max.}$ [°]	50	50
	$-12 \leq h \leq 1$	$-9 \leq h \leq 9$
	$-14 \leq k \leq 1$	$-11 \leq k \leq 11$
	$-23 \leq l \leq 23$	$-12 \leq l \leq 12$

$J_{2,3}$ = 1.6 Hz, 1H, H-2), 5.05 (s, 5H, H-Cp), 4.26 (dd, $J_{6,6'}$ = 11.6 Hz, $J_{5,6}$ = 5.2, 1H, H-6), 3.93 (dd, $J_{6,6'}$= 11.6 Hz, $J_{5,6'}$= 7.2 Hz, 1H, H-6'), 2.13, 2.12, 2.04, 1.98, 1.97 (5 s, 15H). ^{1}H NMR (500 MHz, acetone-D$_6$, 223 K) δ 5.82 (dd, $J_{3,4}$ = 10.1 Hz, $J_{2,3}$ = 1.4 Hz, 1H, H-3), 5.41 (dd, $J_{3,4}$ = 10.1 Hz, $J_{4,5}$ = 1.7 Hz, 1H, H-4), 5.26 (ddd, $J_{5,6'}$ = 7.8 Hz, $J_{5,6}$ = 4.7 Hz, $J_{4,5}$ = 1.7 Hz, 1H, H-5), 5.10 (s, 5 H, H-Cp), 4.88 (d, $J_{2,3}$ = 1.4 Hz, 1H, H-2), 4.24 (dd, $J_{6,6'}$ = 11.6 Hz, $J_{5,6}$ = 4.7, 1H, H-6), 3.88 (dd, $J_{6,6'}$= 11.6 Hz, $J_{5,6'}$= 7.8 Hz, 1H, H-6'), 2.15, 2.14, 2.02, 1.97, 1.94 (5 s, 15H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 253.8 (C-1), 213.8 (CO), 213.6 (CO), 170.5, 170.4, 170.3, 169.6, 169.3 (C-O$\underline{\text{C}}$OCH$_3$), 86.9 (5 C, Cp), 85.5 (C-2), 68.1, 67.5, 65.1 (C-3, C-4, C-5), 62.0 (C-6), 20.7, 20.66, 20.61, 20.56, 20.50 (C-OCO$\underline{\text{C}}$H$_3$). FABMS *m/z* (%) 567 (4) [M$^+$ + H], 539 (0.5) [M$^+$ + H - CO], 507 (1) [M$^+$ + H - C$_2$H$_3$O$_2$], 409 (2) [M$^+$ + H - 2 CO, - Ac$_2$O], 205 (100) [(FeCp(CO)$_3$)$^+$], 177 (19) [(FeCp(CO)$_2$)$^+$]. IR (KBr) 3123 (w), 2963 (w), 2023 (s), 1967 (vs), 1753 (s), 1740 (s), 1655 (s), 1373 (m), 1275 (m), 1238 (s), 1217 (s), 1036 (m), 850 (m), 790 (m).

Anal. Calcd for $C_{23}H_{26}FeO_{13}$ (566.39 g/mol): C, 48.78; H, 4.63. Found: C, 48.76; H 4.65.

Dicarbonylcyclopentadienyl[2,3,4,5,6-penta-*O*-acetyl-D-gluconyl]iron (7). 2.48 g (6.0 mmol) **2** yield 2.10 g (3.7 mmol, 62 %) of 7. Single crystals were obtained by crystallization at -30 °C from petroleum ether/dichloromethane (v/v 8:1). R_f (petroleum ether/diethyl ether/dichloromethane v/v/v 1:1:1): 0.35. ^{1}H NMR (500 MHz, acetone-D$_6$, 298 K) δ 5.84 (dd, $J_{3,4}$ = 5.4 Hz, $J_{2,3}$ = 3.4 Hz, 1H, H-3), 5.44 (dd, $J_{4,5}$ = 6.0 Hz, $J_{3,4}$ = 5.5 Hz, 1H, H-4), 5.14 (d, $J_{2,3}$ = 3.5 Hz, 1H, H-2), 5.09 (s, 5 H, H-Cp), 5.04 (m, 1 H, H-5), 4.40 (dd, $J_{6,6'}$ = 12.3 Hz, $J_{5,6}$ = 3.2, 1H, H-6), 4.17 (dd, $J_{6,6'}$= 12.3 Hz, $J_{5,6'}$= 6.3 Hz, 1H, H-6'), 2.19, 2.09, 2.04, 2.02, 1.99 (5 s, 15H). ^{1}H NMR (500 MHz, acetone-D$_6$, 213 K) δ 6.00 (dd, $J_{3,4}$ = 6.5 Hz, $J_{2,3}$ = 1.8 Hz, 1H, H-3), 5.48 (dd, $J_{3,4}$ = 6.5 Hz, $J_{4,5}$= 5.1 Hz, 1H, H-4), 5.38 (d, $J_{2,3}$ = 1.6 Hz, 1H, H-2), 5.17 (s, 5 H, H-Cp), 4.87 (m, 1 H, H-5), 4.49 (dd, $J_{6,6'}$ = 12.3 Hz, $J_{5,6}$ = 2.2, 1H, H-6), 4.23 (dd, $J_{6,6'}$= 12.3 Hz, $J_{5,6'}$= 7.2 Hz, 1H, H-6'), 2.17, 2.09, 2.07, 1.99, 1.96 (5 s, 15H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 253.5 (C-1), 214.0 (CO), 213.8 (CO), 170.7, 170.1, 170.0, 169.9, 169.7 (C-O$\underline{\text{C}}$OCH$_3$), 87.0 (5 C, Cp), 86.6 (C-2), 70.4, 69.1, 66.4 (C-3, C-4, C-5), 61.7 (C-6), 20.9, 20.8, 20.7, 20.5, (C-OCO$\underline{\text{C}}$H$_3$). FABMS *m/z* (%) 567 (4) [M$^+$ + H], 539 (0.4) [M$^+$ + H - CO], 507 (1) [M$^+$ + H - AcO], 451 (17) [M$^+$ - AcO -2 CO], 409 (4) [M$^+$ + H, -Ac$_2$O - 2 CO], 205 (100) [(FeCp(CO)$_3$)$^+$], 177 (19) [(FeCp(CO)$_2$)$^+$]. IR (KBr) 3126 (w), 3010 (w), 2988 (w), 2023 (vs), 1960 (vs), 1755 (vs), 1740 (vs), 1653 (s), 1429 (m), 1375 (s), 1219 (vs), 1078 (s), 1028 (s), 785 (s).

Anal. Calcd for $C_{23}H_{26}FeO_{13}$ (566.39 g/mol): C, 48.78; H, 4.63. Found: C, 48.55; H 4.64.

Dicarbonylcyclopentadienyl[2,3,4,5-tetra-*O*-acetyl-L-arabinonyl]iron (8). 0.75 g (2.5 mmol) **3** yield 1.04 g (2.1 mmol, 84 %) of **8**. R$_f$ (petroleum ether/diethyl ether/dichlormethane v/v/v 1:1:1): 0.40. ^{1}H NMR (250 MHz, CDCl$_3$) δ 5.87 (dd, $J_{3,4}$ = 8.7 Hz, $J_{2,3}$ = 1.8 Hz, 1H, H-3), 5.15 (ddd, $J_{3,4}$ = 8.7 Hz, $J_{4,5'}$ = 4.9 Hz, $J_{4,5'}$ = 2.6 Hz, 1H, H-4), 5.04 (d, $J_{2,3}$ = 1.8 Hz, 1H, H-2), 4.86 (s, 5H, H-Cp), 4.25 (dd, $J_{5,5'}$ = 12.5 Hz, $J_{4,5}$ = 2.6 Hz, 1H, H-5), 4.09 (dd, $J_{5,5'}$ = 12.5 Hz, $J_{4,5'}$ = 4.9 Hz, 1H, H-5'), 2.14, 2.03 (2 s, 6H), 2.02 (s, 6H). ^{13}C NMR (62.5 MHz, CDCl$_3$) δ 254.0 (C-1), 213.9 (CO), 213.3 (CO), 170.6, 170.1, 169.7, 169.1 (C-O$\underline{C}$OCH$_3$), 86.9 (5 C, Cp), 85.7 (C-2), 68.7, 66.2 (C-3, C-4), 61.7 (C-5), 20.6, 20.5, 20.4, 20.3 (C-OCO$\underline{C}$H$_3$). FABMS *m/z* (%) 495 (6) [M$^+$ + H], 410 (9) [M$^+$ - CO - Cp - H], 379 (88) [M$^+$ - AcO - CO], 337 (3) [M$^+$ + H - Ac$_2$O - 2 CO], 289 (17) [M$^+$ - CO -Fp], 205 (100) [(FeCp(CO)$_3$)$^+$], 177 (21) [(FeCp(CO)$_2$)$^+$]. IR (KBr) 3120 (w), 2970 (w), 2023 (vs), 1965 (vs), 1751 (vs), 1651 (s), 1435 (m), 1373 (s), 1220 (vs), 1040 (s), 850 (m).

Anal. Calcd for $C_{20}H_{22}FeO_{11}$ (494.23 g/mol): C, 48.60; H, 4.49. Found: C, 48.46; H 4.51.

Dicarbonylcyclopentadienyl[2,3,4,5-tetra-*O*-acetyl-D-ribonyl]iron (9). 0.59 g (1.7 mmol) **4** yield 0.49 g (1.0 mmol, 60 %) of **9**. R$_f$ (petroleum ether/diethyl ether/dichlormethane v/v/v 1:1:1): 0.51. ^{1}H NMR (500 MHz, acetone-D$_6$, 298 K) δ 5.93 (dd, $J_{3,4}$ = 7.7 Hz, $J_{2,3}$ = 2.8 Hz, 1H, H-3), 5.30 (ddd, $J_{3,4}$ = 7.7 Hz, $J_{4,5'}$ = 5.2 Hz, $J_{4,5'}$ = 2.6 Hz, 1H, H-4), 5.20 (s, 5H, H-Cp), 5.15 (d, $J_{2,3}$ = 2.8 Hz, 1H, H-2), 4.37 (dd, $J_{5,5'}$ = 12.4 Hz, $J_{4,5}$ = 2.6 Hz, 1H, H-5), 4.17 (dd, $J_{5,5'}$ = 12.4 Hz, $J_{4,5'}$ = 5.2 Hz, 1H, H-5'), 2.12, 2.11, 2.00, 1.97 (4 s, 12H). ^{1}H NMR (500 MHz, acetone-D$_6$, 213 K) δ 6.14 (d, $J_{3,4}$ = 9.7 Hz, 1H, H-3), 5.35 (s, 5H, H-Cp), 5.22 (m, 1H, H-4), 5.11 (d, $J_{2,3}$ = 1.7 Hz, 1H, H-2), 4.33 (dd, $J_{5,5'}$ = 12.5 Hz, $J_{4,5}$ = 1.9 Hz, 1H, H-5), 4.18 (dd, $J_{5,5'}$ = 12.5 Hz, $J_{4,5'}$ = 3.5 Hz, 1H, H-5'), 2.13, 2.05, 1.97, 1.88 (4 s, 12H). ^{13}C NMR (62.5 MHz, CDCl$_3$) δ 250.8 (C-1), 213.4 (CO), 213.1 (CO), 170.2, 169.6, 169.4, 169.1 (C-O$\underline{C}$OCH$_3$), 88.1 (C-2), 86.9 (5 C, Cp), 68.1, 66.7 (C-3, C-4), 61.5 (C-5), 20.5, 20.4, 20.3 (C-OCO$\underline{C}$H$_3$).

FABMS m/z (%) 495 (6) [M^+ + H], 435 (5) [M^+ - AcO], 410 (7) [M^+ - CO - Cp - H], 407 (4) [M^+ - AcO - CO] 379 (21) [M^+ - AcO - 2 CO], 289 (34) [M^+ - Fp - CO], 205 (100) [$(FeCp(CO)_3)^+$], 177 (21) [$(FeCp(CO)_2)^+$]. IR (KBr) 3130 (w), 2980 (w), 2950 (w), 2025 (vs), 1967 (vs), 1750 (vs), 1643 (s), 1435 (m), 1373 (s), 1225 (vs), 1042 (s).

Anal. Calcd for $C_{20}H_{22}FeO_{11}$ (494.23 g/mol): C, 48.60; H, 4.49. Found: C, 48.37; H 4.53.

X-ray crystallographic studies of 6 and 7.[16] The structures were solved by direct methods. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were localized by difference electron density determination and refined using a riding model. The absolute configuration was determined by Flack's x-refinement.[17] Details of data collection and refinement are given in Table 4. Programs used: SHELXTL-Plus[18] and SHELXL-93.[19]

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