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Glucose ferrocenyl-oxazolines: Coordination behavior toward $[Pd(\eta^3\text{-allyl})Cl]_2$ studied by ESI-MS

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Abstract

Several new oxazolin-2-yl-substituted ferrocenes based on 2-amino-2-deoxy-α-D-glucose were synthesized via the corresponding amides followed by closing the oxazoline-ring with $SnCl_4$.

Coordination properties of representatives of the group of mono- and bis-oxazolinyl ferrocenes, 2-ferrocenyl-4,5-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-D-glucopyrano)-[2,1-*d*]-oxazoline and 1,1′-bis{4,5-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-D-glucopyrano)-[2,1-*d*]-oxazolin-2-yl}ferrocene, respectively, toward $[Pd(\eta^3\text{-allyl})Cl]_2$ were investigated by electrospray ionization mass spectrometry in positive ion mode and by MS/MS technique.

With the monooxazoline derivative mainly a 1:1 complex with the Pd-moiety was found in the mass spectrum while the bisoxazoline yields a stoichiometry of 2:1 (oxazoline:Pd). The latter result is attributed to steric hindrance of the coordination of a second Pd-moiety to the bulky bisoxazolinyl-ferrocene.

In the case of 1,1′-bis{4,5-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-D-glucopyrano)-[2,1-*d*]-oxazolin-2-yl}ferrocene **9** overlapping of two signals in the *m*/*z* range from 955–965 was found which can be assigned to the singly charged adduct $[C_{36}H_{40}FeN_2O_{16} + Pd(\eta^3\text{-}C_3H_5)]^+$ and a doubly charged Pd–ligand cluster with the general formula $Pd_2[L(\mathbf{9})]_2$.

In addition, the molecular structure of 1,1′-bis{4,5-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-D-glucopyrano)-[2,1-*d*]-oxazolin-2-yl}ferrocene was determined by X-ray diffraction analysis.

Keywords: Ferrocene; Oxazoline; Pd complex; Glucose; Electrospray ionization mass spectrometry

1. Introduction

Since the 1990s, the numbers of approved drugs shifted clearly into the direction of enantiomerically pure compounds [1–3]. The reason for this development is obvious: frequently only one of the two enantiomers has the desired activity and the other one possesses no activity and/or even shows undesired side effects [4].

The broad applicability of enantioselective catalyses was already proven for many types of reactions and a manifold of catalysts is available [5]. Many types of reactions converting non-chiral compounds into chiral products via catalysis by a transition metal coordinated to a chiral donor group are known, e.g., hydrogenations, hydrometallations, carbometallations, oxidations, carbonylations, carbon-carbon bond-forming reactions [1].

In order to improve the properties of catalysts, new ligands are designed resulting in higher enantiomeric excesses and yields. One class of ligands suitable for the application in many metal-catalyzed asymmetric syntheses are chiral bis(oxazoline)s [6–9]. These 5-membered heterocycles have found their applications in a large

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variety of processes: in natural metal chelators [10–12], in syntheses [6,13,14], in catalytic asymmetric reactions [9,15–22] and possess interesting biological properties [23,24].

Lately, ferrocene derivatives substituted with oxazoline-residues have gained interest for enantioselective catalysis [15,16]. One possibility to introduce a chiral element is to use enantiomerically pure amino alcohols which are easily obtainable by reduction of naturally occurring amino acids. Another natural compound which has the possibility to form an oxazoline group is 2-amino-2-deoxy-α-D-glucose containing the same structural element as the 2-aminoalcohols. Furthermore, it possesses the advantage of many additional functional groups for further derivatization which may influence the activity of a potential catalyst.

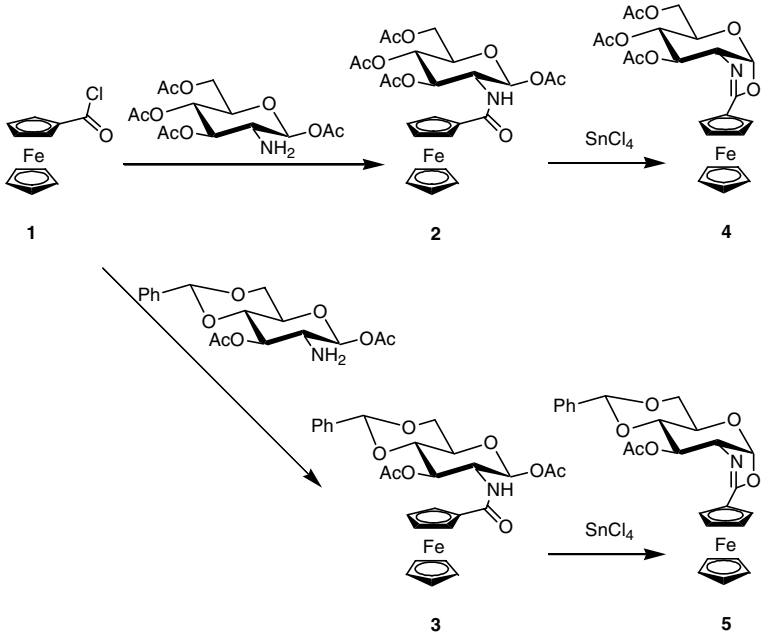
Electrospray ionization mass spectrometry (ESI-MS) is known to be the softest desorption/ionization technique. Originally developed to transfer biomacromolecules into the gaseous phase without degradation, it found its application in many fields of chemistry. Especially for metal coordination compounds the softness of the ionization is highly advantageous over the other common mass spectrometric techniques. Electrospray ionization mass spectrometry represents a versatile tool for the investigation of ligand–metal interactions, e.g., affinity studies [25], and characterization of metal complexes with different metal centers, e.g., Cr [26], Pd(II) [27,28], Pt(II) [29], Ru(II) [30]. ESI-MS delivers fast and reliable information about molecular weight, charge, as well as isotope distribution of molecules.

Recently, we reported the synthesis and electrospray ionization MS studies accompanied by theoretical investigations on alkyl- and aryl-substituted 1,1′-bis(oxazolin-2-yl)ferrocenes. We found that the compounds form monoadducts with $[Pd(\eta^3\text{-allyl})Cl]_2$ which exhibit no catalytic activity in palladium-catalyzed allylic alkylation [27].

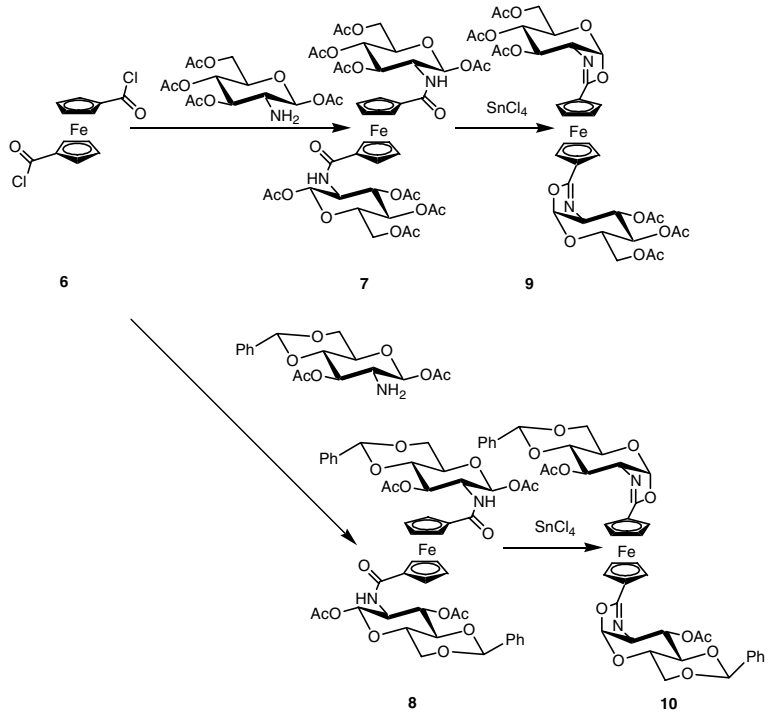
Herein, we describe the synthesis and characterization of several substituted glucose-oxazolines basing on ferrocenecarboxylic acid chloride and 1,1′-ferrocenedicarboxylic acid dichloride. The coordination behavior toward $[Pd(\eta^3\text{-allyl})Cl]_2$ was studied by ESI-MS at different ligand to metal ratios.

2. Results and discussion

The series of new ferrocene glucose-oxazolines was synthesized in two steps: in a first step the mono and bisamides were obtained from reaction between ferrocenecarboxylic acid chloride (see Scheme 1) or ferrocene-1,1′-biscarboxylic acid dichloride (see Scheme 2) and 1,3,4,6-tetra-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside or 1,3-di-*O*-acetyl-2-amino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside. The reactions were carried out in dry dichloromethane and in the presence of triethylamine. The pure amides were isolated after recrystallization from absolute ethanol. In a second step the corresponding mono or bisamides were converted into the oxazolines by a ring closing reaction in the presence of a Lewis acid. In accordance to literature, $SnCl_4$ was found to be the most suitable reagent for the oxaz-



Scheme 1.



Scheme 2.

oline syntheses [31,32]. The reactions were carried out in dry CH_2Cl_2 at room temperature. Amides **3** and **8** (with the benzylidene protecting group) yielded under these conditions only the corresponding oxazolines. If the reaction time for amide **3** and $SnCl_4$ was extended to more than 24 h, on the TLC plate a new spot was observed which was identified as the corresponding oxazoline after cleavage of the benzylidene group (after isolation by column chromatography). No suitable conditions to increase the yield of the unprotected compound were found (extension of the reaction time or using $FeCl_3$ instead of $SnCl_4$ led to decomposition [31–33]).

Also very unusual stability of the benzylidene protecting group was observed in compounds **5** and **10**. All experiments to cleave the benzylidene group in acidic media led to an opened oxazoline ring.

The characterization of the synthesized compounds was done by ^1H and ^{13}C NMR, ESI-MS, and elemental analysis. NMR was found to be a useful tool to follow the oxazoline-ring closing process: in ^1H NMR the disappearance of the protons assigned to the amide functionality and the acetyl group on C1 and in ^{13}C NMR the characteristic high-field shift from about 170 to 166 ppm of the CO-group. Also the disappearance of the signal of the acetyl group and low-field shifts of the C1 from about 93 to 99–102 ppm indicated the complete formation of the oxazoline moiety.

The structure of 1,1′-bis{4,5-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-D-glucopyrano)-[2,1-*d*]-oxazolin-2-yl}ferrocene **9** has been determined by single crystal X-ray diffraction analysis. A suitable crystal for the crystallographic study was obtained by slow evaporation of a solution of **9** in ethyl acetate. Compound **9** crystallized in the monoclinic non-centrosymmetric space group $P2_1$, the result of the X-ray diffraction analysis is summarized in Fig. 1. Selected bond lengths (Å) and angles (°) are quoted in Table 1. The Cp rings are almost parallel to each other, the dihedral angle being at 4.4°. The Cp ··· Fe ··· Cp torsion twist angle $\Theta_{C1\text{-}X1\cdots X2\text{-}C19}$ is at 47.2°, indicating a conformation being closer at

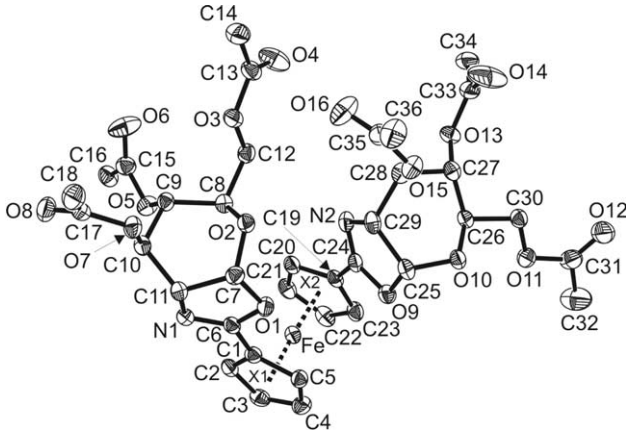


Fig. 1. The molecular structure of 1,1′-bis{4,5-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-D-glucopyrano)-[2,1-*d*]-oxazolin-2-yl}ferrocene **9** drawn at the 50% probability level.

Table 1
Selected bond lengths (Å) and angles (°) in **9**

Atom(1)–atom(2) (Å)		Atom(1)–atom(2)–atom(3) (°)	
N(1)–C(6)	1.271(3)	C(6)–O(1)–C(7)	105.66(16)
N(1)–C(11)	1.478(3)	C(7)–O(2)–C(8)	114.21(17)
O(1)–C(6)	1.372(2)	C(6)–N(1)–C(11)	105.69(18)
O(1)–C(7)	1.454(3)	N(1)–C(6)–O(1)	118.50(19)
O(2)–C(7)	1.393(3)	O(2)–C(7)–O(1)	110.53(18)
O(2)–C(8)	1.437(3)	O(2)–C(7)–C(11)	114.48(18)
C(7)–C(11)	1.537(3)	O(1)–C(7)–C(11)	102.83(17)
C(8)–C(9)	1.537(3)	O(2)–C(8)–C(9)	109.18(18)
C(9)–C(10)	1.530(3)	C(10)–C(9)–C(8)	113.43(19)
C(10)–C(11)	1.516(3)	C(11)–C(10)–C(9)	113.00(18)
N(2)–C(24)	1.277(3)	N(1)–C(11)–C(10)	112.77(19)
N(2)–C(29)	1.478(3)	N(1)–C(11)–C(7)	104.89(18)
O(9)–C(24)	1.371(3)	C(10)–C(11)–C(7)	112.82(18)
O(9)–C(25)	1.454(3)	C(25)–O(10)–C(26)	113.10(17)
O(10)–C(25)	1.406(2)	C(24)–N(2)–C(29)	105.6(2)
O(10)–C(26)	1.429(3)	N(2)–C(24)–O(9)	118.4(2)
C(25)–C(29)	1.534(4)	O(10)–C(25)–O(9)	109.42(17)
C(26)–C(27)	1.516(3)	O(10)–C(25)–C(29)	114.91(19)
C(27)–C(28)	1.530(3)	O(9)–C(25)–C(29)	103.11(18)
C(28)–C(29)	1.530(3)	O(10)–C(26)–C(27)	108.03(18)
		C(26)–C(27)–C(28)	113.23(19)
		C(29)–C(28)–C(27)	114.40(19)
		N(2)–C(29)–C(28)	111.8(2)
		N(2)–C(29)–C(25)	105.42(18)
		C(28)–C(29)–C(25)	114.23(18)
		C(24)–O(9)–C(25)	106.00(18)

synclinal staggered (ideal twist angle of 36°) than at synclinal eclipsed (ideal twist angle of 72°). The orientation of the oxazoline ring with respect to the Cp ring can be characterized by torsion angles $\Theta_{C2\text{-}C1\text{-}C6\text{-}O1}$ at −166.4 and $\Theta_{C23\text{-}C19\text{-}C24\text{-}O9}$ at −24.2°. The D-glucopyranoside rings adopt a half-twist conformation. The C10, C11, C7, O2 atoms in the first ring and C28, C29, C25, O10 atoms in the second ring are coplanar within ±0.07 and ±0.06 Å, correspondingly. The atoms C8, C9 and C26, C27 come out of the mean planes by 1.12, 0.76 and 1.06, 0.57 Å, respectively.

3. Coordination behavior studies by electrospray ionization mass spectrometry

Recently we reported about the application of ESI-MS for studying the binding behavior of alkyl- and aryl-substituted oxazolin-2-ylferrocences toward $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ [27]. In order to compare the glucoseamine-based ferrocenyl-mono- and bis(oxazoline)s with the previously studied organometallic species, compounds **4** and **9** were chosen for MS studies.

4 (with only one oxazoline in the molecule) was incubated with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ at stoichiometries of oxazoline moiety:Pd(II) of 1:4, 1:2, and 1:1 and in the case of the bisoxazoline **9** of 1:1 and 2:1. This mixture was analyzed by electrospray ionization mass spectrometry in the positive ion mode (for calculated *m/z* ratios of the parent compounds and the expected adducts see Table 2). The incubation solution of the Pd-complex and the oxazoline-ligand was directly injected into the mass spectrometer and the MS measurement parameters were kept constant (with exception of one measurement in the mass range 50–3000 *m/z*) in order to maximize signals corresponding to the mass-to-charge ratio of the ligands.

When incubating compound **4** with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ at a stoichiometry of 1:4 the most intense peak (100%) was found at *m/z* 646 assignable to $[C_{23}H_{25}FeNO_8 + Pd(\eta^3\text{-}C_3H_5)]^+$ accompanied by the occurrence of relatively less abundant signals of the ligand at *m/z* 500 ($[M + H]^+$, 63%), of an adduct with two Pd-ions at *m/z* 824 ($[C_{23}H_{25}FeNO_8 + Pd_2(\eta^3\text{-}C_3H_5)Cl_2]^+$, 10%), and other unidentified palladium-allyl-chloride clusters with characteristic isotope pattern.

When reducing the amount of added $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (oxazoline:Pd = 1:2), much less peaks were found which were identified again as the $[C_{23}H_{25}FeNO_8 + Pd(\eta^3\text{-}C_3H_5)]^+$ ion (*m/z* 646, 100%), the protonated ligand at *m/z* 500 (16%), **4** bearing two Pd-centers (*m/z* 830, $[C_{23}H_{25}FeNO_8 + Pd_2(\eta^3\text{-}C_3H_5)_2Cl]^+$, 14%), and two peaks with rich isotope pattern at *m/z* 1329 and 1012 assignable to $[2C_{23}H_{25}FeNO_8 + Pd_2(\eta^3\text{-}C_3H_5)_2Cl]^+$ (2%) and $[C_{23}H_{25}FeNO_8 + Pd_3(\eta^3\text{-}C_3H_5)_3Cl_2]^+$ (2%), respectively. Additionally, a minor intense peak for a 1:2 adduct $[PdL^1_2]$ (L^1 = **4**) was found at *m/z* 1145 (1%).

A further decrease of the Pd-content (1:1) led to a mass spectrum with only four assignable peaks at *m/z* 147, 646, 830, and 1145 which were attributed to $[Pd(\eta^3\text{-}C_3H_5)]^+$ (4%), $[C_{23}H_{25}FeNO_8 + Pd(\eta^3\text{-}C_3H_5)]^+$

Table 2
List of the calculated *m/z* ratios for the ligands and for the formed complexes with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (measured in positive ion mode)

Compound	Formula	*m/z*
$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	$[Pd(\eta^3\text{-}C_3H_5)]^+$	147
4	$[C_{23}H_{25}FeNO_8 + H]^+$	500
4 + $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	$[C_{23}H_{25}FeNO_8 + Pd(\eta^3\text{-}C_3H_5)]^+$	646
	$[C_{23}H_{25}FeNO_8 + PdCl]^+$	642
	$[C_{23}H_{25}FeNO_8 + Pd_2(\eta^3\text{-}C_3H_5)_2Cl]^+$	830
	$[C_{23}H_{25}FeNO_8 + Pd_2(\eta^3\text{-}C_3H_5)Cl_2]^+$	824
	$[C_{23}H_{25}FeNO_8 + Pd_2(\eta^3\text{-}C_3H_5)Cl_2]^+$	1012
	$[2\ C_{23}H_{25}FeNO_8 + Pd(\eta^3\text{-}C_3H_5)]^+$	1145
	$[C_{23}H_{25}FeNO_8 + Pd_3(\eta^3\text{-}C_3H_5)_3Cl_2]^+$	1329
9	$[C_{36}H_{40}FeN_2O_{16} + H]^+$	813
9 + $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	$[C_{36}H_{40}FeN_2O_{16} + PdCl]^+$	953
	$[C_{36}H_{40}FeN_2O_{16} + Pd(\eta^3\text{-}C_3H_5)]^+$	959
	$[2\ C_{36}H_{40}FeN_2O_{16} + Pd_2(\eta^3\text{-}C_3H_5)_2]^+$	961
	$[C_{36}H_{40}FeN_2O_{16} + Pd_2(\eta^3\text{-}C_3H_5)_2\text{-}H]^+$	1107
	$[C_{36}H_{40}FeN_2O_{16} + Pd_2Cl_3]^+$	1131
	$[C_{36}H_{40}FeN_2O_{16} + Pd_2(\eta^3\text{-}C_3H_5)Cl_2]^+$	1137
	$[C_{36}H_{40}FeN_2O_{16} + Pd_2(\eta^3\text{-}C_3H_5)_2Cl]^+$	1143
	$[C_{36}H_{40}FeN_2O_{16} + Pd_3(\eta^3\text{-}C_3H_5)_2Cl_3]^+$	1321
	$[C_{36}H_{40}FeN_2O_{16} + Pd_3(\eta^3\text{-}C_3H_5)_3Cl_2]^+$	1325

(100%), $[C_{23}H_{25}FeNO_8 + Pd_2(\eta^3\text{-}C_3H_5)_2Cl]^+$ (16%), and $[2C_{23}H_{25}FeNO_8 + Pd(\eta^3\text{-}C_3H_5)]^+$ (3%), respectively.

In general, isolation and fragmentation (MS/MS) of the signal at *m*/*z* 830, which was found at stoichiometries of oxazoline-moiety:Pd = 1:1 and 1:2, yielded again a peak with *m*/*z* 646 (100%) indicating the coordination of the $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ dimer to **4** via release of a chloro ligand. The $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ dimer fragmented in the MS/MS experiment gives again the oxazoline:Pd adduct possessing a stoichiometry of 1:1.

The bisoxazoline 1,1′-bis{4,5-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-D-glucopyrano)-[2,1-*d*]-oxazolin-2-yl}ferrocene **9** was incubated with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ at two stoichiometries: 1:2 and 1:1. In the case of 1:2, a main peak with *m*/*z* 959 ($[C_{36}H_{40}FeN_2O_{16} + Pd(\eta^3\text{-}C_3H_5)]^+$) was found accompanied by a less abundant one at *m*/*z* 1137 assignable to $[C_{36}H_{40}FeN_2O_{16} + Pd_2(\eta^3\text{-}C_3H_5)Cl_2]^+$. When changing the measurement parameters and the scan range to 50–3000 *m*/*z* beside the peak at *m*/*z* 959 (14%) a peak at *m*/*z* 1325 (100%), which can be attributed to $[C_{36}H_{40}FeN_2O_{16} + Pd_3(\eta^3\text{-}C_3H_5)_3Cl_2]^+$, arises. At lower abundance, peaks assignable to $[C_{36}H_{40}FeN_2O_{16} + Pd_2(\eta^3\text{-}C_3H_5)_2 - H]^+$ (*m*/*z* 1107, 18%), $[C_{36}H_{40}FeN_2O_{16} + Pd_3(\eta^3\text{-}C_3H_5)_2Cl_3]^+$ (*m*/*z* 1321, 34%), and $[C_{36}H_{40}FeN_2O_{16} + Pd_3(\eta^3\text{-}C_3H_5)_2Cl_3]^+$ (*m*/*z* 1143, 30%) can be identified.

Changing to the stoichiometric ratio of 1:1, beside the main peak at *m*/*z* 959 (100%) and the less abundant one at 1131 (5%, $[C_{36}H_{40}FeN_2O_{16} + Pd_2Cl_3]^+$), no higher ligand–Pd clusters were detected. Having a closer look on the peak at about *m*/*z* 959 allowed the identification of a doubly charged species overlapping with the signal for the monoadduct. The doubly charged species with calculated *m*/*z* 961 can be attributed to a Pd–ligand cluster with the general formula $Pd_2[L(\mathbf{9})]_2$. Unfortunately efforts to isolate the defined $[Pd_2L_2^2]$-complex were not successful.

Comparing the results of the electrospray ionization mass spectrometric study for the bisoxazoline **9** with those obtained for the reactions of the bis(alkyl-oxazoline)s with $[Pd(\eta^3\text{-allyl})Cl]_2$ [27], similar coordination behavior can reported. In contrast to the bisoxazoline **9**, the monooxazoline **4** forms beside complexes of the stoichiometry oxazoline:Pd = 1:1 also complexes of the type $Pd[L(\mathbf{4})]_2$.

4. Conclusions

Bis(oxazoline)s are widely known to be excellent ligands for a manifold of metal centers. Herein, the synthesis and characterization of new glucoseamine-based mono- and bis(oxazolin-2-yl)ferrocenes are presented. The crystal structure of 1,1′-bis{4,5-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-D-glucopyrano)-[2,1-*d*]-oxazolin-2-yl}ferrocene was determined showing that the sugar moiety has half-twist conformation and the two oxazoline groups are arranged nearly synclinal staggered.

The coordination behavior of 2-ferrocenyl-4,5-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-D-glucopyrano)-[2,1-*d*]-oxazoline **4** and 1,1′-bis{4,5-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-D-glucopyrano)-[2,1-*d*]-oxazolin-2-yl}ferrocene **9** toward $[Pd(\eta^3\text{-allyl})Cl]_2$ was studied by electrospray ionization mass spectrometry in the positive ion mode. These experiments revealed that **4** forms at an incubation ratio of 1:1 mainly a monoadduct while when increasing the Pd-content (2:1) also a peak assignable to a bisadduct $Pd[L(\mathbf{4})]_2$ was found. Compound **9** was proven to form 1:1 adducts with Pd(II) indicating that steric hindrance of the bulky sugar-rest limits the binding of a second Pd-center. When incubating the ligand with the Pd-complex at a ratio of 2:1 also a doubly charged peak was detected what is attributed to the formation of a Pd–ligand cluster with the general formula $Pd_2[L(\mathbf{9})]_2$.

The newly developed ligands with their oxazoline-residues might be of interest for a variety of enantioselective reactions being catalyzed by palladium or other transition metal ions. Also the opportunity of functionalization of the hydroxy groups of the carbohydrate with other donor atoms, e.g., phosphorus, can improve or widely extend the catalytic potential of this ligand type.

5. Experimental

All reactions were carried out in dry solvents and under argon atmosphere. The chemicals obtained from commercial suppliers were used as received and were of analytical grade. Ferrocenecarboxylic acid chloride [34], 1,1′-ferrocenedicarboxylic acid dichloride [35], 1,3,4,6-tetra-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside [36], and 1,3-di-*O*-acetyl-2-amino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside [37] were prepared according to literature procedures. The NMR-spectra were recorded on a Bruker Avance DPX 400 instrument (Ultrashield™ Magnet) at 400.13 MHz (^{1}H) and 100.63 MHz (^{13}C) at 25 °C in d_6-DMSO or $CDCl_3$. Melting points were determined with a Büchi B-540 apparatus and are uncorrected. Electrospray ionization mass spectra were recorded on a Bruker esquire$_{3000}$. The elemental analyses were done by the Laboratory for Elemental Analysis of the Institute of Physical Chemistry, University of Vienna, with a Perkin–Elmer 2400 CHN Elemental Analyzer. Silica gel was used for column chromatography (Fluka-60 70–230 mesh) and for thin layer chromatography (Polygram® SIL G/UV$_{254}$). X-ray diffraction measurements were performed on a Nonius Kappa CCD diffractometer at 120 K. The single crystal of **9** was positioned at 35 mm from the detector and 490 frames were measured, each for 75 s over a

2° scan width. The data were processed using Denzo-SMN software. Crystal data, data collection parameters, and structure refinement details are given in Table 3. The structures were solved by direct methods and refined by full-matrix least-squares techniques. Non-hydrogen atoms were refined with anisotropic displacement parameters. H-atoms were placed in calculated positions and allowed to ride. Computer programs: structure solution, SHELXS-97 [38]; refinement, SHELXL-97 [39]; molecular diagrams, ORTEP [40]; scattering factors, [41].

5.1. 1,3,4,6-Tetra-O-acetyl-2-deoxy-2-[(ferrocenecarbonyl)amino]-β-D-glucopyranose (2)

A solution of ferrocenecarboxylic acid chloride (1.34 g, 5.4 mmol) in 20 mL of dichloromethane was added dropwise within 20 min to a solution of 1,3,4,6-tetra-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside (2.28 g, 6.5 mmol) and Et_3N (1.10 g, 11.0 mmol) in dichloromethane (75 mL) at 0 °C. The reaction mixture was stirred for 3 h at room temperature, washed with brine (2 × 25 mL) and water (2 × 25 mL), dried over Na_2SO_4 and the solvent was evaporated in vacuum. The product was recrystallized from ethanol. Yield: 1.72 g (57%), M.p. = 163–165 °C, ^{1}H NMR (400.13 MHz, $CDCl_3$, 25 °C): δ_{ppm} 2.08 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 3.90 (m, 1H, H_5), 4.11 (s, 5H, Cp), 4.18 (dd, 1H, ^3J = 2.0 Hz; $2J$ = 12.0 Hz, $H_{6'}$), 4.32 (dd, 1H, ^3J = 4.5 Hz; ^2J = 12.0 Hz, H_6), 4.35 (m, 2H, Cp), 4.52 (m, 1H, H_2), 4.63 (m, 1H, Cp), 4.67 (m, 1H, Cp), 5.21 (t, 1H, ^3J = 10.0 Hz, H_4), 5.32 (t, 1H, ^3J = 9.5 Hz, H_3), 5.80 (d, 1H, ^3J = 9.5 Hz, H_1), 6.01 (d, 1H, ^3J = 9.5 Hz, NH). ^{13}C NMR (100.63 MHz, $CDCl_3$, 25 °C): δ_{ppm} 21.00 (CH_3), 21.16 (CH_3), 21.25 (CH_3), 21.43 (CH_3), 53.05 (C_2), 62.18 (C_6), 68.36 (C_4), 68.63 (Cp), 68.69 (Cp), 70.18 (Cp), 71.24 (Cp), 71.28 (Cp), 73.20 (C_3), 73.36 (C_5), 75.31 (Cp), 93.27 (C_1), 169.70 (C(O)–N), 170.03 (C(O)), 170.71 (C(O)), 171.11 (C(O)), 171.93 (C(O)). $C_{25}H_{29}FeNO_{10}$: Calc. C, 53.68; H, 5.22; N, 2.50. Found: C, 53.45; H, 5.20; N, 2.50%.

Table 3
Crystallographic data for **9**

Chemical formula	$C_{36}H_{40}FeN_2O_{16}$
Formula weight	812.55
Color	Orange
Crystal size (mm^3)	0.14 × 0.11 × 0.09
T (K)	120
λ (Å)	0.71073
Space group	$P2_1$
a (Å)	15.032(5)
b (Å)	8.314(5)
c (Å)	15.491(5)
β (°)	111.633(5)
V (Å^3)	1799.6(14)
Z	2
μ_{calc} (cm^{-1})	4.99
Flack parameter	−0.003(11)
R_1[a]	0.0395
wR_2[b]	0.0803

[a] $R_1 = \sum|F_o| - |F_c|/\sum|F_o|$.
[b] $wR_2 = [\sum w|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$.

5.2. 1,3-Di-O-acetyl-4,6-O-benzylidene-2-deoxy-2-[(ferrocenecarbonyl)amino]-β-D-glucopyranose (3)

Compound **3** was obtained by following the same procedure as described for **2** starting from ferrocenecarboxylic acid chloride (2.23 g, 9.0 mmol), 1,3-di-*O*-acetyl-2-amino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (3.51 g, 10.0 mmol) and triethylamine (1.00 g, 10.0 mmol). Yield: 2.68 g (53%), M.p. = 221–223 °C, ^{1}H NMR (400.13 MHz, d_6-DMSO, 25 °C): δ_{ppm} 1.97 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 3.62 (m, 1H, H_5), 3.81 (t, 1H, $^{2,3}J$ = 10.0 Hz, $H_{6'}$), 3.89 (t, 1H, ^3J = 9.5 Hz, H_4), 4.13 (s, 5H, Cp), 4.18 (m, 1H, H_2), 4.30 (dd, 1H, ^3J = 5.0 Hz; ^2J = 10.0 Hz, H_6), 4.37 (brs, 2H, Cp), 4.71 (brs, 2H, Cp), 5.44 (t, 1H, ^3J = 10.0 Hz, H_3), 5.69 (s, 1H, PhCH), 5.96 (d, 1H, ^3J = 9.0 Hz, H_1), 7.39 (brs, 5H, Ph), 7.89 (d, 1H, ^3J = 9.0 Hz, NH). ^{13}C NMR (100.63 MHz, d_6-DMSO, 25 °C): δ_{ppm} 21.48 (CH_3), 21.53 (CH_3), 53.29 (C_2), 67.36 (C_5), 68.21 (C_6), 69.09 (Cp), 70.29 (Cp), 71.12 (Cp), 72.36 (C_3), 76.61 (Cp), 78.70 (C_4), 93.42 (C_1), 101.11 (PhCH), 126.93 (Ph), 129.03 (Ph), 129.81 (Ph), 138.12 (Ph), 169.84 (C(O)–N), 169.95 (C(O)), 170.54 (C(O)). $C_{28}H_{29}FeNO_8$: Calc. C, 59.69; H, 5.19; N, 2.49. Found: C, 59.42; H, 4.95; N, 2.56%.

5.3. 2-Ferrocenyl-4,5-(3,4,6-tri-O-acetyl-1,2-dideoxy-D-glucopyrano)-[2,1-d]-oxazoline (4)

$SnCl_4$ (50 mg, 0.2 mmol) was added to a solution of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-[(ferrocenecarbonyl)-amino]-β-D-glucopyranose **2** (1.50 g, 2.6 mmol) in dichloromethane (50 mL). The mixture was stirred for 4 h, neutralized with saturated $NaHCO_3$ solution at 0 °C and filtrated through Celite. The solution was washed with water (2 × 20 mL) and dried over Na_2SO_4. The solvent was removed in vacuum. The product was purified by column chromatography on silica gel with hexane:ethyl acetate = 1:1 as eluent. Yield: 0.79 g (60%), M.p. 49–50 °C, ^{1}H NMR (400.13 MHz, $CDCl_3$, 25 °C): δ_{ppm} 2.10 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 3.79 (m, 1H, H_5), 4.21–4.24 (m, 3H, $H_{6'}$, H_6, H_2), 4.26 (s, 5H, Cp), 4.45 (m, 2H, Cp), 4.84 (m, 1H, Cp), 4.86 (m, 1H, Cp), 4.98 (dd, 1H, ^3J = 2.5 Hz; 9.0 Hz, H_4), 5.42 (t, 1H, ^3J = 2.5 Hz, H_3), 6.01 (d, 1H, ^3J = 7.5 Hz, H_1). ^{13}C NMR (100.63 MHz, $CDCl_3$, 25 °C): δ_{ppm} 21.19 (CH_3), 21.30 (CH_3), 21.37 (CH_3), 63.91 (C_6), 65.67 (C_2), 67.78 (C_5), 69.14 (C_4), 69.08

(Cp), 69.66 (Cp), 69.74 (Cp), 70.11 (Cp), 70.73 (C_3), 71.34 (Cp), 71.38 (Cp), 99.22 (C_1), 169.01 (C=N), 169.61 (C(O)), 169.90 (C(O)), 170.97 (C(O)). $C_{23}H_{25}FeNO_8$: Calc. C, 55.32; H, 5.05; N, 2.81. Found: C, 55.47; H, 4.98; N, 2.70%.

5.4. 2-Ferrocenyl-4,5-(3-O-acetyl-4,6-O-benzylidene-1,2-dideoxy-2-ferrocenyl-D-glucopyrano)-[2,1-d]-oxazoline (5)

Compound **5** was obtained by following the same procedure as described for **4** starting from $SnCl_4$ (100 mg, 0.4 mmol) and 1,3-di-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-[(ferrocenecarbonyl)amino]-β-D-glucopyranose **3** (2.0 g, 3.50 mmol). Yield: 1.16 g (66%), M.p. 160–161 °C, ^{1}H NMR (400.13 MHz, $CDCl_3$, 25 °C): δ_{ppm} 2.17 (s, 3H, CH_3), 3.73–3.88 (m, 3H, $H_{6'}$, H_5, H_4), 4.15 (dd, 1H, ^3J = 4.5 Hz; 7.5 Hz, H_2), 4.26 (s, 5H, Cp), 4.42 (m, 2H, Cp), 4.45 (dd, 1H, ^3J = 4.5 Hz; ^2J = 9.5 Hz, H_6), 4.82 (m, 1H, Cp), 4.85 (m, 1H, Cp), 5.28 (dd, 1H, ^3J = 4.5 Hz; 7.5 Hz, H_3), 5.57 (s, 1H, PhH), 6.07 (d, 1H, ^3J = 7.5 Hz, H_1), 7.37 (m, 3H, Ph), 7.47 (m, 2H, Ph). ^{13}C NMR (100.63 MHz, $CDCl_3$, 25 °C): δ_{ppm} 21.62 (CH_3), 63.85 (C_5), 67.98 (C_2), 69.17 (C_6), 69.45 (Cp), 69.58 (Cp), 70.11 (Cp), 71.28 (C_p), 74.48 (C_3), 78.50 (C_4), 101.98 (C_1), 102.09 (PhCH), 126.58 (Ph), 126.68 (Ph), 129.57 (Ph), 137.25 (Ph), 168.02 (C=N), 170.26 (C(O)). $C_{26}H_{25}FeNO_6$: Calc. C, 62.04; H, 5.01; N, 2.78. Found: C, 62.23; H, 4.93; N, 2.61%.

5.5. 1,1′-Bis[(carbonylamino)-N,N′-(1,3,4,6-tetra-O-acetyl-2-deoxy-β-D-glucopyranose)]ferrocene (7)

Compound **7** was obtained by following the same procedure as described for **2** starting from 1,1′-ferrocenedicarboxylic acid dichloride (270 mg, 0.9 mmol), 1,3,4,6-tetra-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside (700 mg, 2.0 mmol) and triethylamine (200 mg, 2.0 mmol). Yield: 440 mg, (52%), M.p. = 197–199 °C, ^{1}H NMR (400.13 MHz, $CDCl_3$, 25 °C): δ_{ppm} 2.08 (s, 6H, CH_3), 2.09 (s, 6H, CH_3), 2.13 (s, 6H, CH_3), 2.15 (s, 6H, CH_3), 3.95 (m, 2H, H_5), 4.17 (dd, 2H, ^3J = 2.5 Hz; ^2J = 12.5 Hz, $H_{6'}$), 4.35 (dd, 2H, ^3J = 4.5 Hz; ^2J = 12.5 Hz, H_6), 4.38 (m, 4H, Cp), 4.41 (m, 4H, Cp), 4.77 (m, 2H, H_2), 5.23 (t, 2H, ^3J = 9.5 Hz, H_4,), 5.44 (d, 2H, ^3J = 9.5 Hz, H_3), 6.00 (d, 2H, ^3J = 9.0 Hz, H_1,), 6.99 (d, 2H, ^3J = 9.5 Hz, NH). ^{13}C NMR (100.63 MHz, $CDCl_3$, 25 °C): δ_{ppm} 21.08 (CH_3), 21.19 (CH_3), 21.32 (CH_3), 21.41 (CH_3), 53.70 (C_2), 62.18 (C_6), 68.49 (C_4), 70.00 (Cp), 71.40 (Cp), 71.56 (Cp), 71.74 (Cp), 73.11 (C_3), 73.61 (C_5), 78.00 (C_p), 93.02 (C_1), 169.79 (C(O)–N), 170.19 (C(O)), 170.56 (C(O)), 171.14 (C(O)), 171.90 (C(O)). $C_{40}H_{48}FeN_2O_{20}$: Calc. C, 51.51; H, 5.18; N, 3.00. Found: C, 51.29; H, 5.06; N, 2.87%.

5.6. 1,1′-Bis[(carbonylamino)-N,N′-(1,3-di-O-acetyl-4,6-O-benzylidene-2-deoxy-β-D-glucopyranose)] ferrocene (8)

Following the same procedure as described for **2** starting from 1,1′-ferrocenedicarboxylic acid dichloride (1.55 g, 5.0 mmol), 1,3-di-*O*-acetyl-2-amino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (4.21 g, 12.0 mmol) and triethylamine (1.21 g, 12.0 mmol) yielded compound **8** (2.20 g, 47%). M.p. = 295–296 °C, ^{1}H NMR (400.13 MHz, d_6-DMSO, 25 °C): δ_{ppm} 1.99 (s, 6H, CH_3), 2.06 (s, 6H, CH_3), 3.62 (m, 2H, H_5), 3.81 (t, 2H, $^{2,3}J$ = 10.0 Hz, $H_{6'}$), 3.90 (t, 2H, ^3J = 9.5 Hz, H_4), 4.14 (m, 2H, H_2), 4.23 (brs, 4H, Cp), 4.30 (m, 2H, H_6), 4.68 (brs, 4H, Cp), 5.42 (t, 2H, ^3J = 9.5 Hz, H_3), 5.69 (s, 2H, PhCH), 5.96 (d, 2H, ^3J = 8.0 Hz, H_1), 7.39 (brs, 10H, Ph), 8.02 (d, 2H, ^3J = 9.0 Hz, NH). ^{13}C NMR (100.63 MHz, d_6-DMSO, 25 °C): δ_{ppm} 21.44 (CH_3), 21.50 (CH_3), 53.48 (C_2), 67.38 (C_5), 68.21 (C_6), 70.27 (Cp), 70.35 (Cp), 72.30 (C_3), 73.01 (Cp),73.06 (Cp), 77.89 (Cp), 78.62 (C_4), 93.32 (C_1), 101.14 (PhCH), 126.94 (Ph), 129.03 (Ph), 129.82 (Ph), 138.11 (Ph), 169.30 (C(O)-N), 169.83 (C(O)), 170.57 (C(O)). $C_{46}H_{48}FeN_2O_{16}$: Calc. C, 58.73; H, 5.14; N, 2.98. Found: C, 58.45; H, 5.02; N, 2.90%.

5.7. 1,1′-Bis{4,5-(3,4,6-tri-O-acetyl-1,2-dideoxy-D-glucopyrano)-[2,1-d]-oxazolin-2-yl}ferrocene (9)

Following the same procedure as described for **4** starting from $SnCl_4$ (10 mg, 0.05 mmol) and 1,1′-bis[(carbonylamino)-*N*,*N*′-(1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-glucopyranose)]ferrocene **7** (0.4 g, 0.47 mmol) yielded compound **9** (0.19 g, 49%). M.p. 110–112 °C, ^{1}H NMR (400.13 MHz, $CDCl_3$, 25 °C): δ_{ppm} 2.09 (s, 6H, CH_3), 2.13 (s, 6H, CH_3), 2.16 (s, 6H, CH_3), 3.78 (m, 2H, H_5), 4.23–4.25 (m, 6H, $H_{6'}$, H_6, H_2), 4.52 (m, 2H, Cp), 4.56 (m, 2H, Cp), 4.87 (m, 4H, Cp), 5.00 (d, 2H, ^3J = 9.0 Hz, H_4), 5.38 (t, 2H, ^3J = 2.0 Hz, H_3), 6.12 (d, 2H, ^3J = 7.0 Hz, H_1).^{13}C NMR (100.63 MHz, $CDCl_3$, 25 °C): δ_{ppm} 21.18 (CH_3), 21.28 (CH_3), 21.34 (CH_3), 63.74 (C_6), 65.68 (C_2), 67.81 (C_5), 69.09 (C_4), 70.68 (C_3), 70.88 (Cp), 71.26 (Cp), 72.75 (Cp), 73.09 (Cp), 99.53 (C_1), 167.49 (C=N), 169.71 (C(O)), 169.89 (C(O)), 171.00 (C(O)). $C_{36}H_{40}FeN_2O_{16}$: Calc. C, 53.21; H, 4.96; N, 3.44. Found: C, 53.49; H, 5.03: N, 3.36%.

5.8. 1,1′-Bis{4,5-(3-O-acetyl-4,6-O-benzylidene-α-D-glucopyrano)-[2,1-d]-oxazolin-2-yl}ferrocene (10)

Following the same procedure as described for **4** starting from $SnCl_4$ (30 mg, 0.12 mmol) and 1,1′-bis[(carbonylamino)-*N*,*N*′-(1,3-di-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranose)]ferrocene **8** (1.12 g, 1.2 mmol) yielded compound **10** (0.61 g, 62%). M.p. 196–197 °C, ^{1}H NMR (400.13 MHz, $CDCl_3$, 25 °C): δ_{ppm} 2.17 (s,

6H, CH_3), 3.71–3.90 (m, 6H, $H_{6'}$, H_5, H_4), 4.15 (dd, 2H, ^3J = 4.0 Hz; 7.0 Hz, H_2), 4.45–4.52 (m, 6H, Cp, H_6), 4.80 (m, 4H, Cp), 5.28 (dd, 2H, ^3J = 4.5 Hz; 7.5 Hz, H_3), 5.57 (s, 2H, PhH), 6.14 (d, 2H, ^3J = 7.5 Hz, H_1), 7.36 (m, 6H, Ph), 7.47 (m, 4H, Ph). ^{13}C NMR (100.63 MHz, $CDCl_3$, 25 °C): δ_{ppm} 21.62 (CH_3), 63.78 (C_5), 67.93 (C_2), 69.14 (C_6), 71.04 (Cp), 71.18 (Cp), 71.52 (Cp), 72.52 (Cp), 72.69 (Cp), 74.46 (C_3), 78.43 (C_4), 102.08 (C_1), 102.21 (PhCH), 126.60 (Ph), 128.67 (Ph), 129.54 (Ph), 137.30 (Ph), 166.82 (C=N), 170.28 (C(O)). $C_{42}H_{40}FeN_2O_{12}$: Calc. C, 61.47; H, 4.91; N, 3.41. Found: C, 62.23; H, 5.11; N, 3.33%.

6. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 261083 for compound **9**.

Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK. Fax. (int code) +44 1223 336 003 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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