Systematizing structural motifs and nomenclature in 1,*n*′-disubstituted ferrocene peptides

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Received 11th November 2005
First published as an Advance Article on the web 23rd January 2006
DOI: 10.1039/b511332f

Ferrocene peptide conjugates display an array of structural features including helical ferrocene based chirality and a number of different intramolecular hydrogen bonding patterns. In this *tutorial review* we present a rigorous nomenclature for these systems, followed by a section that summarises and categorises the structures known to date. The issues discussed herein are of general relevance for all metallocene-based chiral transition metal catalysts and peptide turn mimetics.

1 Introduction

The disubstituted ferrocene framework is widespread in chemistry. Applications include organic synthesis, homogeneous catalysis, medicinal diagnostics and crystal engineering.[1–4] The molecules of interest described here are chiral disubstituted ferrocene peptide conjugates (Fig. 1), readily obtained from enantiopure amino acids and suitably substituted ferrocene derivatives using peptide coupling techniques.[5,6] These systems are currently being investigated for their applications in biomedical, nano, and material sciences. Although, a large number of disubstituted Fc peptides have been reported, a uniform stereochemical description is lacking.

In this tutorial review, we will outline a nomenclature that will uniquely define the conformations of disubstituted

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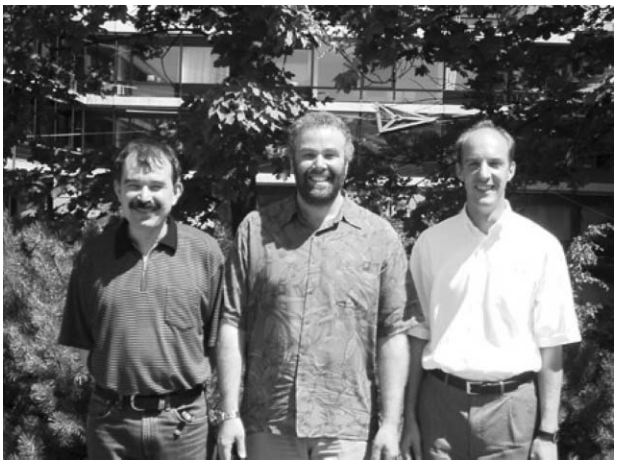

Srecko I. Kirin (left on picture) graduated from the University of Zagreb (1991, natural product synthesis, with A. Deljac) and worked as research chemist at PLIVA Pharmaceutical industry, Zagreb. He obtained his Masters (1994, enantioselective catalysis, with V. Sunjic) and Doctoral degrees (1998, organosilicon chemisty, with M. Eckert-Maksic) at the Rudjer Boskovic Institute, Zagreb (1993–2001). In 2001 he joined the group of N. Metzler-Nolte in Heidelberg as postdoctoral assistant. His current research interests focus on the development of artificial metalloenzymes and organometallic peptide mimics.

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Nils Metzler-Nolte (right on picture) obtained his PhD from the University of Munich in 1994 (Organoboron chemistry, with H. Nöth). After a postdoctoral year with M. L. H. Green in Oxford, he started independent research at the Max-Planck-Institut für Strahlenchemie (now MPI for Bioinorganic Chemistry). He obtained his Habilitation at the University of Bochum in May 2000 and was soon after appointed Professor for bioinorganic chemistry at the University of Heidelberg. He took up a Chair in Inorganic Chemistry at the University of Bochum in 2006. His work has been recognized by several awards and he has organized national and international meetings. He is the organizer of an interdisciplinary Research Unit on "Biological Function of Organometallic Compounds" funded by the German Research Foundation DFG. His research interest is in bioorganometallic chemistry and functional bioconjugates with transition metals, including aspects of medicinal inorganic chemistry.

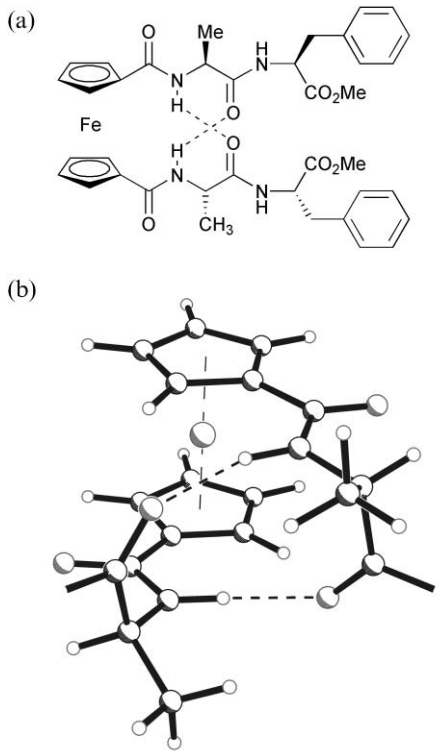

Fig. 1

ferrocene peptide conjugates. Although ferrocene is used as the prototype metallocene throughout this text, the systematic nomenclature outlined herein can be applied to all metallocenes. L-Amino acid chirality is assumed throughout this article, unless otherwise specified. Also herein, Fc denotes $(C_5H_4)_2Fe$, a disubstituted ferrocene moiety. As an example, we have chosen Fc[CO-Ala-Phe-OMe]$_2$ to guide the reader and to illustrate the nomenclature (Fig. 1a).

In taking a look at the molecule, the reader will notice various stereochemical elements of which the stereogenicity (L/D) of the carbon center of individual amino acids is the most obvious. However, we also need to consider the geometrical isomerism of the amide groups directly bound to the Cp rings (*E*/*Z*) and most importantly the helical chirality at the Fc core itself (*M*/*P*). Furthermore, we need to consider intramolecular and inter-peptide strand hydrogen bonding, which was first demonstrated by Herrick.[7]

2 General considerations

Both peptide substituents are connected to the Cp ring *via* an amide linkage. Fig. 2 illustrates the difference between 1,*n*′- and 1,*n*-disubstituted Fc peptides. In molecule A, one substituent is attached on each of the two Cp rings, potentially giving rotational isomers. In molecules of type B, both substituent are attached on the same Cp ring.[8,9] At present, only peptide derivatives of type A are known and will be discussed here. For ease of discussion, the eclipsed conformation of the Fc moiety is represented in a top down view and this representation will be used throughout (see section 3.1 for the definition of *n* in 1,*n*′-disubstituted ferrocenes).

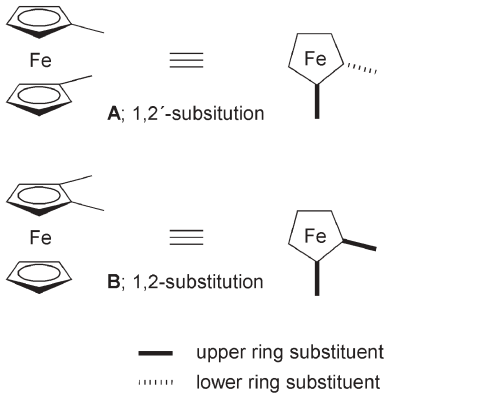

Fig. 2

We can consider three different types of disubstituted ferrocene peptide systems: those derived from Fc-dicarboxylic acid (**I**), Fc-amino acid (Fca, **II**) and Fc-diamine (**III**) (Fig. 3). The parent compounds are boxed in the Figure. Most Fc peptide conjugates known to date are class-**I** derivatives, in which Fc dicarboxylic acid is connected to the amino acid *via* an amide bond.[6] Only recently some peptide derivatives of Fc amino acid and Fc diamine became available, forming class-**II** and class-**III**, respectively.[10,11] It was proposed that Fc peptide conjugates derived from the Fc-diacid or Fc-diamine would allow modelling of parallel β-sheets, whereas conjugates derived from Fc amino acid may give rise to anti-parallel β-sheet models.

X-ray crystallography provides detailed information about molecular structures including intra- and inter-molecular

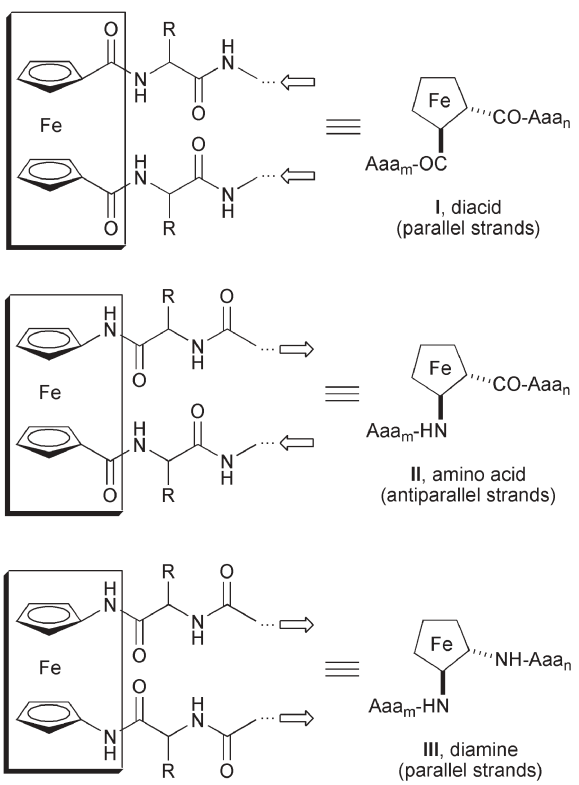

Fig. 3

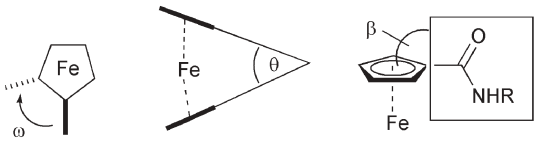

Fig. 4

H-bonding patterns, but is limited to crystalline materials. For non-crystalline materials, spectroscopic techniques such as NMR, IR and CD are extremely useful tools that allow the identification of conformational parameters and H-bonding. For example, in the ^{1}H NMR spectra the presence of amide resonances above a chemical shift $\delta = 7$ in non-hydrogen bonding solvents ($CDCl_3$, CD_2Cl_2, CD_3CN) indicates the presence of H-bonding. In the IR, spectrum absorptions under 3400 cm^{-1} indicate H-bonded amides. A comparison between IR spectra in the solid state (KBr) and in solution (CH_2Cl_2) gives additional information about inter-molecular H-bonding in the solid state. CD bands above 400 nm are particularly useful to assign helical conformations about the ferrocene core. The strength of H-bonds may be investigated by temperature dependent NMR or CD spectroscopy, or the addition of methanol or other hydrogen bonding solvents.[10,12]

Some important structural parameters of Fc peptides are shown in Fig. 4, and include the torsion angle ω between the two peptides, the tilt angle θ between the two Cp rings and the twist angle β between the Cp ring and the amide plane.[12]

3 Stereochemical descriptors

3.1 Helical chirality of the ferrocene moiety: *M*/*P* isomers

The two substituents on the cyclopentadienyl rings can exist as rotational isomers with respect to the Cp–Fe–Cp axis. For 1,*n*′-disubstituted metallocenes with chiral substituents, we use the following nomenclature (Fig. 5). A 1,1′-isomer is defined with the value of ω being between $-36°$ and $+36°$. A torsional angle of $36° < \omega < 108°$ defines a 1,2′-isomer, and so forth. Other isomers are defined as shown in Fig. 5. Helical chirality descriptors are useful in this context. The *P*-isomer has the substituent with higher priority in position 1 on the top Cp ring and the other substituent with lower priority in position 2′ or 3′on the bottom ring, giving a clockwise rotation. The *M*-isomer is present if the substituent on the bottom Cp ring is in the 4′ or 5′ position, giving a counter-clockwise rotation. This will give rise to *P*-1,1′, *P*-1,2′ or *P*-1,3′ and *M*-1,1′, *M*-1,4′ or *M*-1,5′ configurations. If we require the two Cp rings to be frozen in their relative position, then *P*-1,2′ and

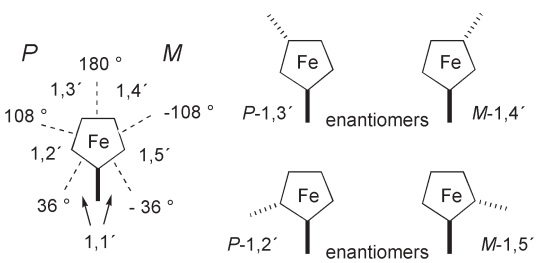

Fig. 5

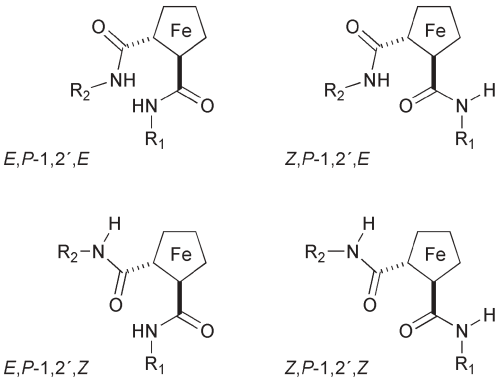

Fig. 6

M-1,5′ and *P*-1,3′ and *M*-1,4′ are pairs of enantiomers. The same applies for *P*-1,1′ and *M*-1,1′, if $\omega \neq 0$. The priority is defined by the Kahn–Ingold–Prelog rules.[13] Using this approach, our example from Fig. 1b is present in the *P*-1,2′ conformation.

3.2 Orientation of the Cp–amide bonds: *E*/*Z* isomers

Next, the position of the two amide C=O or N–H groups directly attached to the Cp rings of the Fc group must be considered. Conjugation results in hindered rotation about the Cp–amide bond. Both groups directly attached to the Fc can point in opposite directions, towards each other, or they can point in the same direction. In essence, for any given helical isomer, this could result in 4 different geometrical isomers. Fig. 6 shows the possible geometric isomers for Fc peptide conjugates in *P*-1,2′ configuration (class-**I**). The *E* configuration for one Cp–amide bond is defined as described by modified Kahn–Ingold–Prelog rules, where the substituted other ring must be considered as well, Fig. 7. The vast majority of class-**I** ferrocene peptides have the *E*,*E* configuration, with both bulky C=O pointing outwards and the small N–H groups pointing inwards. A central cleft is created by this arrangement. This can be easily seen by inspection of our example shown in Fig. 1b which exists as the *E*,*E* isomer. This molecule can be described as the *E*,*P*-1,2′,*E* conformation. The first geometrical descriptor refers to the *E*-configuration of the amide and Cp groups of the top ring, whereas the second descriptor refers to the bottom ring. For the case that $R^1 = R^2$, the *Z*,*E*- and *E*,*Z*-isomers of Fig. 6 are identical, since the

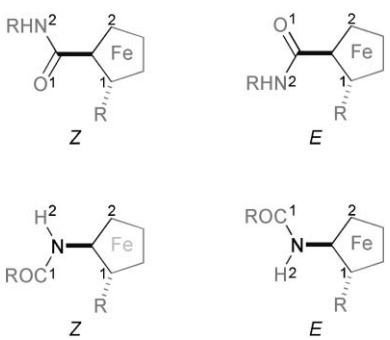

Fig. 7

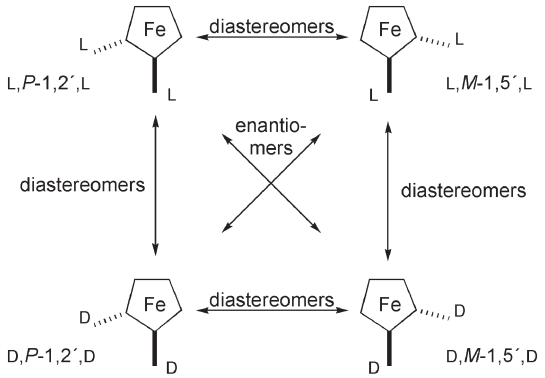

Fig. 8

molecule has a C_2-symmetry axis. This kind of *E*/*Z* isomerism will not be observed in monosubstituted ferrocenes, but it is of course not limited to 1,*n*′-disubstituted derivatives.

Presently, class-**I** Fc peptide conjugates with *Z*,*Z* conformation are unknown. This configuration would undoubtedly lead to high steric crowding. However, the non-peptidic diamide {Fc[CO-NH-CH_2-bipy]$_2$Fe}, adopts a *Z*,*Z* conformation.[14] In this compound, the coordination to the additional iron atom forces the two carbonyl groups into the otherwise unfavourable *Z*,*Z* configuration.

3.3 Chiral elements in the podant peptide chain: L/D isomers

The presence of a stereogenic centre at the first amino acid attached to each of the Cp rings of the Fc core gives rise to several enantiomers and diastereomers. Their relationship for a combination of *P*-1,2′/*M*-1,5′ helical and L,L/D,D isomers is displayed in Fig. 8. The relationship between *P*-1,3′ and *M*-1,4′ with L and D chiral elements in the podant peptide is analogous.

Our example shown in Fig. 1 has an L,L,*E*,*P*-1,2′,*E*,L,L configuration. Again, L and *E* before the helical descriptor refer to the relationship of peptide and amide-Cp on the top ring.

3.4 Interstrand H-bond pattern

Two turn structures in peptide chemistry are shown in Fig. 9. They differ in their H-bonding pattern. If the carbonyl group is closer to the peptide N-terminus than the H-bonding amide proton, the direction is defined as N → C (Fig. 9, left). Depending on the size of the H-bonded ring, γ-turns (7-membered ring) and β-turn (10 membered ring) form, whereas

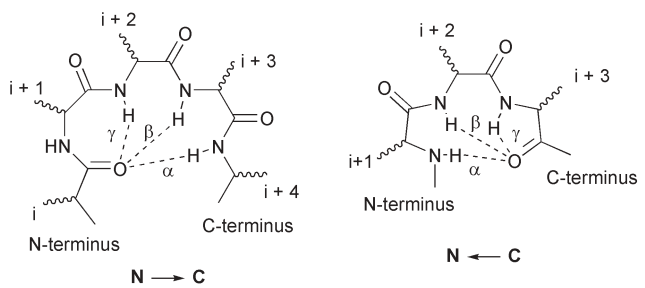

Fig. 9

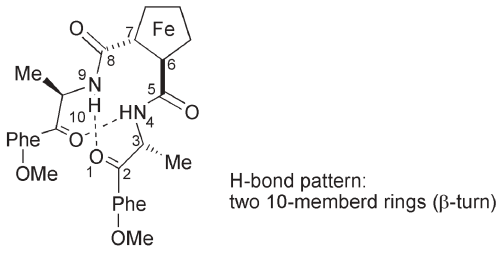

Fig. 10

13 membered rings are present in α-helices. The "reverse turns" (C → N, Fig. 9 right) rvs-γ (5-membered ring), rvs-β (8 membered rings) and rvs-α (11 membered ring) are energetically disfavoured and rarely observed in protein structures.[15]

One of the intriguing aspects of the Fc peptide conjugates is their potential for intramolecular H-bonding between the podant peptide chains. Consequently, we can apply peptide-derived turn nomenclature to Fc peptides. In our example Fc[CO-Ala-Phe-Ome]$_2$, two ten-membered H-bonded rings are formed (Fig. 10). These structural elements are classified as β-turns. This is a typical intramolecular H-bonding pattern in Fc peptides termed "Herrick conformation" (see below).

If only weak H-bonds are present, an equilibrium of different, interconverting *conformational* isomers in solution will be observed. In the "Herrick conformation" discussed above, the hydrogen bonds are sufficiently stable to allow isolation of one single isomer without interconversion in solution. Therefore, the example in Fig. 10 matches the definition of a *configurational* isomer.

4 Systematisation

4.1 Class-I ferrocene peptides

Fc peptides derived from Fc dicarboxylic acid are known in three major conformational families: the "Herrick conformation", the "van Staveren conformation" and the open "Xu conformation" (Fig. 11).

In $CDCl_3$ solution, the amide protons of a "Herrick conformer" show resonances at chemical shift $\delta > 7$ ppm, as expected for protons involved in H-bonding. The characteristic CD pattern for Fc[Ala-OMe]$_2$ in the region from 300–600 nm is shown in Fig. 12 and displays a Fc based transition with a positive Cotton effect at about 480 nm.[16] From the literature it is apparent that L amino acids induce *P*-helicity of the Fc

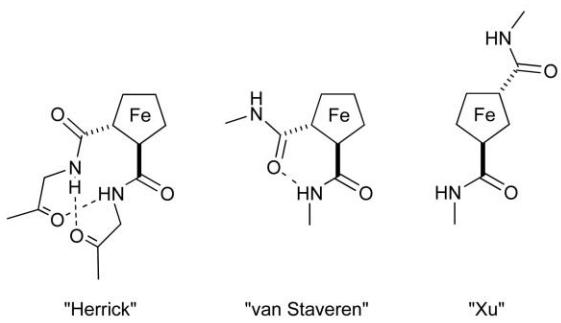

Fig. 11

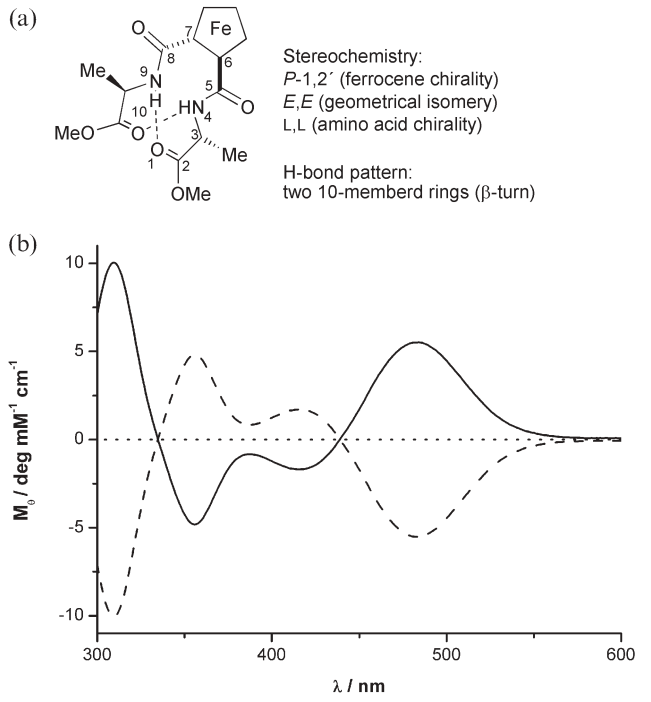

Fig. 12

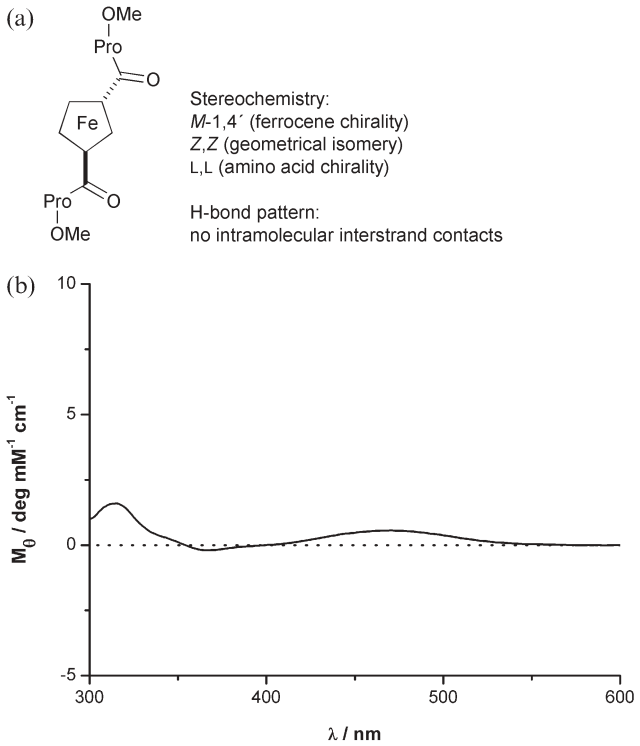

Fig. 13

group (full line in Fig. 12), while D amino acids induce *M*-helicity (broken line in Fig. 12).

In the solid state, structures with the general formula Fc[CO-Aaa$_1$-Aaa$_2$-PG]$_2$ (Aaa$_1$ = Gly or Ala) adopt the "Herrick conformation". The first example was provided by Hirao *et al.*, who studied the enantiomers Fc[CO-Ala-Pro-OMe]$_2$ and Fc[CO-DAla-DPro-OMe]$_2$ and obtained *P*-1,2′ and *M*-1,5′ configurations as shown by X-ray crystallography, respectively.[17,18] The nature of the ester group has no influence on the stereochemistry of the Fc core.[19] In addition, the "Herrick conformation" persists even for cyclic structures.[20,21] The CD spectra of molecules in *P*-1,2′ configuration described by Hirao are similar to that in Fig. 12.

The solid state structure of Fc[CO-Val-OMe]$_2$ also shows a "Herrick-like conformation" in the solid state, but the N–H···O interstrand contacts are too long to be defined as H-bonds, d(N···O) = 3.25 Å.[22]

Compound Fc[CO-Pro-OMe]$_2$ is an example for an open "Xu conformation", Fig. 13. In the solid state no intramolecular interstrand contacts are present, $\omega = -123.2^{\circ}$.[23] This is not surprising, since Pro has no amide protons that can engage in H-bonding. The CD spectrum of this compound is shown in Fig. 13. For a "Xu conformer", it is not expected that any rotational barriers are present that will stabilise either the *P* or *M* helicity or the *E* or *Z* geometric isomers.

Fc[CO-Gly-OEt]$_2$ as well as Fc[CO-Cys(OBzl)-OMe]$_2$ are present as "Xu conformers" in the solid state.[24,25] However, both compounds give a "Herrick conformer" in solution, as judged by their ^{1}H NMR ($CDCl_3$) with δ(NH) 8.1 ppm and 7.5 ppm, respectively. In addition, the CD spectrum of the latter peptide shows a "Herrick pattern",[25] with a molar ellipticity $M_\theta \sim 5$ deg mM^{-1} cm^{-1}, while the Gly derivatives are racemic and have only very weak CD signals ($M_\theta \sim 0.1$ deg mM^{-1} cm^{-1}).[16]

In addition, four Fc glycine conjugates are known. Since no "chiral information" is present in the amino acid, a racemic mixture of *M* and *P* helical isomers is formed and either one or both isomers are crystallized by chance. Three derivatives form a "Herrick conformation" in the crystal, and one a racemic mixture of "Xu conformers" composed of the *E*,*M*-1,4′,*Z* and *E*,*P*-1,3′,*Z* isomers.[24,26]

A very interesting example is provided by the structure of Fc[CO-Phe-OMe]$_2$. In the solid state, an unsymmetrical "van Staveren conformation" with a *E*,*P*-1,2′,*Z* configuration is found, Fig. 14.[12] Presumably, the "Herrick conformer" is present in solution, with a C_2-symmetrical ^{1}H NMR spectrum displaying the amide resonance at 7.7 ppm. A characteristic CD pattern of a *P*-helical structure is observed in solution, similar to the one shown in Fig. 12.[16]

Up to this point, we have learned that L amino acids are *P* directing, while D amino acids direct the helical chirality to the *M* conformer. This raises the question as to which conformer is obtained, if the two amino acids are of opposite chirality. The stereochemical analysis of the unsymmetrical diastereomers

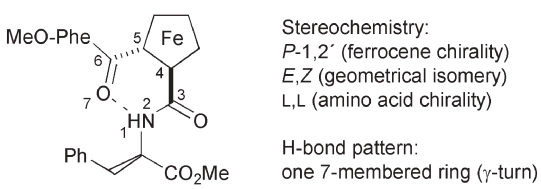

Fig. 14

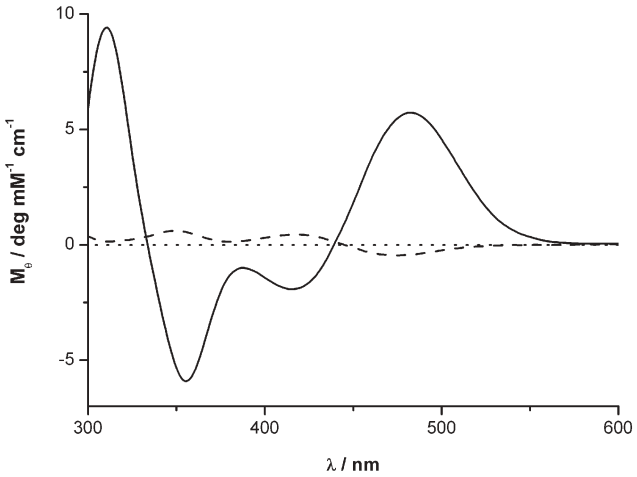

Fig. 15

Fc[CO-Phe-OMe][CO-Ala-OMe] and Fc[CO-D-Phe-OMe][CO-Ala-OMe] shows that while the former displays a CD spectrum characteristic for a "Herrick conformation" (full line in Fig. 15), the later shows much weaker CD signals indicating a mixture of *M* and *P* helical conformers in solution (Fig. 15, broken line)).[16] This is presumably due to a lack of energetic preference for one conformation.

4.2 Class-II ferrocene peptides

The synthesis of 1-amino-1′-carboxyferrocene (ferrocene amino acid, Fca) has been published by a number of authors.[27–29] Different routes have been applied and multi-gram quantities have been prepared.[10] However, the coupling of Fca to amino acids and peptides has been reported only recently, describing the synthesis and structural analysis of Boc-Ala-Fca-Ala-Ala-OMe. An L,*E*,*P*-1,2′,*E*,L,L isomer is present in the solid state, with two hydrogen bonds, Fig. 16. The presence of H-bonding was confirmed in solution by ^{1}H NMR and CD spectroscopy (Fig. 16). This H-bonding pattern can be classified as a "Herrick-like" with two interstrand H bonds resulting in an 11-membered and a 9-membered ring.

4.3 Class-III ferrocene peptides

The only known examples of class-**III** ferrocene peptides are [Boc-Ala-NH]$_2$Fc and its enantiomer [Boc-D-Ala-NH]$_2$Fc.[11] The geometrical isomer found in the crystal is *E*,*E*, with both NH groups bound directly to the Cp rings pointing "inside", Fig. 17. In class-**III** derivatives, the small NH can turn "inside" easier than the sterically more demanding CO in the class-**I** compounds. In [Boc-Ala-NH]$_2$Fc the ω angle is only 27° and the helical chirality can be defined as *M*-1,1′. In the solid state, this compound gives a C_2 symmetrical structure, where the H-bonds form two 10-membered rings (β-turn). Dissolved in chlorinated hydrocarbons, [Boc-Ala-NH]$_2$Fc shows clearly interstrand H-bonding with chemical shift of the amide NHs at 9.00 ppm and a strong positive signal at 470 nm in the CD spectrum, Fig. 17. However, the CD-signals are significantly weaker than those of the class-**I** derivatives displayed in Fig. 12.

5. Conclusion and outlook

Ferrocene peptides may exist in a large number of stereo-isomers, with possible sources of chirality being amino acid chirality, *E*/*Z* isomerism at the amide bonds, and helical and positional isomers of the metallocene. Out of this theoretical structural variety, only a limited number of isomers are

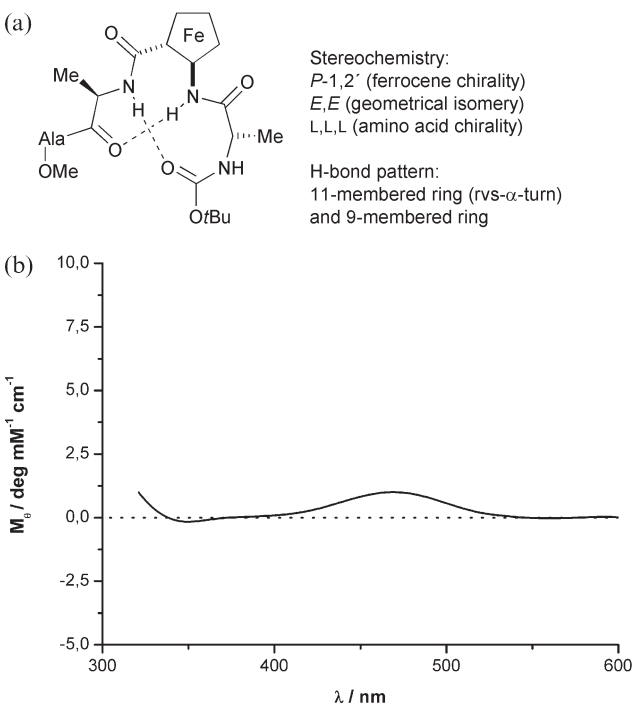

Fig. 16

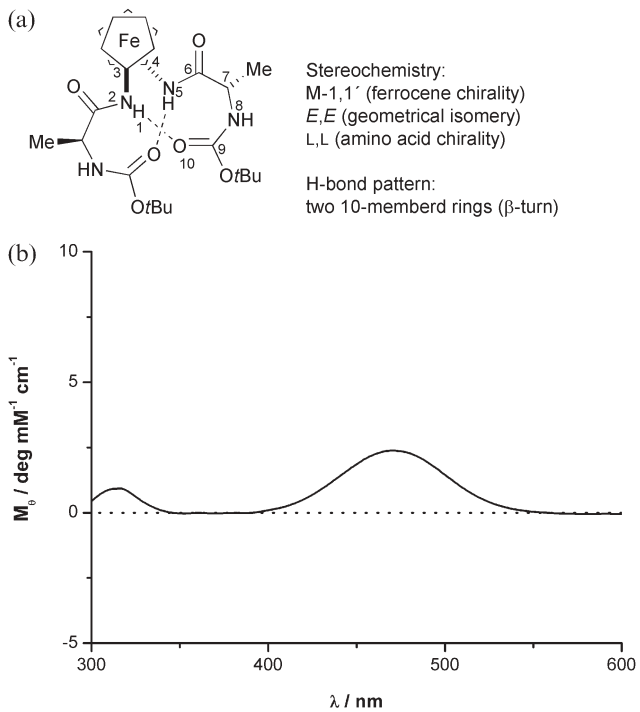

Fig. 17

actually found. Wherever possible, strong intramolecular hydrogen bonds form between amide NH and carbonyl oxygen atoms. As a consequence, helical chirality is induced in the metallocene core and a *P* helix is the major isomer for naturally occurring L amino acids.

In this article, the nomenclature is outlined and exemplified for ferrocenes with podant peptides on the two Cp rings. However, it is not restricted to such cases. A large number of 1,2-disubstituted sandwich or half-sandwich compounds were prepared and used, for instance as ligands in asymmetric catalysis.[1] Surprisingly, much less work was devoted to 1,*n*′-disubstituted derivatives, although an additional element of helical chirality of the metallocene may be exploited.[4]

Secondly, 1,*n*′-disubtituted metallocenes may serve as turn mimetics in peptide turn structures. Because of the low barrier of rotation of the two Cp rings against one another, these compounds are more flexible than most purely organic turn mimetics.[30] In addition, most of the ferrocene peptides investigated so far present hydrogen bond patterns which are not observed in natural systems. Minimal models for naturally occurring β-turns and β-sheet structures were reviewed.[31,32] The metallocene peptides may provide an alternative approach to uncommon lead structures for medicinal chemistry or structural biology.

6. Note added in proof

A few papers of interest to the issues discussed herein appeared in the mean time. Heinze and Beckmann give a conformational analysis of class-**II** Fca derivatives, also covering dynamic aspects.[33] Two papers by Hirao and coworkers[34,35] presents two different turn types simultaneously on a class-**I** scaffold.

Acknowledgements

The authors are grateful to all co-workers who contributed to the work discussed herein. Financial support from the DFG (SFB 623) and Volkswagenstiftung (fellowship to S. I. K.) is also gratefully acknowledged.

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