1,1′-Bis(oxazolin-2-yl)ferrocenes: An Investigation of Their Complexation Behavior toward $[Pd(\eta^3\text{-allyl})Cl]_2$

Christian G. Hartinger,*[a] Alexey A. Nazarov,*[a] Vladimir B. Arion,[a] Gerald Giester,[b] Maxim L. Kuznetsov,[c] Markus Galanski,[a] and Bernhard K. Keppler*[a]

Keywords: Asymmetric catalysis / Density functional calculations / Mass spectrometry / Metallocenes / Palladium

The coordination behavior of several aryl- and alkyl-bis(oxazolinyl)ferrocenes, which were prepared in high yields from ferrocene-1,1′-dicarbonyl dichloride and enantiomerically pure or racemic amino alcohols via the corresponding bis(β-hydroxyamide)s and dimesylates or ditosylates as intermediates, toward $[Pd(\eta^3\text{-allyl})Cl]_2$ was investigated by ESI mass spectrometry. The synthesized compounds were characterized by NMR spectroscopy and elemental analysis and the molecular structures of 1,1′-bis[(*R*)-4-isopropyloxazolin-2-yl]-ferrocene (**6b**), 1,1′-bis[(*S*)-4-isopropyloxazolin-2-yl]ferrocene (**7b**), 1,1′-bis[(*S*)-4-*sec*-butyloxazolin-2-yl]ferrocene (**11b**), 1,1′-bis[(*S*)-4-*tert*-butyloxazolin-2-yl]ferrocene (**12b**), 1,1′-bis[(*R*)-4-phenyloxazolin-2-yl]ferrocene (**13b**), and 1,1′-bis[(*S*)-4-phenyloxazolin-2-yl]ferrocene (**14b**) were determined by single-crystal X-ray diffraction analysis. The coordination behavior studies by ESI-MS show a strong preference for monodentate complex formation. This result is supported by theoretical studies carried out at the B3LYP level of theory. It was found that the latter coordination type of 1,1′-bis[(*S*)-4-methyloxazolin-2-yl]ferrocene (**1b**) to an allylpalladium moiety is kinetically favored over the bidentate one.

Introduction

Oxazolines are an intensively studied class of compounds. These five-membered heterocycles are found in natural metal chelators,[1–3] show interesting biological properties,[4,5] and also play an important role in synthesis[6–10] as well as have a remarkable range of applicability. Their uses vary widely from organic[6–8] and coordination chemistry,[9,10] via polymer chemistry,[11–13] to antiacaricide as well as antiinsecticidic purposes.[14] Oxazolines are used in a manifold variety of catalytic processes, for example hydrosilylation,[15] transfer hydrogenation,[16] allylic substitution,[17] allylic oxidation,[18] aziridination of olefins,[19] aziridination of imines,[20] cyclopropanation,[21–23] and the Diels–Alder reaction.[24] Furthermore, it should be noted that there is a great interest in oxazolines as they possess interesting properties in asymmetric synthesis when coordinated to transition metals.

Beside the natural occurrence of oxazolines, there are several methods that are useful for constructing the oxazoline or 4,5-dihydrooxazole moiety in the laboratory (for reviews see refs.[6,7,11]): the dehydration and ring formation of some carboxamides, for example hydroxy amides, the reaction between halo carboxamides and strong bases, as well as the addition of oxiranes to nitriles and of amino alcohols to carboxylic acids or imino esters offer a synthetic pathway to build up the required five-membered heterocycle. Lately, coordination-chemistry-driven approaches have moved into the focus of synthetic chemists' interest,[25,26] and the addition of haloalcohol/base or oxirane/chloride systems to Pt^{II}-bound nitrile,[27,28] and reactions between nitriles and amino alcohols catalyzed or mediated by a variety of metal ions, for example Zn^{II}, Cd^{II}, Ni^{II}, Al^{III}, Co^{II}, Cu^{II}, show high potential for the assembly of the oxazoline system.[29–32]

An impressive number of reports and essays show the applicability but also the popularity of ferrocene and its derivatives in many fields of organic, materials, synthetic, and also medicinal chemistry,[33–37] and the use of substituted ferrocenes in metal-catalyzed enantioselective synthesis has been a very important application for more than twenty years. Herein chiral ferrocene derivatives are involved which either bear the center of chirality on a substituent or contain an element of planar chirality.[38]

The combination of the coordinating oxazoline structure, which is easily obtainable (also in an enantiomerically pure form) from reactions involving nonracemic starting materials, such as α-amino alcohols, and ferrocene (with the possibility to introduce planar chirality) has led to the develop-

[a] Institute of Inorganic Chemistry, University of Vienna,
Waehringer Str. 42, 1090 Vienna, Austria
Fax: +43-1-4277-52680
E-mail: bernhard.keppler@univie.ac.at,
christian.hartinger@univie.ac.at
alex.nazarov@univie.ac.at
[b] Institute of Mineralogy and Crystallography, University of Vienna,
Althanstr. 14, 1090 Vienna, Austria
[c] Department of Chemistry, Moscow Pedagogical State University,
Nesvigskiy per. 3, 119021 Moscow, Russian Federation

ment of compounds containing both moieties, i.e., ferrocene and an oxazolinyl moiety.[39–43] This method offers a straightforward way to synthesize chiral ferrocene derivatives which are, due to their distinct structural features, applicable in asymmetric synthesis. Surprisingly, Ahn et al. have reported a lack of catalytic activity for 1,1′-bis[(*S*)-4-*tert*-butyloxazolin-2-yl]ferrocene (**12b**) in the palladium-catalyzed allylic alkylation, while there are many examples of non-metallocene complexes with bisoxazoline ligands that give high enantiomeric excesses and turnover rates.[17,44–48]

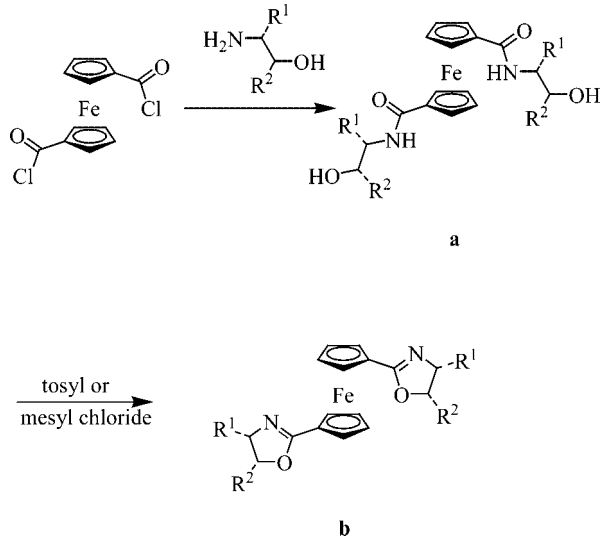
Electrospray ionization mass spectrometry (ESI-MS) is the softest desorption/ionization method, and its suitability to determine the coordination behavior of transition metal cations toward ligands has been studied extensively (for examples see refs.[49–52] and for a review see ref.[53]). The desolvation process mainly leads to the presence of ions in the gas phase that are also found in solution.[54] ESI-MS has a number of advantages over other techniques; in particular, it provides information on the characteristic isotopic patterns of compounds (especially metal compounds) and allows low sample consumption and use of many compatible solvents.[49]

In order to clarify the influence of the nature of the substituents on the catalytic potential of 1,1′-bis(oxazolin-2-yl)ferrocenes, several derivatives of the parent compound 1,1′-bis[(*S*)-4-*tert*-butyloxazolin-2-yl]ferrocene (**12b**) were synthesized and tested with respect to their catalytic potential in asymmetric allylic substitution, where the catalytic activity depends strongly on the formation of chelate structures between multidentate ligands and transition metals.[55,56] The coordination behavior of new 1,1′-bis(oxazolin-2-yl)ferrocenes bearing alkyl (**1b**, **7b**, and **12b**) or aryl substituents (**14b**) in the 4-position of the oxazoline ring toward $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ was studied in detail by ESI-MS. In order to elucidate the energetic preference for the coordination of 1,1′-bis[(*S*)-4-methyloxazolin-2-yl]ferrocene (**1b**) to an allylpalladium moiety, DFT calculations at the B3LYP level of theory were also carried out.

Results and Discussion

Synthesis

The oxazolines bearing alkyl and aryl substituents at the 4- and/or 5-position of the oxazoline residue (see Scheme 1 and Table 1) were synthesized by a condensation reaction of 1,1′-ferrocenedicarbonyl dichloride with the corresponding α-amino alcohols at room temperature, followed by a ring-closing procedure with either methanesulfonyl chloride and triethylamine or *p*-toluenesulfonyl chloride, triethylamine and a catalytic amount of 4-(dimethylamino)pyridine at 0 °C.[41,57–62] The yield for the syntheses of the methyl- and aryl-substituted compounds was higher when using *p*-toluenesulfonyl chloride, and the methyl and diphenyl amides that precipitated during the synthesis were obtained in high purity by filtration. All oxazolines and other amides were isolated by flash column chromatography on silica gel using a mixture of ethyl acetate and *n*-hexane as eluent.



Scheme 1. General scheme for the synthesis of the 1,1′-bis-(oxazolin-2-yl)ferrocenes.

Table 1. List of the synthesized 1,1′-bis(oxazolin-2-yl)ferrocenes.

	Substituents		Tosyl/mesyl chloride	
	R^1	R^2	tosyl	mesyl
1	(*S*)-methyl	H	X	
2	H	(*S*)-methyl	X	
3	(*R*)-ethyl	H		X
4	(*S*)-ethyl	H		X
5	*n*-propyl	H		X
6	(*R*)-isopropyl	H		X
7	(*S*)-isopropyl	H		X
8	*n*-butyl	H		X
9	(*R*)-isobutyl	H		X
10	(*S*)-isobutyl	H		X
11	(*S*)-*sec*-butyl	H		X
12	(*S*)-*tert*-butyl	H		X
13	(*R*)-phenyl	H	X	
14	(*S*)-phenyl	H	X	
15	H	phenyl	X	
16	(*R*)-benzyl	H	X	
17	(*S*)-benzyl	H	X	
18	(*S*)-phenyl	(*R*)-phenyl	X	

NMR spectroscopy was found to be a useful tool to follow the ring-closing process, i.e., the transformation from hydroxy amides to oxazolines. This process is marked in the ^{1}H NMR spectrum by the disappearance of the protons of the hydroxy and amide groups and in the ^{13}C NMR spectrum by a characteristic high-field shift from about δ = 170 to 166 ppm of the CO group, as well as by low-field shifts of the primary (for **2**, **15**, and **18**) or secondary amino alcohol carbon atoms from about δ = 64 ppm to about δ = 73 ppm [with the exception of **8** (from ca. δ = 52 to 73 ppm) and **18** (from ca. δ = 75 to 79 ppm] as well as of the amino alcohol carbon atoms next to the nitrogen from about δ = 50 to about 69 ppm (with the exception of **18**: from approximately δ = 60 to 89 ppm).

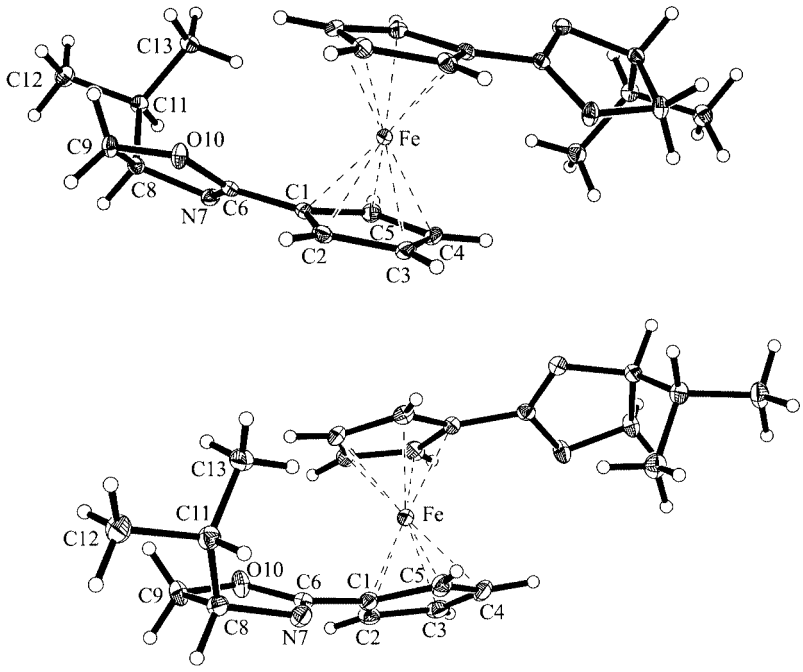


Figure 1. The molecular structure and labeling scheme of 1,1′-bis[(*R*)-4-isopropyloxazolin-2-yl]ferrocene (**6b**; top) and 1,1′-bis[(*S*)-4-isopropyloxazolin-2-yl]ferrocene (**7b**; bottom) with displacement ellipsoids drawn at the 50% probability level.

The syntheses of hydroxy amides as well as of the corresponding oxazolines with (*S*)-isopropyl, (*S*)-*tert*-butyl,[41] and (*S*)-phenyl moieties[39] in the 4-position of the oxazoline moiety have been reported earlier, but no crystal structure data were published. The synthesis of the 1,1′-ferrocenedicarboxamide **6a** has been reported, but no analytical data were presented.[42]

Crystal Structure Analysis

Crystal structure analysis has been performed to elucidate the influence of different substituents, viz., isopropyl, phenyl, *sec*- and *tert*-butyl, at oxazoline rings on the torsional twist angle of the Cp rings around the iron atom.

The results of the X-ray diffraction study of **6b** and **7b**, which crystallized as pure enantiomers in the noncentrosymmetric C_2 space group, are summarized in Figure 1. The asymmetric unit consists of one half of the molecule in **6b** and **7b**. The C8 atom in **6b** and **7b** possesses an (*R*) and (*S*) absolute configuration, respectively. The Cp rings in **6b** and **7b** approach an anticlinal eclipsed arrangement with a torsional twist angle Cp···Fe···Cp of 140.0° and 138.3°, respectively. The Cp rings are almost parallel to each other, the dihedral angles being 2.2° (**6b**) and 2.3° (**7b**). The orientation of the oxazoline ring with respect to the Cp ring can be characterized by the torsion angle C2–C1–C6–O10, which is 28.1° and –28.0° in **6b** and **7b**, respectively. The distribution of the electron density in the 4-isopropyloxazoline fragments in both **6b** and **7b** is very similar (see Table 2). The bond lengths and angles in the ferrocene moiety in both complexes are normal.[39]

Table 2. Selected bond lengths [Å] and angles [°] in **6b**, **7b**, **11b**, and **12b**.

	6b	7b	11b	12b
C1–C6	1.4685(18)	1.468(2)	1.479(8)	1.458(4)
C6–N7	1.2643(18)	1.264(2)	1.259(8)	1.265(3)
C6–O10	1.3641(17)	1.364(2)	1.345(8)	1.361(3)
N7–C8	1.4854(17)	1.487(2)	1.481(8)	1.474(4)
C8–C9	1.5397(19)	1.538(2)	1.520(9)	1.534(4)
C9–O10	1.4586(16)	1.4586(19)	1.455(8)	1.461(3)
C8–C11	1.530(2)	1.525(2)	1.510(8)	1.543(3)
C11–C12	1.5314(19)	1.534(2)	1.466(14)	1.511(4)
C11–C13	1.5312(17)	1.533(2)	1.586(12)	1.517(5)
N7–C8–C9	103.97(11)	103.95(13)	104.8(5)	104.1(2)
N7–C8–C11	110.08(11)	110.03(13)	110.8(6)	111.8(2)
C9–C8–C11	116.23(12)	116.36(15)	116.8(6)	115.5(2)

Like **6b** and **7b**, complex **11b** crystallizes as the (*S*)-enantiomer in the noncentrosymmetric $C222_1$ space group (see Figure 2 top) and the asymmetric unit consists of half the molecule. The Cp rings in **11b** adopt an antiperiplanar (staggered) arrangement with a torsional twist angle Cp···Fe···Cp of 176.5°. The Cp rings are almost parallel to each other, with a dihedral angle of 1.6°. The oxazoline ring is almost parallel to the Cp ring. The torsion angle C2–C1–C6–O10 is 3.2°. Like **11b**, complex **12b** crystallizes as the (*S*)-enantiomer in the noncentrosymmetric $C222_1$ space group (see Figure 2 bottom) and the asymmetric unit consists of half the molecule. The Cp rings in **12b** adopt an antiperiplanar (staggered) arrangement with a torsional twist angle Cp···Fe···Cp of 174.9°. The Cp rings are almost parallel to each other, with a dihedral angle of 0.4°. The oxazoline ring is almost parallel to the Cp ring. The torsion

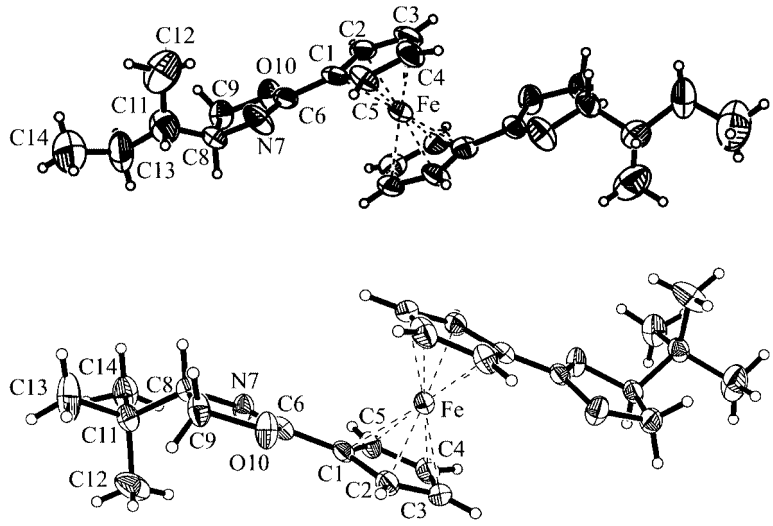


Figure 2. The molecular structure and labeling scheme of 1,1′-bis[(*S*)-4-*sec*-butyloxazolin-2-yl]ferrocene (**11b**; top) and 1,1′-bis[(*S*)-4-*tert*-butyloxazolin-2-yl]ferrocene (**12b**; bottom) with displacement ellipsoids drawn at the 50% probability level.

angle C2–C1–C6–O10 is 8.1°. Selected bond lengths and angles of **11b** and **12b** are given in Table 2.

Figure 3 shows one of the two independent molecules in the crystal structures of **13b** (*R*) and **14b** (*S*). Like in all previous compounds, the ferrocene moiety shows the expected geometry, with no unusual bond lengths or angles. The two Cp rings are almost parallel to each other, with dihedral angles of 4.5° and 2.0° in the two independent molecules of **13b** and 4.4° and 2.0° in **14b**. The Cp···Fe···Cp torsional twist angle is 54.2° and 52.9° for the independent molecules in **13b**, and –54.2° and –53.0° in **14b**, thus indicating a conformation between synclinal staggered (ideal twist angle of 36°) and synclinal eclipsed (ideal twist angle of 72°). As in **12b**, the oxazoline rings are almost parallel to the Cp rings, the torsional angles C2–C1–C6–O10, C18–C17–C22–O26 and C34–C33–C38–O42, C50–C49–C54–O58 being 6.1°, –11.5° and 4.7°, –3.6° in **13b** and –6.6°, 11.4°, –4.2°, 3.3° in **14b** (see Table 3 for selected bond lengths and angles).

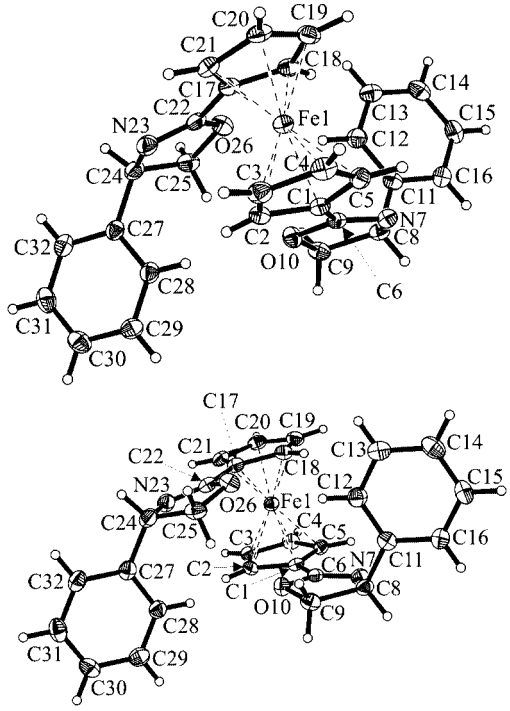


Figure 3. The molecular structure and labeling scheme of 1,1′-bis[(*R*)-4-phenyloxazolin-2-yl]ferrocene (**13b**; top) and 1,1′-bis[(*S*)-4-phenyloxazolin-2-yl]ferrocene (**14b**; bottom) with displacement ellipsoids drawn at the 50% probability level.

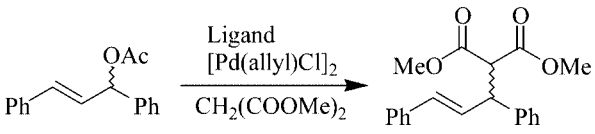
Investigation of the Coordination Properties

The application of bisoxazoline-based ligands in palladium-catalyzed allylic alkylation and in many other metal-catalyzed enantioselective reactions is well known.[9,17,44–48] Therefore the results of a study done by Ahn and co-workers, who found no catalytic activity for 1,1′-bis[(*S*)-4-*tert*-butyloxazolin-2-yl]ferrocene (**12b**), is rather surprising, although the ligand does bear a bulky *tert*-butyl group.

The catalytic potential of the ligands applied depends on several structural features, especially the bite angle and the bulkiness of the substituents. In order to study the influence of the substituents nature and of their bulkiness, a series of analogues was synthesized and their catalytic potential in the asymmetric allylic substitution investigated. The experiments were carried out with palladium complexes generated in situ by stirring the corresponding chiral ligand and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ under standard conditions, i.e., (*E*)-1,3-diphenylprop-2-enyl acetate as substrate and dimethyl malonate as nucleophile with the *N*,*O*-bis(trimethylsilyl)acetamide base system (BSA-KOAc; see Scheme 2).[63] In agreement with the results of Ahn and co-workers, we did not observe any catalytic activity for any of the synthesized compounds. The variation of the ligand/Pd ratio from 1:1 to a large excess of the Pd compound (up to 10 times excess) did not affect the catalytic activity, and all efforts to isolate a defined Pd complex were unsuccessful.

Table 3. Selected bond lengths [Å] and angles [°] in **13b** and **14b**.

	13b	**14b**
C1–C6	1.462(3)	1.465(3)
C6–N7	1.269(2)	1.269(3)
C6–O10	1.370(2)	1.367(2)
N7–C8	1.485(2)	1.489(3)
C8–C9	1.542(3)	1.541(3)
C9–O10	1.456(2)	1.455(3)
C8–C11	1.515(3)	1.506(3)
C11–C12	1.396(3)	1.398(3)
C11–C16	1.386(3)	1.394(3)
N7–C8–C9	103.72(14)	103.36(17)
N7–C8–C11	108.53(14)	108.55(17)
C9–C8–C11	115.39(16)	115.73(18)



Scheme 2. General scheme for the palladium-catalyzed allylic alkylation.

In order to investigate the reasons for this lack of catalytic activity, the coordination of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ toward several 1,1′-bis(oxazolin-2-yl)ferrocenes was studied by ESI-MS in the positive-ion mode (for calculated *m*/*z* ratios of the parent compound and the expected adducts see Table 4). The incubation solution of the Pd complex and the oxazoline ligand was injected directly into the mass spectrometer and the MS measurement parameters were optimized in order to maximize signals corresponding to the mass-to-charge ratio of the ligands (see Table 5).

Table 4. List of the calculated *m*/*z* ratios for the ligands and for the complexes formed with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (measured in positive-ion mode).

	Formula	*m*/*z* ratio
1b	$[C_{18}H_{20}FeN_2O_2 + H]^+$	353
1b + $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	$[C_{18}H_{20}FeN_2O_2 + Pd(\eta^3\text{-}C_3H_5)]^+$	499
1b + $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	$[C_{18}H_{20}FeN_2O_2 + PdCl]^+$	495
1b + $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	$[C_{18}H_{20}FeN_2O_2 + Pd_2(\eta^3\text{-}C_3H_5)_2Cl]^+$	683
7b	$[C_{22}H_{28}FeN_2O_2 + H]^+$	409
7b + $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	$[C_{22}H_{28}FeN_2O_2 + Pd(\eta^3\text{-}C_3H_5)]^+$	555
7b + $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	$[C_{22}H_{28}FeN_2O_2 + PdCl]^+$	551
7b + $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	$[C_{22}H_{28}FeN_2O_2 + Pd_2(\eta^3\text{-}C_3H_5)_2Cl]^+$	739
12b	$[C_{24}H_{32}FeN_2O_2 + H]^+$	437
12b + $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	$[C_{24}H_{32}FeN_2O_2 + Pd(\eta^3\text{-}C_3H_5)]^+$	583
12b + $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	$[C_{24}H_{32}FeN_2O_2 + PdCl]^+$	577
12b + $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	$[C_{24}H_{32}FeN_2O_2 + Pd_2(\eta^3\text{-}C_3H_5)_2Cl]^+$	767
12b + $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	$[C_{24}H_{32}FeN_2O_2 + Pd_2(\eta^3\text{-}C_3H_5)Cl_2]^+$	761
14b	$[C_{28}H_{24}FeN_2O_2 + H]^+$	477
14b + $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	$[C_{28}H_{24}FeN_2O_2 + Pd(\eta^3\text{-}C_3H_5)]^+$	623
14b + $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	$[C_{28}H_{24}FeN_2O_2 + PdCl]^+$	617
14b + $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	$[C_{28}H_{24}FeN_2O_2 + Pd_2(\eta^3\text{-}C_3H_5)Cl_2]^+$	807

For 1,1′-bis[(*S*)-4-methyloxazolin-2-yl]ferrocene (**1b**), a signal at *m*/*z* = 353 was observed as the most intense peak $[C_{18}H_{20}FeN_2O_2 + H]^+$. Addition of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ in 1:1 ligand/Pd molar ratio resulted in the formation of a peak at *m*/*z* = 499 assignable to the mono-palladium complex $[C_{18}H_{20}FeN_2O_2 + Pd(\eta^3\text{-}C_3H_5)]^+$ and a relatively much less abundant one at *m*/*z* = 683 for the bis-palladium one $[C_{18}H_{20}FeN_2O_2 + Pd_2(\eta^3\text{-}C_3H_5)_2Cl]^+$. Increasing the amount of palladium (molar ratio 1:2) in the incubation mixture resulted only in a minor increase of the peak at *m*/*z* = 683; the signal assigned to $[C_{18}H_{20}FeN_2O_2 + Pd(\eta^3\text{-}C_3H_5)]^+$ remained the most intense.

Table 5. Operational MS parameters chosen for investigations on the complexation behavior of **1b**, **7b**, **12b**, and **14b**.

Parameters	Values
HV capillary [V]	4000
Dry gas flow [L min^{-1}]	5
Dry gas temperature [°C]	80
Nebulizer gas [psi]	10
Skimmer 1 [V]	35.7
Capillary exit offset [V]	73.6
Octopole [V]	2.50
Octopole Δ [V]	2.40
Trap drive	30.6
Injection rate [μL min^{-1}]	6
Polarity	positive
Scan range, *m*/*z*	50–1200

Similar investigations were performed for 1,1′-bis[(*S*)-4-isopropyloxazolin-2-yl]ferrocene (**7b**): at a molar ratio of 1:1 the most intense peak was again the ligand coordinated to one Pd^{II} center, which in this case also bears an allyl ligand. At the lower ligand/transition metal molar ratio (1:1) a remarkable amount of $[C_{22}H_{28}FeN_2O_2 + Pd_2(\eta^3\text{-}C_3H_5)_2Cl]^+$ is already detectable in this case. Addition of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ to obtain molar ratios of 1:2 and 1:10 influenced the mass spectra by increasing the signal with *m*/*z* = 739, and at a molar ratio of 1:10 there are already peaks with equal relative intensities for the mono-palladium (*m*/*z* = 555) and the bis-palladium conjugates (*m*/*z* = 739; see Figure 4). Additionally, MS/MS experiments of both adducts were done and it was found that the fragmentation of *m*/*z* = 739 leads to a peak for the mono adduct (*m*/*z* = 555).

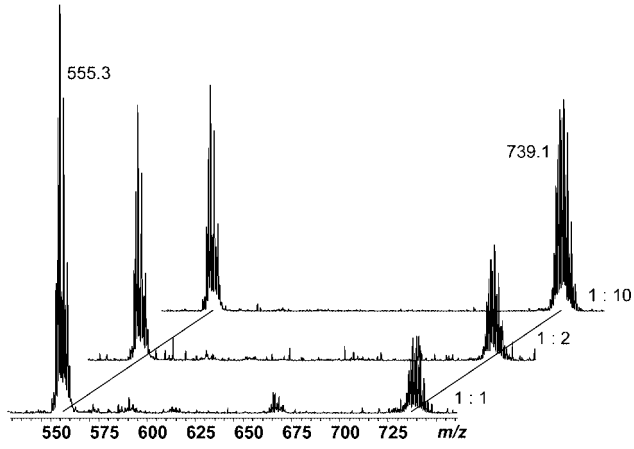


Figure 4. Mass spectrometric investigation of the coordination behavior of 1,1′-bis[(*S*)-4-isopropyloxazolin-2-yl]ferrocene (**7b**) toward $[Pd(allyl)Cl]_2$ at molar ratios of 1:1, 1:2, and 1:10 (ligand/palladium), with peaks found at *m*/*z* = 555 and 739 assignable to the mono- and bis-palladium complexes, respectively.

Further MS^3 experiments did not result in any assignable signals.

In the case of (*S*)-*tert*-butyloxazoline (**12b**) a major adduct with *m*/*z* = 767 is formed which was assigned to $[C_{24}H_{32}FeN_2O_2 + Pd_2(\eta^3\text{-}C_3H_5)_2Cl]^+$. Additionally, a coordination compound was detected which contains one allyl and two chloro ligands instead of two allyl and one chloro ligand. Note that due to the broad isotope distribution of palladium and chloro ligands an overlapping of the signals with *m*/*z* = 761 and 767 can not be avoided.

The (*S*)-phenyloxazoline **14b** was chosen as representative for the aryloxazolines for the MS experiments. At a molar ratio of 1:1 the monoadduct with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ is the most intense peak, while at a 1:2 ratio the dinuclear Pd species is formed. Extension of the reaction times for all the MS experiments did not influence the appearance of the mass spectra. The increase of the peak with two Pd atoms coordinated to the 1,1′-bis(oxazolin-2-yl)ferrocene ligands reveals that there is no stable chelate formed between the two oxazoline rings and the Pd^{II} cation. These results are in good agreement with a report published by Imai et al., who showed by NMR spectroscopy that 1,1′-bis[(*S*)-4-isopropyloxazolin-2-yl]ferrocene (**7b**) functions, independently of the Pd/oxazoline ratio, as a monodentate ligand.[64]

In order to study the experimentally found monodentate coordination of the ferrocene ligand to the allylpalladium moiety instead of the expected chelate formation, quantum-chemical calculations of equilibrium structures of the parent methyl-substituted ligand 1,1′-bis[(*S*)-4-methyloxazolin-2-yl]ferrocene (**1b**) and possible complexes with mono- and bidentate coordination of **1b** to Pd^{II} (**1c** and **1d**, respectively) were carried out at the B3LYP level of theory. The calculated structural parameters of **1b** are in perfect agreement with those found experimentally for **12b**, with a maximum deviation of 0.021 Å for the C8–C9 bond. For the other bonds, the difference between the calculated and experimental bond lengths often appears within the 3σ interval of the X-ray data.

The minima corresponding to both **1c** and **1d** were located (see Figure 5). A comparison of the total energies of these structures shows that the chelate complex **1d** is 19.07 kcal mol^{-1} more stable than complex **1c**. In terms of Gibbs free energy, when the entropic factor is taken into account, the stability of **1d** relative to **1c** decreases slightly but is still significant ($\Delta G = G_{1d} - G_{1c} = -15.83$ kcal mol^{-1}). Consideration of the solvent effects at the CPCM level (for CH_2Cl_2 as a solvent) results in a further, but only moderate, lowering of the energy difference between **1d** and **1c** (by 3.16 kcal mol^{-1}). Thus, the chelate complex displays a significantly higher stability than the monodentate structure despite the possible steric hindrances in the former; the exclusive formation of the monodentate-type complexes must therefore be determined by kinetic factors rather than by thermodynamic ones. Indeed, the formation of chelates is accompanied by the mutual rotation of two Cp cycles and by significant conformational changes in the ligand that should increase the activation energy compared to the formation of **1c** and similar structures.

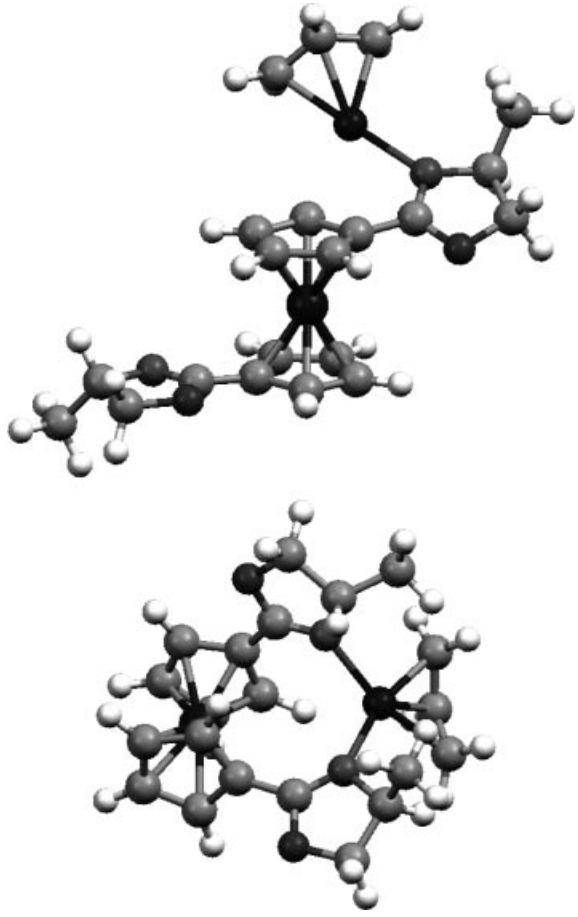


Figure 5. Equilibrium structures of complexes **1c** (top) and **1d** (bottom).

A possible explanation for the preferred monodenticity of the ligands might be the hindrance of rotation of the oxazoline moiety around the C–C axis. Taking into account the crystal structure analyses, the nitrogen atoms are not orientated toward each other and therefore the nitrogen lone-pairs in the solid state point in opposite directions.

Conclusions

Bisoxazolines are known to be excellent ligands in many enantioselective syntheses. A central factor in enantioselective synthesis is the formation of chelate structures by coordination of multidentate ligands to transition metals. The chelation process therefore has a great influence on the success of metal complexes in many catalytic processes.

We have described the synthesis and characterization of a wide variety of differently substituted 1,1′-bis(oxazolin-2-yl)ferrocenes with substituents located in either the 4- or 5-position of the oxazoline rings and being either alkyl or aryl groups. The synthesized compounds were characterized by standard analytical methods (NMR, elemental analysis). Additionally, for compounds **6b**, **7b**, **11b**, **12b**, **13b**, and **14b** the absolute configuration was determined by single-crystal X-ray diffraction analysis.

The catalytic activity of these compounds was tested in the palladium-catalyzed allylic alkylation. These experiments showed that this type of ligand possesses no activity in the test reaction and that a change of the substituent on the oxazoline ring does not influence this. We suppose that the lack of catalytic activity results from the insufficient coordination properties of the studied 1,1′-bis(oxazolin-2-yl)ferrocenes, i.e., chelate formation with the palladium center, a fact that was enlightened in mass spectrometric studies: the bisoxazolines are not capable of functioning as bidentate ligands. This feature was found to be independent of the type of substituents as well as their positions on the oxazoline ring. Comparing the presented results with the outcome of an NMR study reported by Imai and coworkers it can be assumed that the effect is also independent of the type of palladium complex.

In contrast, DFT calculations for this type of compounds revealed, as expected, that chelating structures are energetically more stable than the equivalent monodentate complexes. Therefore it is suggested that the chelate formation of the ferrocene ligands with an allylpalladium moiety instead of the bidentate one is kinetically controlled.

Experimental Section

General Remarks: All reactions were carried out in dry solvents under argon. 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 298 K in [D$_6$]DMSO or $CDCl_3$. Optical rotations were measured with a Perkin–Elmer 341 polarimeter using a 10 cm cell. Melting points were determined with a Büchi B-540 apparatus and are uncorrected. Electrospray ionization mass spectra were recorded on a Bruker esquire$_{3000}$ spectrometer in positive-ion mode (see Table 5 for measurement parameters). 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 (Fluka-60 70–230 mesh) was used for column chromatography and silica gel (Polygram® SIL G/UV$_{254}$) for thin layer chromatography.

The full geometry optimization of all structures was carried out in Cartesian coordinates with the Gaussian 98[69] program package at the DFT level of theory. The calculations were performed using Becke's three-parameter hybrid exchange functional[70] in combination with the gradient-corrected correlation functional of Lee et al.[71] (B3LYP). A quasi-relativistic Stuttgart pseudopotential was used for the 28 core-electrons, the appropriate contracted basis set (8s7p6d)/[6s5p3d][72] for the palladium atom, and the 6-31G* basis set[73–76] for other atoms. For the Fe atom, the relativistic Stuttgart pseudopotential describing 10 core-electrons and the appropriate contracted basis set (8s7p6d1f)/[6s5p3d1f][77] was also used in some calculations. Symmetry operations were not applied for all structures. The Hessian matrix was calculated analytically for all equilibrium structures to prove the location of correct minima (no imaginary frequencies were found) and to estimate the thermodynamic functions calculated at 25 °C. Solvent effects were taken into account at the single-point calculations based on the gas-phase equilibrium geometries by using the polarizable continuum model[78] in the CPCM version[79] with CH_2Cl_2 as a solvent.

The *N*-substituted 1,1′-ferrocenedicarboxamides **7a**, **12a**, and **14a**, 1,1′-bis[(*S*)-4-isopropyloxazolin-2-yl]ferrocene (**7b**), 1,1′-bis[(*S*)-4-*tert*-butyloxazolin-2-yl]ferrocene (**12b**), and 1,1′-bis[(*S*)-4-phenyloxazolin-2-yl]ferrocene (**14b**) were prepared following a literature procedure.[39] The synthesized amides were stable for more than one year at room temperature while the oxazolines degraded over time. Therefore they should be stored under argon and in the refrigerator.

***N*,*N*′-Bis[(1*S*)-(2-hydroxy-1-methylethyl)]ferrocene-1,1′-dicarboxamide (1a):** A solution of 1,1′-ferrocenyldicarbonyl dichloride (0.78 g, 2.50 mmol) in CH_2Cl_2 (30 mL) was added slowly at 0 °C to a solution of (*R*)-(–)-2-amino-1-propanol (0.37 g, 5.00 mmol) and triethylamine (0.7 mL, 5.05 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred for 4 h, the formed precipitate was filtered off and washed five times with CH_2Cl_2 (30 mL). This procedure yielded 0.69 g (71%) of pure product after drying in vacuo. $[\alpha]_D^{20}$ = +18 (*c* = 0.25, DMSO); m.p. 200–201 °C decomp. ^{1}H NMR ([D$_6$]DMSO): δ = 7.52 (d, ^3J = 7.6 Hz, 2 H, N*H*), 4.75 (br. s, 4 H, Fc-*H*), 4.29 (br. s, 4 H, Fc-*H*), 3.97 (m, 2 H, NHC*H*), 3.45 (m, 2 H, HOCH_2), 3.38 (m, 2 H, HOCH_2), 1.12 (d, ^3J = 6.5 Hz, 6 H, CH_3) ppm. ^{13}C{^{1}H} NMR: δ = 169.24 (*C*O), 78.83 (Fc-*C*), 72.46 (Fc-*C*), 70.95 (Fc-*C*), 70.65 (Fc-*C*), 65.34 (HO*C*H$_2$), 47.78 (NH*C*H), 18.19 (*C*H$_3$) ppm. $C_{18}H_{24}FeN_2O_4$ (388.2): calcd. C 55.69, H 6.23, N 7.22; found C 55.50, H 6.08, N 6.96.

***N*,*N*′-Bis[(1*S*)-(1-hydroxy-1-methylethyl)]ferrocene-1,1′-dicarboxamide (2a):** Following the same procedure as described for **1a** yielded 0.95 g (98%) of **2a**. $[\alpha]_D^{20}$ = +4 (*c* = 0.25, DMSO); m.p. 122–123 °C decomp. ^{1}H NMR ([D$_6$]DMSO): δ = 7.92 (br. s, 2 H, N*H*), 4.87 (br. s, 2 H, O*H*), 4.77 (br. s, 2 H, Fc-*H*), 4.74 (br. s, 4 H, Fc-*H*), 3.81 (m, 2 H, HOC*H*), 3.15 (m, 2 H, NHCH_2), 3.14 (m, 2 H, NHCH_2), 1.10 (d, ^3J = 6.5 Hz, 6 H, CH_3) ppm. ^{13}C{^{1}H} NMR: δ = 169.66 (*C*O), 78.83 (Fc-*C*), 72.33 (Fc-*C*), 70.74 (Fc-*C*), 70.45 (Fc-*C*), 66.16 (HO*C*H), 47.78 (NH*C*H), 18.19 (*C*H$_3$) ppm. $C_{18}H_{24}FeN_2O_4$ (388.2): calcd. C 55.69, H 6.23, N 7.22; found C 55.41, H 6.44, N 7.15.

***N*,*N*′-Bis[(1*R*)-(1-(hydroxymethyl)propyl]ferrocene-1,1′-dicarboxamide (3a):** A solution of 1,1′-ferrocenyldicarbonyl dichloride (0.78 g, 2.50 mmol) in CH_2Cl_2 (20 mL) was added slowly at 0 °C to a solution of (*R*)-(–)-2-amino-1-butanol (0.45 g, 5.00 mmol) and triethylamine (0.70 mL, 5.05 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred for 4 h and washed with a saturated solution of $NaHCO_3$ and then with brine. The organic phase was dried with Na_2SO_4 and the solvent was removed in vacuo. This procedure yielded 0.68 g (65%) of the title compound **3a** after purification by column chromatography. $[\alpha]_D^{20}$ = –17 (*c* = 0.25, DMSO); m.p. 181–182 °C decomp. ^{1}H NMR ($CDCl_3$): δ = 6.73 (d, ^3J = 6.0 Hz, 2 H, N*H*), 4.70 (br. s, 2 H, Fc-*H*), 4.45 (br. s, 4 H, Fc-*H*), 4.30 (br. s, 2 H, Fc-*H*), 4.26 (br. s, 2 H, O*H*), 3.91 (br. s, 2 H, NHC*H*), 3.83 (br. s, 2 H, HOCH_2), 3.78 (br. s, 2 H, HOCH_2), 1.97 (m, 4 H, CH_2CH$_3$), 1.01 (dd, ^3J = 7.0, 8.5 Hz, 6 H, CH$_2$CH_3) ppm. ^{13}C{^{1}H} NMR: δ = 170.91 (*C*O), 78.28 (Fc-*C*), 72.60 (Fc-*C*), 71.81 (Fc-*C*), 71.34 (Fc-*C*), 69.37 (Fc-*C*), 63.25 (HO*C*H$_2$), 57.51 (NH*C*H), 29.75 (*C*H$_2$CH$_3$), 20.04 (CH$_2$*C*H$_3$) ppm. $C_{20}H_{28}FeN_2O_4$ (416.3): calcd. C 57.70, H 6.78, N 6.73; found C 57.59, H 6.66, N 6.51.

Ferrocene-1,1′-dicarboxamide 4a: Following the same procedure as described for **3a** yielded 0.89 g (86%) of **4a**. $[\alpha]_D^{20}$ = +20 (*c* = 0.25, DMSO); m.p. 181–182 °C decomp. ^{1}H NMR ($CDCl_3$): δ = 6.70 (d, ^3J = 8.5 Hz, 2 H, N*H*), 4.71 (br. s, 2 H, Fc-*H*), 4.49 (br. s, 2 H, Fc-*H*), 4.44 (br. s, 2 H, Fc-*H*), 4.35 (br. s, 2 H, O*H*), 4.33 (br. s, 2 H, Fc-*H*), 4.05 (m, 2 H, NHC*H*), 3.87 (dd, ^3J = 3.0, 11.5 Hz, 2 H, HOCH_2), 3.67 (dd, ^3J = 6.0, 11.5 Hz, 2 H, HOCH_2), 1.65 (m, 4 H, CH_2CH$_3$), 1.00 (dd, *J* = 6.0, 11.5 Hz, 6 H, CH$_2$CH_3) ppm. ^{13}C{^{1}H} NMR: δ = 170.88 (*C*O), 78.28 (Fc-*C*), 71.77 (Fc-*C*), 71.46 (Fc-*C*), 69.87 (Fc-*C*), 64.77 (HO*C*H$_2$), 53.77 (NH*C*H), 24.79 (*C*H$_2$CH$_3$),

11.19 (CH_2CH_3) ppm. $C_{20}H_{28}FeN_2O_4$ (416.3): calcd. C 57.70, H 6.78, N 6.73; found C 57.63, H 6.83, N 6.68.

Ferrocene-1,1′-dicarboxamide 5a: Following the same procedure as described for **3a** yielded 0.88 g (79%) of **5a**. M.p. 47–48 °C. ^{1}H NMR ($CDCl_3$): δ = 6.77 (d, ^3J = 8.5 Hz, 1 H, N*H*), 6.69 (d, ^3J = 9.0 Hz, 1 H, N*H*), 4.73 (br. s, 2 H, Fc-*H*), 4.55 (br. s, 1 H, Fc-*H*), 4.50 (br. s, 1 H, Fc-*H*), 4.45 (br. s, 1 H, Fc-*H*), 4.41 (br. s, 2 H, Fc-*H*), 4.34 (br. s, 1 H, Fc-*H*), 4.15 (m, 2 H, NHC*H*), 3.87 (dd, ^3J = 3.0, 11.0 Hz, 2 H, HOCH_2), 3.65 (dd, ^3J = 5.0, 11.0 Hz, 2 H, HOCH_2), 1.61–1.52 (m, 4 H, CH_2CH$_2$CH$_3$), 1.47–1.36 (m, 4 H, CH$_2$CH_2CH$_3$), 0.97 (t, ^3J = 8.0 Hz, 3 H, CH$_2$CH$_2$CH_3), 0.94 (t, ^3J = 7.0, 3 H, CH$_2$CH$_2$CH_3) ppm. ^{13}C{^{1}H} NMR: δ = 170.89 (*C*O), 170.86 (*C*O), 78.26 (Fc-*C*), 77.87 (Fc-*C*), 72.43 (Fc-*C*),72.21 (Fc-*C*), 71.81 (Fc-*C*), 71.57 (Fc-*C*), 71.44 (Fc-*C*), 70.11 (Fc-*C*), 69.83 (Fc-*C*), 65.64 (HO*C*H$_2$), 65.23 (HO*C*H$_2$), 52.00 (NH*C*H), 51.95 (NH*C*H), 33.88 (*C*H$_2$CH$_2$CH$_3$) 33.58 (*C*H$_2$CH$_2$CH$_3$), 19.82 (CH$_2$*C*H$_2$CH$_3$), 14.43 (CH$_2$CH$_2$*C*H$_3$), 14.39 (CH$_2$CH$_2$*C*H$_3$) ppm. $C_{22}H_{32}FeN_2O_4$ (444.3): calcd. C 59.47, H 7.26, N 6.30; found C 59.28, H 7.30, N 6.21.

Ferrocene-1,1′-dicarboxamide 6a:[42] Yield: 0.97 g (87%). $[\alpha]_D^{20}$ = –53 (*c* = 0.25, DMSO); m.p. 108–109 °C. ^{1}H NMR ($CDCl_3$): δ = 6.65 (d, ^3J = 9.0 Hz, 2 H, N*H*), 4.72 (br. s, 2 H, Fc-*H*), 4.46 (br. s, 4 H, Fc-*H*), 4.32 (br. s, 2 H, Fc-*H*), 4.16 (br. s, 2 H, O*H*), 3.92 (m, 2 H, NHC*H*), 3.85 (dd, ^3J = 3.0, 11.5 Hz, 2 H, HOCH_2) 3.76 (dd, ^3J = 6.0, 11.5 Hz, 2 H, HOCH_2), 1.97 (m, ^3J = 7.0 Hz, 2 H, C*H*(CH$_3$)$_2$], 1.03 (d, ^3J = 7.0 Hz, 6 H, CH_3), 1.00 (d, ^3J = 7.0 Hz, 6 H, CH_3) ppm. ^{13}C{^{1}H} NMR: δ = 170.84 (*C*O), 78.32 (Fc-*C*), 72.45 (Fc-*C*), 71.79 (Fc-*C*), 71.37 (Fc-*C*), 69.43 (Fc-*C*), 63.30 (HO*C*H$_2$), 57.50 (NH*C*H), 29.80 [*C*H(CH$_3$)$_2$], 20.02 (*C*H$_3$), 19.70 (*C*H$_3$) ppm. $C_{22}H_{32}FeN_2O_4$ (444.3): calcd. C 59.47, H 7.26, N 6.30; found C 59.35, H 7.09, N 6.35.

Ferrocene-1,1′-dicarboxamide 8a: Following the same procedure as described for **3a** yielded 0.73 g (62%) of **8a**. M.p. 39–40 °C. ^{1}H NMR ($CDCl_3$): δ = 6.68 (d, ^3J = 8.0 Hz, 1 H, N*H*), 6.59 (d, ^3J = 8.5 Hz, 1 H, N*H*), 4.75 (br. s, 2 H, Fc-*H*), 4.55 (br. s, 1 H, Fc-*H*), 4.51 (br. s, 1 H, Fc-*H*), 4.46 (br. s, 1 H, Fc-*H*), 4.43 (br. s, 2 H, Fc-*H*), 4.36 (br. s, 1 H, Fc-*H*), 4.14 (m, 2 H, NHC*H*), 3.89 (dd, ^3J = 3.0, 12.0 Hz, 2 H, HOCH_2), 3.65 (dd, ^3J = 5.5, 11.0 Hz, 2 H, HOCH_2), 1.59 [m, 4 H, CH_2(CH$_2$)$_2$CH$_3$], 1.36 [m, 8 H, CH$_2$(CH_2)$_2$CH$_3$], 0.92 [m, 6 H, CH$_2$(CH$_2$)$_2$CH_3]. ^{13}C{^{1}H} NMR: δ = 170.82 (*C*O), 170.78 (*C*O), 78.30 (Fc-*C*), 77.88 (Fc-*C*), 72.51 (Fc-*C*), 72.18 (Fc-*C*), 71.80 (Fc-*C*), 71.53 (Fc-*C*), 71.46 (Fc-*C*), 70.03 (Fc-*C*), 69.82 (Fc-*C*), 65.74 (NH*C*H), 65.29 (NH*C*H), 52.27 (HO*C*H$_2$), 52.19 (HO*C*H$_2$), 31.52 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 31.18 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 28.79 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 23.02 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 22.97 (CH$_2$CH$_2$-*C*H$_2$CH$_3$), 14.45 (CH$_2$CH$_2$CH$_2$*C*H$_3$), 14.41 (CH$_2$CH$_2$CH$_2$*C*H$_3$) ppm. $C_{24}H_{36}FeN_2O_4$ (472.4): calcd. C 61.02, H 7.68, N 5.93; found C 61.15, N 5.93.

Ferrocene-1,1′-dicarboxamide 9a: Following the same procedure as described for **3a** yielded 0.81 g (68%) of **9a**. $[\alpha]_D^{20}$ = –19 (*c* = 0.25, DMSO); m.p. 59–60 °C. ^{1}H NMR ($CDCl_3$): δ = 6.78 (d, ^3J = 8.5 Hz, 2 H, N*H*,), 4.69 (br. s, 2 H, Fc-*H*), 4.45 (br. s, 2 H, Fc-*H*), 4.43 (br. s, 2 H, Fc-*H*), 4.30 (br. s, 2 H, Fc-*H*), 4.25 (m, 2 H, NHC*H*), 3.85 (dd, ^3J = 3.0, 11.0 Hz, 2 H, HOCH_2), 3.61 (dd, ^3J = 5.5, 11.5 Hz, 2 H, HOCH_2), 1.69 [m, 2 H, CH_2CH(CH$_3$)$_2$], 1.57 [m, 2 H, CH_2CH(CH$_3$)$_2$], 1.38 [m, 2 H, CH$_2$C*H*(CH$_3$)$_2$], 0.98 (d, ^3J = 6.6 Hz, 12 H, CH_3) ppm. ^{13}C{^{1}H} NMR: δ = 170.88 (*C*O), 78.14 (Fc-*C*), 72.50 (Fc-*C*), 71.84 (Fc-*C*), 71.42 (Fc-*C*), 69.63 (Fc-*C*), 65.73 (HO*C*H$_2$), 50.34 (NH*C*H), 40.80 [*C*H$_2$CH(CH$_3$)$_2$], 25.46 [CH$_2$*C*H(CH$_3$)$_2$], 23.59 (*C*H$_3$), 22.67 (*C*H$_3$) ppm. $C_{24}H_{36}FeN_2O_4$ (472.4): calcd. C 61.02, H 7.68, N 5.93; found C 60.81, H 7.52, N 5.75.

Ferrocene-1,1′-dicarboxamide 10a: Following the same procedure as described for **3a** yielded 1.14 g (96%) of **10a**. $[\alpha]_D^{20}$ = +18 (*c* = 0.25, DMSO); m.p. 53–54 °C. ^{1}H NMR ($CDCl_3$): δ = 6.70 (d, ^3J = 9.0 Hz, 2 H, N*H*,), 4.69 (br. s, 2 H, Fc-*H*), 4.45 (br. s, 2 H, Fc-*H*), 4.26 (m, 2 H, NHC*H*), 3.87 (dd, ^3J = 3.0, 11.0 Hz, 2 H, HOCH_2), 3.61 (dd, ^3J = 5.5, 11.0 Hz, 2 H, HOCH_2), 1.70 [m, 2 H, CH_2CH(CH$_3$)$_2$], 1.57 [m, 2 H, CH_2CH(CH$_3$)$_2$], 1.38 [m, 2 H, CH$_2$C*H*(CH$_3$)$_2$], 0.98 (d, ^3J = 6.0 Hz, 12 H, CH_3) ppm. ^{13}C{^{1}H} NMR δ = 170.83 (*C*O), 78.16 (Fc-*C*), 72.48 (Fc-*C*), 71.81 (Fc-*C*), 71.42 (Fc-*C*), 69.60 (Fc-*C*), 65.77 (HO*C*H$_2$), 50.35 (NH*C*H), 40.82 [*C*H$_2$CH(CH$_3$)$_2$], 25.46 [CH$_2$*C*H(CH$_3$)$_2$], 23.58 (*C*H$_3$), 22.66 (*C*H$_3$) ppm. $C_{24}H_{36}FeN_2O_4$ (472.4): calcd. C 61.02, H 7.68, N 5.93; found C 60.80, H 7.83, N 5.82.

Ferrocene-1,1′-dicarboxamide 11a: Following the same procedure as described for **3a** yielded 1.08 g (91%) of **11a**. $[\alpha]_D^{20}$ = +23 (*c* = 0.25, DMSO); m.p. 60–61 °C. ^{1}H NMR ($CDCl_3$): δ = 6.66 (d, ^3J = 8.5 Hz, 2 H, N*H*), 4.72 (br. s, 2 H, Fc-*H*), 4.46 (br. s, 4 H, Fc-*H*), 4.32 (br. s, 2 H, Fc-*H*), 3.99 (m, 2 H, NHC*H*), 3.85 (dd, ^3J = 3.0, 11.5 Hz, 2 H, HOCH_2), 3.77 (dd, ^3J = 6.0, 11.5 Hz, 2 H, HOCH_2), 1.78 [m, 2 H, C*H*(CH$_3$)CH$_2$CH$_3$], 1.58 [m, 2 H, CH(CH$_3$) CH_2CH$_3$], 1.24 [m, 2 H, CH(CH$_3$)CH_2CH$_3$], 1.00 (d, ^3J = 6.5 Hz, 6 H, CH_3), 0.95 (t, ^3J = 7.0 Hz, 6 H, CH_3) ppm. ^{13}C{^{1}H} NMR: δ = 170.73 (*C*O), 78.27 (Fc-*C*), 72.49 (Fc-*C*), 71.79 (Fc-*C*), 71.36 (Fc-*C*), 69.36 (Fc-*C*), 63.03 (HO*C*H$_2$), 56.05 (NH*C*H), 36.12 [*C*H(CH$_3$)CH$_2$CH$_3$], 26.21 [CH(CH$_3$)*C*H$_2$CH$_3$], 15.96 (CH$_3$), 11.63 (CH$_3$) ppm. $C_{24}H_{36}FeN_2O_4$ (472.4): calcd. C 61.02, H 7.68, N 5.93; found C 61.12, H 7.70, N 5.83.

Ferrocene-1,1′-dicarboxamide 13a: Following the same procedure as described for **3a** yielded 1.30 g (83%) of **13a**. $[\alpha]_D^{20}$ = –88 (*c* = 0.25, DMSO); m.p. 207–208 °C decomp. ^{1}H NMR ([D$_6$]DMSO): δ = 8.22 (d, ^3J = 7.5 Hz, 2 H, N*H*,), 7.41–7.26 (m, 10 H, Ph-*H*), 5.04 (m, 4 H, NHC*H*, O*H*), 4.91 (br. s, 2 H, Fc-*H*), 4.60 (br. s, 2 H, Fc-*H*), 4.31 (br. s, 2 H, Fc-*H*), 4.26 (br. s, 2 H, Fc-*H*), 3.70.(m, 4 H, HOCH_2) ppm. ^{13}C{^{1}H} NMR: δ = 169.53 (*C*O), 142.36 (Ph-*C*), 128.97 (Ph-*C*), 127.90 (Ph-*C*), 127.73 (Ph-*C*), 78.48 (Fc-*C*), 72.46 (Fc-*C*), 72.25 (Fc-*C*), 71.90 (Fc-*C*), 69.67 (Fc-*C*), 65.23 (HO*C*H$_2$), 56.49 (NH*C*H) ppm. $C_{28}H_{28}FeN_2O_4$ (512.4): calcd. C 65.64, H 5.51, N 5.47; found C 65.52, H 5.41, N 5.25.

Ferrocene-1,1′-dicarboxamide 15a: Following the same procedure as described for **3a** yielded 1.37 g (87%) of **15a**. M.p. 207–208 °C decomp. ^{1}H NMR ([D$_6$]DMSO): δ = 7.96 (m, 2 H, N*H*), 7.42–7.27 (m, 10 H, Ph-*H*), 5.61 (dd, ^3J = 4.5, 9.0 Hz, 2 H, HOC*H*), 4.82 (br. s, 2 H, O*H*), 4.71 (br. s, 4 H, Fc-*H*), 4.29 (br. s, 4 *H*, Fc-*H*), 3.46 (m, 2 H, NHCH_2), 3.26 (m, 2 H, NHCH_2) ppm. ^{13}C{^{1}H} NMR: δ = 169.60 (*C*O), 144.69 (Ph-*C*), 128.94 (Ph-*C*), 127.94 (Ph-*C*), 126.93 (Ph-*C*), 78.52 (Fc-*C*), 72.43 (Fc-*C*), 72.19 (Fc-*C*),70.65 (Fc-*C*), 70.53 (Fc-*C*), 70.43 (HO*C*H), 48.15 (NH*C*H$_2$) ppm. $C_{28}H_{28}FeN_2O_4$ (512.4): calcd. C 65.64, H 5.51, N 5.47; found C 65.34, H 5.69, N 5.31.

Ferrocene-1,1′-dicarboxamide 16a: Following the same procedure as described for **3a** yielded 1.31 g (79%) of **16a**. $[\alpha]_D^{20}$ = +41 (*c* = 0.25, DMSO); m.p. 173–174 °C decomp. ^{1}H NMR ([D$_6$]DMSO): δ = 7.67 (d, ^3J = 8.5, 2 H, N*H*), 7.31 (m, 8 H, Ph-*H*), 7.18 (m, 2 H, Ph-*H*), 4.91 (t, ^3J = 5.5 Hz, 2 H, NHC*H*,), 4.66 (br. s, 2 H, Fc-*H*), 4.32 (br. s, 2 H, Fc-*H*), 4.16 (br. s, 2 H, O*H*), 4.08 (br. s, 2 H, Fc-*H*), 4.05 (br. s, 2 H, Fc-*H*), 3.51 (m, 2 H, HOCH_2), 3.43 (m, 2 H, HOCH_2), 2.99 (m, 2 H, CH_2Ph), 2.76 (m, 2 H, CH_2Ph) ppm. ^{13}C{^{1}H} NMR: δ = 169.33 (*C*O), 140.53 (Ph-*C*), 129.94 (Ph-*C*), 128.99 (Ph-*C*), 126.77 (Ph-*C*), 78.62 (Fc-*C*), 72.37 (Fc-*C*), 72.20 (Fc-*C*), 71.94 (Fc-*C*), 69.12 (Fc-*C*), 64.21 (HO*C*H$_2$), 53.65 (NH*C*H), 37.39 (*C*H$_2$Ph) ppm. $C_{30}H_{32}FeN_2O_4$ (540.4): calcd. C 66.67, H 5.97, N 5.18; found C 66.33, H 5.96, N 5.04.

Ferrocene-1,1′-dicarboxamide 17a: Following the same procedure as described for **3a** yielded 1.19 g (72%) of **17a**. $[\alpha]_D^{20}$ = –37 (*c* = 0.25, DMSO); m.p. 175–176 °C decomp. ^{1}H NMR ([D$_6$]DMSO): δ = 7.68 (d, ^3J = 8.5 Hz, 2 H, N*H*), 7.31 (m, 8 H, Ph-*H*), 7.18 (m, 2 H, Ph-*H*), 4.92 (t, ^3J = 5.0 Hz, 2 H, NHC*H*), 4.66 (br. s, 2 H, Fc-*H*), 4.32 (br. s, 2 H, Fc-*H*), 4.16 (br. s, 2 H, O*H*), 4.07 (br. s, 2 H, Fc-*H*), 4.04 (br. s, 2 H, Fc-*H*), 3.51(m, 2 H, HOCH_2), 3.42 (m, 2 H, HOCH_2), 2.99 (m, 2 H, CH_2Ph), 2.75 (m, 2 H, CH_2Ph) ppm. ^{13}C{^{1}H} NMR: δ = 169.34 (*C*O), 140.53 (Ph-*C*), 129.94 (Ph-*C*), 128.99 (Ph-*C*), 126.77 (Ph-*C*), 78.62 (Fc-*C*), 72.37 (Fc-*C*), 72.20 (Fc-*C*), 71.94 (Fc-*C*), 69.12 (Fc-*C*), 64.21 (HO*C*H$_2$), 53.65 (NH*C*H), 37.39 (*C*H$_2$Ph) ppm. $C_{30}H_{32}FeN_2O_4$ (540.4): calcd. C 66.67, H 5.97, N 5.18; found C 66.57, H 5.90, N 4.99.

Ferrocene-1,1′-dicarboxamide 18a: Following the same procedure as described for **1a** yielded 1.61 g (79%) of **18a**. $[\alpha]_D^{20}$ = +76 (*c* = 0.25, DMSO); m.p. 277–278 °C decomp. ^{1}H NMR ([D$_6$]DMSO): δ = 8.25 (d, ^3J = 9.0 Hz, 2 H, N*H*), 7.59–7.48 (m, 8 H, Ph-*H*), 7.44–7.02 (m, 12 H, Ph-*H*), 5.44 (br. s, 2 H, O*H*), 5.04 (t, ^3J = 9.0 Hz, 2 H, NHC*H*,), 4.91 (dd, ^3J = 5.5, 8.5 Hz, 2 H, C*H*OH,), 4.35 (br. s, 2 H, Fc-*H*), 4.18 (br. s, 2 H, Fc-*H*), 3.82 (br. s, 2 H, Fc-*H*), 3.78 (br. s, 2 H, Fc-*H*) ppm. ^{13}C{^{1}H} NMR: δ = 168.54 (*C*O), 145.00 (Ph-*C*), 143.07 (Ph-*C*), 129.15 (Ph-*C*), 128.70 (Ph-*C*), 128.55 (Ph-*C*), 128.10 (Ph-*C*), 127.94 (Ph-*C*), 127.57 (Ph-*C*), 78.44 (Fc-*C*), 75.39 (*C*HOH), 72.23 (Fc-*C*), 71.81 (Fc-*C*), 71.07 (Fc-*C*), 69.17 (Fc-*C*), 59.77 (NH*C*H) ppm. $C_{40}H_{36}FeN_2O_4$ (664.6): calcd. C 72.29, H 5.46, N 4.22; found C 72.46, H 5.45, N 4.14.

1,1′-Bis[(*S*)-4-methyloxazolin-2-yl]ferrocene (1b): A solution of *p*-toluenesulfonyl chloride (0.42 g, 2.20 mmol) in CH_2Cl_2 (20 mL) was added dropwise at 0 °C to a solution of **1a** (0.39 g, 1.00 mmol), triethylamine (0.70 mL, 5.00 mmol), and a catalytic amount of 4-(dimethylamino)pyridine in CH_2Cl_2 (50 mL). The reaction mixture was stirred at room temperature for 10 h and then washed with a saturated solution of $NaHCO_3$ and with brine. The water layer was extracted with CH_2Cl_2 and the combined organic phases were dried with Na_2SO_4. Purification by column chromatography gave 0.31 g (88%) of **1b**. $[\alpha]_D^{20}$ = +77 (*c* = 0.25, CH_2Cl_2); m.p. 85–86 °C. ^{1}H NMR ($CDCl_3$): δ = 4.72 (br. s, 4 H, Fc-*H*), 4.41 (t, ^3J = 8.5, 2 H, OCH_2), 4.34 (br. s, 4 H, Fc-*H*), 4.20 (m, 2 H, NC*H*), 3.84 (t, ^3J = 8.0 Hz, 2 H, OCH_2), 1.30 (d, ^3J = 6.6 Hz, 6 H, CH_3) ppm. ^{13}C{^{1}H} NMR: δ = 165.39 (*C*O), 74.15 (OCH$_2$), 72.38 (Fc-*C*), 72.26 (Fc-*C*), 72.01 (Fc-*C*), 71.02 (Fc-*C*), 70.94 (Fc-*C*), 62.26 (NCH), 21.91(*C*H$_3$) ppm. $C_{18}H_{20}FeN_2O_2$ (352.2): calcd. C 61.38, H 5.72, N 7.95; found C 61.36, H 5.80, N 7.76.

1,1′-Bis[(*S*)-5-methyloxazolin-2-yl]ferrocene (2b): Following the same procedure as described for **1b** yielded 0.28 g (79%) of **2b**. $[\alpha]_D^{20}$ = +22 (*c* = 0.25, CH_2Cl_2); m.p. 101–102 °C. ^{1}H NMR ($CDCl_3$): δ = 4.73 (m, 6 H, Fc–*H*, OC*H*), 4.35 (br. s, 2 H, Fc-*H*), 4.32 (br. s, 2 H, Fc-*H*), 3.97 (dd, $^{3,2}J$ = 9.5, 14.0 Hz, 2 H, NCH_2), 3.44 (dd, $^{3,2}J$ = 7.0, 14.0 Hz, 2 H, NCH_2), 1.40 (d, ^3J = 6.5 Hz, 6 H, CH_3) ppm. ^{13}C{^{1}H} NMR: δ = 165.64 (*C*O), 76.20 (O*C*H), 72.42 (Fc-*C*), 72.32 (Fc-*C*), 72.15 (Fc-*C*), 70.78 (Fc-*C*), 70.59 (Fc-*C*), 62.00 (NCH$_2$), 21.62(*C*H$_3$) ppm. $C_{18}H_{20}FeN_2O_2$ (352.2): calcd. C 61.38, H 5.72, N 7.95; found C 61.50, H 5.52, N 7.93.

1,1′-Bis[(*R*)-4-ethyloxazolin-2-yl]ferrocene (3b): Following a similar procedure as described for **1b**, but changing *p*-toluenesulfonyl chloride for methanesulfonyl chloride, yielded 0.29 g (77%) of **3b**. $[\alpha]_D^{20}$ = –63 (*c* = 0.25, CH_2Cl_2); m.p. 75–76 °C. ^{1}H NMR ($CDCl_3$): δ = 4.75 (br. s, 4 H, Fc-*H*), 4.38 (t, ^3J = 9.0 Hz, 2 H, OCH_2,), 4.35 (br. s, 4 H, Fc-*H*), 4.10 (m, 2 H, NC*H*), 3.97 (t, ^3J = 8.0 Hz, 2 H, OCH_2), 1.75 (m, 2 H, CH_2CH$_3$), 1.48 (m, 2 H, CH_2CH$_3$), 0.99 (t, ^3J = 7.5 Hz, 6 H, CH_3) ppm. ^{13}C{^{1}H} NMR: δ = 165.39 (*C*O), 72.37 (Fc-*C*), 72.32 (Fc-*C*), 72.13 (Fc–*C*, OCH$_2$), 71.01 (Fc-*C*), 70.82 (Fc-*C*), 68.27 (NCH), 28.87 (*C*H$_2$), 10.37(*C*H$_3$) ppm. $C_{20}H_{24}FeN_2O_2$ (380.3): calcd. C 63.17, H 6.36, N 7.37; found C 63.28, H 6.36, N 7.45.

1,1′-Bis[(*S*)-4-ethyloxazolin-2-yl]ferrocene (4b): Following the same procedure as described for **3b** yielded 0.30 g (79%) of **4b**. $[\alpha]_D^{20}$ = +52 (*c* = 0.25, CH_2Cl_2); m.p. 72–73 °C. ^{1}H NMR ($CDCl_3$): δ = 4.75 (br. s, 4 H, Fc-*H*), 4.39 (t, ^3J = 8.0 Hz, 2 H, OCH_2,), 4.36 (br. s, 4 H, Fc-*H*), 4.10 (m, 2 H, NC*H*), 3.98 (t, ^3J = 8.0 Hz, 2 H, OCH_2), 1.76 (m, 2 H, CH_2CH$_3$), 1.59 (m, 2 H, CH_2CH$_3$), 1.00 (t, ^3J = 7.5 Hz, 6 H, CH_3) ppm. ^{13}C{^{1}H} NMR: δ = 165.39 (*C*O), 72.37 (Fc-*C*), 72.32 (Fc-*C*), 72.13 (Fc–*C*, OCH$_2$), 71.01 (Fc-*C*), 70.82 (Fc-*C*), 68.30 (NCH), 28.88 (*C*H$_2$), 10.38 (*C*H$_3$) ppm. $C_{20}H_{24}FeN_2O_2$ (380.3): calcd. C 63.17, H 6.36, N 7.37; found C 63.40, H 6.24, N 7.34.

1,1′-Bis(4-propyloxazolin-2-yl)ferrocene (5b): Following the same procedure as described for **3b** yielded 0.18 g (44%) of **5b** as an oil. ^{1}H NMR ($CDCl_3$): δ = 4.74 (br. s, 4 H, Fc-*H*), 4.39 (dd, $^{3,2}J$ = 2.5, 9.0 Hz, 2 H, OCH_2), 4.35 (br. s, 4 H, Fc-*H*), 4.15 (m, 2 H, NC*H*), 3.96 (dd, $^{3,2}J$ = 3.0, 7.5 Hz, 2 H, OCH_2), 1.72 [m, 2 H, (CH_2)$_2$CH$_3$], 1.47 [m, 6 H, (CH_2)$_2$CH$_3$], 0.99 (t, ^3J = 7.0 Hz, 6 H, CH_3) ppm. ^{13}C{^{1}H} NMR: δ = 165.30 (*C*O), 72.60 (OCH$_2$), 72.38 (Fc-*C*), 72.34 (Fc-*C*), 72.32 (Fc-*C*), 72.15 (Fc-*C*), 72.12 (Fc-*C*), 71.01 (Fc-*C*), 70.97 (Fc-*C*), 70.90 (Fc-*C*), 70.84 (Fc-*C*), 66.86 (NCH), 38.49 (*C*H$_2$), 19.51 (*C*H$_2$), 14.55 (*C*H$_3$) ppm. $C_{22}H_{28}FeN_2O_2$ (408.3): calcd. C 64.71, H 6.91, N 6.86; found C 64.54, H 6.83, N 6.83.

1,1′-Bis[(*R*)-4-isopropyloxazolin-2-yl]ferrocene (6b):[42] Yield: 0.37 g (90%). $[\alpha]_D^{20}$ = –83 (*c* = 0.25, CH_2Cl_2); m.p. 64–65 °C. ^{1}H NMR ($CDCl_3$): δ = 4.77 (br. s, 2 H, Fc-*H*), 4.75 (br. s, 2 H, Fc-*H*), 4.36 (br. s, 4 H, Fc-*H*), 4.31 (t, 2 H, OCH_2, J = 9.0), 4.07 (t, ^3J = 9.0 Hz, 2 H, OCH_2), 4.00 (m, 2 H, NC*H*), 1.87 [m, 2 H, C*H*(CH$_3$)$_2$], 1.03 (d, ^3J = 7.0 Hz, 6 H, CH_3,), 0.95 (d, ^3J = 6.5 Hz, 6 H, CH_3) ppm. ^{13}C{^{1}H} NMR: δ = 165.26 (*C*O), 72.84 (NCH), 72.32 (Fc-*C*), 72.27 (Fc-*C*), 70.01 (Fc-*C*), 70.69 (Fc-*C*), 69.91 (OCH$_2$), 32.78 (*C*H), 19.40 (*C*H$_3$), 18.32 (*C*H$_3$) ppm. $C_{22}H_{28}FeN_2O_2$ (408.3): calcd. C 64.71, H 6.91, N 6.86; found C 64.62, H 6.95, N 6.67.

1,1′-Bis(4-butyloxazolin-2-yl)ferrocene (8b): Following the same procedure as described for **3b** yielded 0.34 g (78%) of **8b** as an oil. ^{1}H NMR ($CDCl_3$): δ = 4.76 (br. s, 4 H, Fc-*H*), 4.40 (m, 2 H, OCH_2), 4.36 (br. s, 4 H, Fc-*H*), 4.14 (m, 2 H, OCH_2), 3.96 (m, 2 H, NC*H*), 1.76 [m, 2 H, (CH_2)$_3$CH$_3$], 1.54 [m, 2 H, (CH_2)$_2$CH$_3$], 1.40 [m, 8 H, (CH_2)$_2$CH$_3$], 0.95 (t, ^3J = 7.0 Hz, 6 H, CH_3) ppm. ^{13}C{^{1}H} NMR: δ = 165.31 (*C*O), 72.60 (OCH$_2$), 72.40 (Fc-*C*), 72.37 (Fc-*C*), 72.33 (Fc-*C*), 72.15 (Fc-*C*), 70.98 (Fc-*C*), 70.96 (Fc-*C*), 70.90 (Fc-*C*), 70.84 (Fc-*C*), 67.07 (NCH), 36.00 (*C*H$_2$), 28.41 (*C*H$_2$), 23.16 (*C*H$_2$), 14.44 (*C*H$_3$) ppm. $C_{24}H_{32}FeN_2O_2$ (436.4): calcd. C 66.06, H 7.39, N 6.42; found C 66.00, H 7.27, N 6.36.

1,1′-Bis[(*R*)-4-isobutyloxazolin-2-yl]ferrocene (9b): Following the same procedure as described for **3b** yielded 0.32 g (73%) of **9b** as an oil. $[\alpha]_D^{20}$ = –83 (*c* = 0.25, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ = 4.75 (br. s, 4 H, Fc-*H*), 4.43 (t, ^3J = 8.5 Hz, 2 H, OCH_2), 4.36 (br. s, 4 H, Fc-*H*), 4.19 (m, 2 H, NC*H*), 3.92 (t, ^3J = 7.5 Hz, 2 H, OCH_2), 1.77 (m, 2 H, CH_2CH), 1.71 (m, 2 H, CH_2CH), 1.37 (m, 2 H, CH$_2$C*H*), 0.98 (t, ^3J = 6.5 Hz, 12 H, CH_3) ppm. ^{13}C{^{1}H} NMR: δ = 165.28 (*C*O), 73.21 (OCH$_2$), 72.44 (Fc-*C*), 72.33 (Fc-*C*), 72.08 (Fc-*C*), 71.04 (Fc-*C*), 70.92 (Fc-*C*), 65.41 (NCH), 46.04 (*C*H$_2$), 25.87 (*C*H), 23.49 (*C*H$_3$), 23.01 (*C*H$_3$) ppm. $C_{24}H_{32}FeN_2O_2$ (436.4): calcd. C 66.06, H 7.39, N 6.42; found C 66.02, H 7.45, N 6.34.

1,1′-Bis[(*S*)-4-isobutyloxazolin-2-yl]ferrocene (10b): Following the same procedure as described for **3b** yielded 0.36 g (82%) of **10b** as an oil. $[\alpha]_D^{20}$ = –83 (*c* = 0.25, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ = 4.73 (br. s, 4 H, Fc-*H*), 4.40 (t, ^3J = 8.5 Hz, 2 H, OCH_2), 4.43 (br. s, 4

H, Fc-*H*), 4.16 (m, 2 H, NC*H*), 3.90 (t, ^3J = 7.5 Hz, 2 H, OCH_2), 1.77 (m, 2 H, CH_2CH), 1.69 (m, 2 H, CH_2CH), 1.35 (m, 2 H, CH_2C*H*), 0.97 (t, ^3J = 6.0 Hz, 12 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR: δ = 165.10 (*C*O), 73.15 (O*C*H_2), 72.35 (Fc-*C*), 72.26 (Fc-*C*), 72.17 (Fc-*C*), 70.98 (Fc-*C*), 70.86 (Fc-*C*), 65.50 (N*C*H), 46.06 (*C*H_2), 25.86 (*C*H), 23.50 (*C*H_3), 23.00 (*C*H_3) ppm. $C_{24}H_{32}FeN_2O_2$ (436.4): calcd. C 66.06, H 7.39, N 6.42; found C 66.12, H 7.42, N 6.47.

1,1′-Bis[(*S*)-4-*sec*-butyloxazolin-2-yl]ferrocene (11b): Following the same procedure as described for **3b** yielded 0.35 g (80%) of **11b**. $[\alpha]_D^{20}$ = –83 (*c* = 0.25, CH_2Cl_2); m.p. 78–79 °C. ^1H NMR ($CDCl_3$): δ = 4.77 (br. s, 2 H, Fc-*H*), 4.75 (br. s, 2 H, Fc-*H*), 4.36 (br. s, 4 H, Fc-*H*), 4.29 (t, ^3J = 7.5 Hz, 2 H, OCH_2), 4.11 (m, 2 H, NC*H*), 4.08 (m, 2 H, OCH_2), 1.73 (m, 2 H, C*H*), 1.57 (m, 2 H, CH_2), 1.24 (m, 2 H, CH_2), 0.97 (t, ^3J = 7.0 Hz, 6 H, CH_2CH_3), 0.90 (d, ^3J = 6.5 Hz, 6 H, CHCH_3) ppm. $^{13}C\{^1H\}$ NMR: δ = 165.14 (*C*O), 72.32 (Fc-*C*), 71.36 (N*C*H), 70.83 (Fc-*C*), 70.65 (Fc-*C*), 69.29 (O*C*H_2), 39.10 (*C*H), 26.65 (*C*H_2), 14.55 (*C*H_3), 12.17 (*C*H_3) ppm. $C_{24}H_{32}FeN_2O_2$ (436.4): calcd. C 66.06, H 7.39, N 6.42; found C 65.95, H 7.26, N 6.29.

1,1′-Bis[(*R*)-4-phenyloxazolin-2-yl]ferrocene (13b): Following the same procedure as described for **1b** yielded 0.43 g (91%) of **13b**. $[\alpha]_D^{20}$ = +190 (*c* = 0.25, CH_2Cl_2); m.p. 92–93 °C. ^1H NMR ($CDCl_3$): δ = 7.41–7.28 (m, 10 H, Ph-*H*), 5.26 (dd, $^{3,2}J$ = 8.5, 10.0 Hz, 2 H, NC*H*), 4.91 (br. s, 2 H, Fc-*H*), 4.89 (br. s, 2 H, Fc-*H*), 4.73 (dd, $^{3,2}J$ = 8.5, 10.0 Hz, 2 H, OCH_2), 4.47 (m, 4 H, Fc-*H*), 4.22 (t, ^3J = 8.5 Hz, 2 H, OCH_2) ppm. $^{13}C\{^1H\}$ NMR: δ = 166.92 (*C*O), 142.79 (Ph-*C*), 129.18 (Ph-*C*), 128.03 (Ph-*C*), 127.22 (Ph-*C*), 75.08 (O*C*H_2), 72.61(Fc-*C*), 72.46 (Fc-*C*), 71.81 (Fc-*C*), 71.28 (Fc-*C*), 70.50 (N*C*H) ppm. $C_{28}H_{24}FeN_2O_2$ (476.3): calcd. C 70.60, H 5.08, N 5.88; found C 70.45,<ztabr6" pos="x22> H 5.30, N 5.88.

1,1′-Bis(5-phenyloxazolin-2-yl)ferrocene (15b): Following the same procedure as described for **1b** yielded 0.36 g (76%) of **15b** as an oil. ^1H NMR ($CDCl_3$): δ = 7.43–7.32 (m, 10 H, Ph-*H*), 5.58 (m, 2 H, OC*H*), 4.88 (br. s, 2 H, Fc-*H*), 4.86 (br. s, 2 H, Fc-*H*), 4.44 (br. s, 4 H, Fc-*H*), 4.34 (m, 2 H,NCH_2), 3.86 (m, 2 H, NCH_2) ppm. $^{13}C\{^1H\}$ NMR: δ = 161.21 (*C*O), 141.31 (Ph-*C*), 129.21 (Ph-*C*), 128.71 (Ph-*C*), 126.38 (Ph-*C*),126.30 (Ph-*C*), 81.28 (O*C*H), 72.59(Fc-*C*), 72.49 (Fc-*C*), 72.45 (Fc-*C*), 72.32 (Fc-*C*), 72.15 (Fc-*C*), 71.91 (Fc-*C*), 71.33 (Fc-*C*), 70.93 (Fc-*C*), 70.86 (Fc-*C*), 70.59 (Fc-*C*), 63.53 (N*C*H_2) ppm. $C_{28}H_{24}FeN_2O_2$ (476.3): calcd. C 70.60, H 5.08, N 5.88; found C 70.71, H 5.12, N 5.91.

1,1′-Bis[(*R*)-4-benzyloxazolin-2-yl]ferrocene (16b): Following the same procedure as described for **1b** yielded 0.47 g (93%) of **16b** as an oil. $[\alpha]_D^{20}$ = +34 (*c* = 0.25, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ = 7.34 (m, 4 H, Ph-*H*), 7.27 (m, 6 H, Ph-*H*), 4.78 (br. s, 2 H, Fc-*H*), 4.75 (br. s, 2 H, Fc-*H*), 4.45 (m, 2 H, NC*H*), 4.36 (br. s, 2 H, Fc-*H*), 4.34 (br. s, 2 H, Fc-*H*), 4.27(t, ^3J = 8.0 Hz, 2 H, OCH_2), 4.07 (t, ^3J = 8.0 Hz, 2 H, OCH_2), 3.23 (dd, $^{3,2}J$ = 5.0, 13.5 Hz, 2 H, CH_2Ph), 2.72 (dd, $^{3,2}J$ = 9.0, 13.5 Hz, 2 H, CH_2Ph) ppm. $^{13}C\{^1H\}$ NMR: δ = 166.08 (*C*O), 139.55 (Ph-*C*), 129.71 (Ph-*C*), 128.99 (Ph-*C*), 126.93 (Ph-*C*), 72.50 (Fc-*C*), 72.45 (Fc-*C*), 71.89 (O*C*H_2), 71.08 (Fc-*C*), 70.95 (Fc-*C*), 68.85 (Fc-*C*), 68.27 (N*C*H), 42.17 (*C*H_2Ph) ppm. $C_{30}H_{28}FeN_2O_2$ (504.4): calcd. C 71.44, H 5.60, N 5.55; found C 71.31, H 5.89, N 5.74.

1,1′-Bis[(*S*)-4-benzyloxazolin-2-yl]ferrocene (17b): Following the same procedure as described for **1b** yielded 0.40 g (79%) of **17b** as an oil. $[\alpha]_D^{20}$ = +3 (*c* = 0.25, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ = 7.34 (m, 4 H, Ph-*H*), 7.27 (m, 6 H, Ph-*H*), 4.78 (br. s, 2 H, Fc-*H*), 4.76 (br. s, 2 H, Fc-*H*), 4.45 (m, 2 H, NC*H*), 4.36 (br. s, 2 H, Fc-*H*), 4.34 (br. s, 2 H, Fc-*H*), 4.27 (t, ^3J = 9.0 Hz, 2 H, OCH_2), 4.07 (t, ^3J = 9.0 Hz, 2 H, OCH_2), 3.24 (dd, $^{3,2}J$ = 4.5, 13.5 Hz, 2 H, CH_2Ph), 2.73 (dd, $^{3,2}J$ = 9.0, 13.5 Hz, 2 H, CH_2Ph) ppm. $^{13}C\{^1H\}$ NMR: δ = 166.11 (*C*O), 138.43 (Ph-*C*), 129.71 (Ph-*C*), 128.99 (Ph-*C*), 126.93 (Ph-*C*), 72.51 (Fc-*C*), 72.45 (Fc-*C*), 71.90 (O*C*H_2), 71.08 (Fc-*C*), 70.97 (Fc-*C*), 69.84 (Fc-*C*), 68.25 (N*C*H), 42.16 (*C*H_2Ph) ppm. $C_{30}H_{28}FeN_2O_2$ (504.4): calcd. C 71.44, H 5.60, N 5.55; found C 71.24, H 5.52, N 5.65.

1,1′-Bis[(4*R*,5*S*)-4,5-diphenyloxazolin-2-yl]ferrocene (18b): Following the same procedure as described for **1b** yielded 0.13 g (21%) of **18b** as an oil. ^1H NMR ($CDCl_3$): δ = 7.43–7.28 (m, 20 H, Ph-*H*), 5.36 (d, ^3J = 8.0 Hz, 2 H, NC*H*), 5.12 (d, ^3J = 7.5 Hz, 2 H, OC*H*), 5.07 (m, 2 H, Fc-*H*), 5.02 (m, 2 H, Fc-*H*), 4.60 (m, 2 H, Fc-*H*), 4.51 (m, 2 H, Fc-*H*) ppm. $^{13}C\{^1H\}$ NMR: δ = 166.22 (*C*O), 142.36 (Ph-*C*), 140.71 (Ph-*C*), 129.30 (Ph-*C*), 129.26 (Ph-*C*), 128.87 (Ph-*C*), 128.14 (Ph-*C*), 127.23 (Ph-*C*), 126.33 (Ph-*C*), 89.24 (N*C*H), 79.37 (O*C*H), 73.02 (Fc-*C*), 72.62 (Fc-*C*), 71.93 (Fc-*C*), 71.75 (Fc-*C*), 70.80 (Fc-*C*) ppm. $C_{40}H_{32}FeN_2O_2$ (628.5): calcd. C 76.44, H 5.13, N 4.46; found C 76.28, H 5.13, N 4.20.

X-ray diffraction measurements were performed on a Nonius Kappa CCD diffractometer. Single crystals were positioned at 40 mm from the detector and 567 and 495 frames were measured, each for 60 and 40 s over a 1.5° scan for **13b** and **14b**, respectively. The data were processed using the Denzo-SMN software package. Crystal data, data collection parameters, and structure refinement details for **6b**, **7b**, **11b**–**14b** are given in Table 6. 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 located on difference Fourier

Table 6. Crystallographic data for **6b**, **7b**, **11b**–**14b**.

Compound	**6b**	**7b**	**11b**	**12b**	**13b**	**14b**
Chemical formula	$C_{22}H_{28}FeN_2O_2$	$C_{22}H_{28}FeN_2O_2$	$C_{24}H_{32}FeN_2O_2$	$C_{24}H_{32}FeN_2O_2$	$C_{112}H_{96}Fe_4N_8O_{8.4}$	$C_{112}H_{96}Fe_4N_8O_{8.60}$
Formula mass	408.31	408.31	436.37	436.37	1911.77	1914.97
T [K]	110	110	110	120	120	120
Space group	*C*2	*C*2	$C222_1$	$C222_1$	*C*2	*C*2
a [Å]	20.099(3)	20.092(7)	6.786(6)	6.839(4)	13.637(3)	13.640(2)
b [Å]	6.388(1)	6.387(2)	10.068(1)	10.316(6)	15.431(3)	15.427(3)
c [Å]	7.833(2)	7.872(2)	32.13(4)	30.799(2)	21.698(4)	21.733(3)
β [°]	108.20(1)	108.18(2)			102.03(3)	102.03(2)
V [Å^3]	960.26(4)	959.78(5)	2195.4(7)	2172.9(2)	4465.7(15)	4471.85(13)
Z	2	2	4	4	2	2
$\mu_{calcd.}$ [cm^{-1}]	8.05	8.05	7.09	7.16	7.05	7.04
Flack parameter	0.008(10)	–0.002(12)	0.07(6)	0.03(3)	–0.011(7)	0.001(8)
R_1[a]	0.019	0.023	0.065	0.033	0.0322	0.0463
wR_2[b]	0.0468	0.0552	0.1829	0.0765	0.0643	0.0746

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

maps and isotropically refined or calculated. In **13b** and **14b** the positions of the hydrogen atoms at O5 were not determined. Computer programs: structure solution, SHELXS-97,[65] refinement, SHELXL-97,[66] molecular diagrams, ORTEP,[67] scattering factors.[68]

CCDC-240819, -240820, -240821, -240822, -240823, and -240824 (for **6b**, **7b**, **11b**–**14b**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We are grateful for financial support from the FWF (Austrian Science Fund, P12381-CHE) and for technical support and computer time at the Linux-PC clusters Schroedinger I and Schroedinger II of the computer center of the University of Vienna.

[1] R. J. Bergeron, J. S. McManis, J. Dionis, J. R. Garlich, *J. Org. Chem.* **1985**, *50*, 2780–2782.
[2] P. F. Cavanaugh Jr., C. W. Porter, D. Tukalo, O. S. Frankfurt, Z. P. Pavelic, R. J. Bergeron, *Cancer Res.* **1985**, *45*, 4754–4759.
[3] T. Miyasaka, Y. Nagao, E. Fujita, H. Sakurai, K. Ishizu, *J. Chem. Soc., Perkin Trans. 2* **1987**, *11*, 1543–1549.
[4] D. D. Nekrasov, *Khim. Geterosikl. Soedin.* **1996**, *8*, 1011–1025.
[5] C. Camoutsis, *J. Heterocycl. Chem.* **1996**, *33*, 539–557.
[6] J. A. Frump, *Chem. Rev.* **1971**, *71*, 483–506.
[7] S. Robin, G. Rousseau, *Tetrahedron* **1998**, *54*, 13 681–13 736.
[8] G. V. Boyd, *Prog. Heterocycl. Chem.* **1998**, *10*, 209–225.
[9] A. K. Ghosh, P. Mathivanan, J. Cappiello, *Tetrahedron: Asymmetry* **1998**, *9*, 1–45.
[10] M. Gómez, G. Muller, M. Rocamora, *Coord. Chem. Rev.* **1999**, *193–195*, 769–835.
[11] B. M. Culbertson, *Prog. Polym. Sci.* **2002**, *27*, 579–626.
[12] S. Kobayashi, H. Uyama, *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 192–209.
[13] O. Nuyken, P. Persigehl, R. Weberskirch, *Macromol. Symp.* **2002**, *177*, 163–173.
[14] T. M. Stevenson, V. E. Amoo, G. C. Chiang, E. Keskeny, J. K. Long, B. A. Crouse, P. Sharpe, K. Hillegass, L. Jones, C. Yatsko, *ACS Symp. Ser.* **2002**, *800*, 188–198.
[15] G. Helmchen, A. Krotz, K. T. Ganz, D. Hansen, *Synlett* **1991**, *4*, 257–259.
[16] D. Mueller, G. Umbricht, B. Weber, A. Pfaltz, *Helv. Chim. Acta* **1991**, *74*, 232–240.
[17] P. von Matt, G. C. Lloyd-Jones, A. B. E. Minidis, A. Pfaltz, L. Macko, M. Neuburger, M. Zehnder, H. Rueegger, P. S. Pregosin, *Helv. Chim. Acta* **1995**, *78*, 265–284.
[18] M. B. Andrus, A. B. Argade, X. Chen, M. G. Pamment, *Tetrahedron Lett.* **1995**, *36*, 2945–2948.
[19] D. A. Evans, M. M. Faul, M. T. Bilodeau, B. A. Anderson, D. M. Barnes, *J. Am. Chem. Soc.* **1993**, *115*, 5328–5329.
[20] K. B. Hansen, N. S. Finney, E. N. Jacobsen, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 676–678.
[21] R. E. Lowenthal, A. Abiko, S. Masamune, *Tetrahedron Lett.* **1990**, *31*, 6005–6008.
[22] T. G. Gant, M. C. Noe, E. J. Corey, *Tetrahedron Lett.* **1995**, *36*, 8745–8748.
[23] A. V. Bedekar, P. G. Andersson, *Tetrahedron Lett.* **1996**, *37*, 4073–4076.
[24] E. J. Corey, N. Imai, H. Y. Zhang, *J. Am. Chem. Soc.* **1991**, *113*, 728–729.
[25] R. A. Michelin, M. Mozzon, R. Bertani, *Coord. Chem. Rev.* **1996**, *147*, 299–338.
[26] V. Yu. Kukushkin, A. J. L. Pombeiro, *Chem. Rev.* **2002**, *102*, 1771–1802.
[27] R. A. Michelin, U. Belluco, M. Mozzon, P. Berin, R. Bertani, F. Benetollo, G. Bombieri, R. J. Angelici, *Inorg. Chim. Acta* **1994**, *220*, 21–33.
[28] R. A. Michelin, M. Mozzon, P. Berin, R. Bertani, F. Benetollo, G. Bombieri, R. J. Angelici, *Organometallics* **1994**, *13*, 1341–1350.
[29] M. A. Stark, G. Jones, C. J. Richards, *Organometallics* **2000**, *19*, 1282–1291.
[30] P. Segl'a, M. Jamnicky, *Inorg. Chim. Acta* **1993**, *205*, 221–229.
[31] K. M. Button, R. A. Gossage, R. K. R. Phillips, *Synth. Commun.* **2002**, *32*, 363–368.
[32] P. Segl'a, M. Jamnicky, M. Koman, T. Glowiak, *Polyhedron* **1998**, *17*, 2765–2772.
[33] *Ferrocenes* (Eds.: A. Togni, T. Hayashi), Wiley-VCH, Weinheim, **1995**.
[34] *Metallocenes* (Eds.: A. Togni, R. L. Halterman), Wiley-VCH, Weinheim, **1998**.
[35] I. Manners, *Chem. Commun.* **1999**, 857–865.
[36] I. Manners, *Adv. Mater.* **1994**, *6*, 68–71.
[37] P. Koepf-Maier, *Anticancer Res.* **1999**, *19*, 493–504.
[38] M. Sawamura, Y. Ito, *Chem. Rev.* **1992**, *92*, 857–871.
[39] W. Zhang, Y. Adachi, T. Hirao, I. Ikeda, *Tetrahedron: Asymmetry* **1996**, *7*, 451–460.
[40] W. Zhang, T. Hirao, I. Ikeda, *Tetrahedron Lett.* **1996**, *37*, 4545–4548.
[41] J. Park, S. Lee, K. H. Ahn, C.-W. Cho, *Tetrahedron Lett.* **1995**, *36*, 7263–7266.
[42] A. A. Nazarov, Ch. G. Hartinger, T. H. Brehmer, G. Giester, M. Galanski, B. K. Keppler, *Phosphorus, Sulfur Silicon Relat. Elem.* **2001**, *168–169*, 465–468.
[43] S. Lee, J. H. Koh, J. Park, *J. Organomet. Chem.* **2001**, *637–639*, 99–106.
[44] B. M. Trost, M. L. Crawley, *Chem. Rev.* **2003**, *103*, 2921–2944.
[45] O. Hoarau, H. Ait-Haddou, M. Castro, G. G. A. Balavoine, *Tetrahedron: Asymmetry* **1997**, *8*, 3755–3764.
[46] O. Hoarau, H. Ait-Haddou, J.-C. Daran, D. Cramailere, G. G. A. Balavoine, *Organometallics* **1999**, *18*, 4718–4723.
[47] W. Zhang, H. Yoshinaga, Y. Imai, T. Kida, Y. Nakatsuji, I. Ikeda, *Synlett* **2000**, *10*, 1512–1514.
[48] K. H. Ahn, C.-W. Cho, J. Park, S. Lee, *Tetrahedron: Asymmetry* **1997**, *8*, 1179–1185.
[49] S. M. Williams, J. S. Brodbelt, A. P. Marchand, D. Cal, K. Mlinaric-Majerski, *Anal. Chem.* **2002**, *74*, 4423–4433.
[50] S. F. Ralph, M. M. Sheil, L. A. Hick, R. J. Geue, A. M. Sargeson, *J. Chem. Soc., Dalton Trans.* **1996**, *23*, 4417–4424.
[51] Ch. G. Hartinger, A. A. Nazarov, V. Chevchenko, V. B. Arion, M. Galanski, B. K. Keppler, *Dalton Trans.* **2003**, *15*, 3098–3102.
[52] C. Markert, A Pfaltz, *Angew. Chem. Int. Ed.* **2004**, *43*, 2498–2500.
[53] *Electrospray Ionization Mass Spectrometry* (Ed.: R. B. Cole), John Wiley & Sons, New York, **1997**.
[54] R. Dessapt, C. Simonnet-Jegat, A. Mallard, H. Lavanant, J. Marrot, F. Secheresse, *Inorg. Chem.* **2003**, *42*, 6425–6431.
[55] P. W. N. M. Van Leeuwen, P. C. J. Kamer, J. N. H. Reek, *Pure Appl. Chem.* **1999**, *71*, 1443–1452.
[56] D. Rechavi, M. Lemaire, *Chem. Rev.* **2002**, *102*, 3467–3493.
[57] T. Sammakia, H. A. Latham, D. R. Schaad, *J. Org. Chem.* **1995**, *60*, 10–11.
[58] Y. Nishibayashi, K. Segawa, Y. Arikawa, K. Ohe, M. Hidai, S. Uemura, *J. Organomet. Chem.* **1997**, *545–546*, 381–398.
[59] E. Manoury, J. S. Fossey, H. Ait-Haddou, J.-C. Daran, G. G. A. Balavoine, *Organometallics* **2000**, *19*, 3736–3739.
[60] A. Chesney, M. R. Bryce, R. W. J. Chubb, A. S. Batsanov, J. A. K. Howard, *Tetrahedron: Asymmetry* **1997**, *8*, 2337–2346.
[61] C. Bolm, N. Hermanns, M. Kesselgruber, J. P. Hildebrand, *J. Organomet. Chem.* **2001**, *624*, 157–161.
[62] C. Bolm, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 542–543.
[63] B. M. Trost, D. J. Murphy, *Organometallics* **1985**, *4*, 1143–1145.

[64] Y. Imai, W. Zhang, T. Kida, Y. Nakatsuji, I. Ikeda, *Chem. Lett.* **1999**, *3*, 243–244.
[65] G. M. Sheldrick, *SHELXS-97,* University of Göttingen, **1997**.
[66] G. M. Sheldrick, *SHELXL-97,* University of Göttingen, **1997**.
[67] C. K. Johnson, Rep. ORNL-5138, OAK Ridge National Laboratory, OAK Ridge, TN, **1976**.
[68] *International Tables for X-ray Crystallography*, Kluwer Academic Press, Dordrecht, vol. C, Tables 4.2.6.8 and 6.1.1.4, **1992**.
[69] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98*, revision A.11.1; Gaussian Inc., Pittsburgh PA, **2001**.
[70] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.
[71] C. Lee, W. Young, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.
[72] D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123–141.
[73] R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* **1971**, *54*, 724–728.
[74] W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257–2261.
[75] P. C. Hariharan, J. A. Pople, *Theoret. Chim. Acta* **1973**, *28*, 213–222.
[76] V. Rassolov, J. A. Pople, M. Ratner, T. L. Windus, *J. Chem. Phys.* **1998**, *109*, 1223–1229.
[77] M. Dolg, U. Wedig, H. Stoll, H. Preuss, *J. Chem. Phys.* **1987**, *86*, 866–872.
[78] J. Tomasi, M. Persico, *Chem. Rev.* **1997**, *94*, 2027–2094.
[79] V. Barone, M. Cossi, *J. Phys. Chem.* **1998**, *102*, 1995–2001.
Received: September 01, 2004

