α-Amino Acids with Metallocenyl Side Chains**

Harald Dialer, Kurt Polborn, Walter Ponikwar, Karlheinz Sünkel, and Wolfgang Beck*[a]

Dedicated to Professor Max Herberhold on the occasion of his 65th birthday

Abstract: A straightforward method for the synthesis of enantiomerically pure bis(valine)metallocenes is presented. Derivatives of lithium cyclopentadienyl-valine **1a, b** were obtained by addition of the (*R*)- or (*S*)-Schöllkopf reagents to 6,6-dimethylfulvene as single enantiomers and gave with $FeCl_2$ or $[RuCl_2(dmso)_4]$ the chiral metallocenes $[Fe\{C_5H_4\text{-}CMe_2\text{-}[C_4H_2N_2(OMe)_2iPr]\}_2]$ (**2a, b**) and $[Ru\{C_5H_4\text{-}CMe_2\text{-}[C_4H_2N_2\text{-}(OMe)_2iPr]\}_2]$ (**3a, b**). Complex **2b** was hydrolyzed to the ferrocenylene-bis-(valine-methylester) $[\{Fe[C_5H_4\text{-}CMe_2\text{-}CH(NH_3^+)COOMe]_2\}^{2+}(Cl^-)_2]$ (**7**) without racemization. Complex **7** could be used as ligand and was treated with $[\{Cp^*IrCl_2\}_2]$ to afford $[Fe\{C_5H_4\text{-}CMe_2\text{-}CH(COOMe)(NH_2\text{-}IrCp^*Cl_2)\}_2]$ (**10**). The reactions of **1** with $CoCl_2$, $[Re(CO)_5Br]$, $[\{(cod)RhCl_2\}_2]$ (cod = 1,5-cyclooctadiene) or $[Cp^*MCl_3]$ (M = Ti, Zr) gave the cyclopentadienyl complexes $[\{Co\{C_5H_4\text{-}CMe_2\text{-}[C_4H_2N_2\text{-}(OMe)_2iPr]\}_2\}^+I^-]$ (**11**) and $[Re\{C_5H_4\text{-}CMe_2\text{-}[C_4H_2N_2(OMe)_2iPr]\}(CO)_3]$ (**13**), $[(C_8H_{12})Rh\{C_5H_4\text{-}CMe_2\text{-}[C_4H_2N_2(OMe)_2\text{-}(iPr)]\}]$ (**14**), $[\{Rh\{C_5H_4\text{-}CMe_2\text{-}[C_4H_2N_2\text{-}(OMe)_2(iPr)]\}\}I]_2(\mu\text{-}I)_2]$ (**15**), $[Cp^*Cl_2Ti\{C_5H_4\text{-}CMe_2\text{-}[C_4H_2N_2(OMe)_2(iPr)]\}]$ (**16**), and $[Cp^*Cl_2Zr\{C_5H_4\text{-}CMe_2\text{-}[C_4H_2N_2\text{-}(OMe)_2(iPr)]\}]$ (**17**), with chiral valine derivatives as substituents on the cyclopentadienyl ring and with excellent diastereoselectivities. Also the Seebach reagent (Boc-BMI) or O′Donnell reagent could be added to 6,6-dimethylfulvene to give the lithium cyclopentadienides $Li[C_5H_4\text{-}CMe_2\text{-}\{C_3H_2(tBu)\text{-}(N\text{-}Boc)(NMe)O\}]$ (**18**) and $Li[C_5H_4\text{-}CMe_2\text{-}CH(NCPh_2)(COOEt)]$ (**21**), which formed the ferrocene derivatives $[Fe\{C_5H_4\text{-}CMe_2\text{-}[C_3H_2(tBu)(N\text{-}Boc)\text{-}(NMe)O]\}_2]$ (**19**) and $[Fe\{C_5H_4\text{-}CMe_2\text{-}CH(NCPh_2)(COOEt)\}_2]$ (**22**). The stable cobaltocinium cation in **11** and the complex **19** could be hydrolyzed to the metallocenes **12** and $[Fe\{C_5H_4\text{-}CMe_2\text{-}CH(NH_3^+)(COO^-)\}_2]$ (**20**) with two valines in the 1,1′-position. The structures of **2a, b**, **11**, **15**, and **16** were determined by X-ray diffraction and confirm the diastereomeric purity of the compounds.

Keywords: amino acids · bioorganometallic chemistry · heterocycles · metallocenes · transition metals

Introduction

Recently, organometallic compounds that contain amino acids and peptides have found considerable interest.[1, 2] The first example of a metallocene with an amino acid as substituent, ferrocenylalanine, was discovered in 1957.[3–6] Also ruthenocenylalanine[7] and ferrocenylene bis(alanine)[8] have been reported. Meanwhile several amino acids and peptides with metal π-coordinated aromatic side chains have been synthesized,[9–16] for example, for the selective labeling of aromatic amino acids.[11, 13] Optically active ferrocenylalanine was obtained by asymmetric hydrogenation of prochiral precursors[8a, 14] or by enzymatic resolution of the racemate.[15, 16] The Schöllkopf reagent[17] was added to $[(arene)\text{-}Mn(CO)_3]^+$ ions to give optically active phenylglycines.[18] Recently cyclopentadienides with amino acid derived substituents could be prepared from N-protected alanine and LiCp.[19] Herein we report a general route for the synthesis of enantiomerically pure amino acid metallocenes.[20]

We have applied the addition of nucleophiles to 6,6-dimethylfulvene, a method which was established by Pauson for the preparation of substituted metallocenes.[21] Using the Schöllkopf,[17] the Seebach,[22] and O′Donnell[23] reagents as nucleophiles optically active metallocenes were accessible.

Results and Discussion

The reaction of the deprotonated Schöllkopf reagent[17] (from (*S*)- and (*R*)-valine) with 6,6-dimethylfulvene afforded the lithium cyclopentadienides **1a** ($R_{C2}S_{C5}$) and **1b** ($S_{C2}R_{C5}$) as single enantiomers which were characterized by their ^1H NMR spectra and which gave with $FeCl_2$ or $[RuCl_2$-

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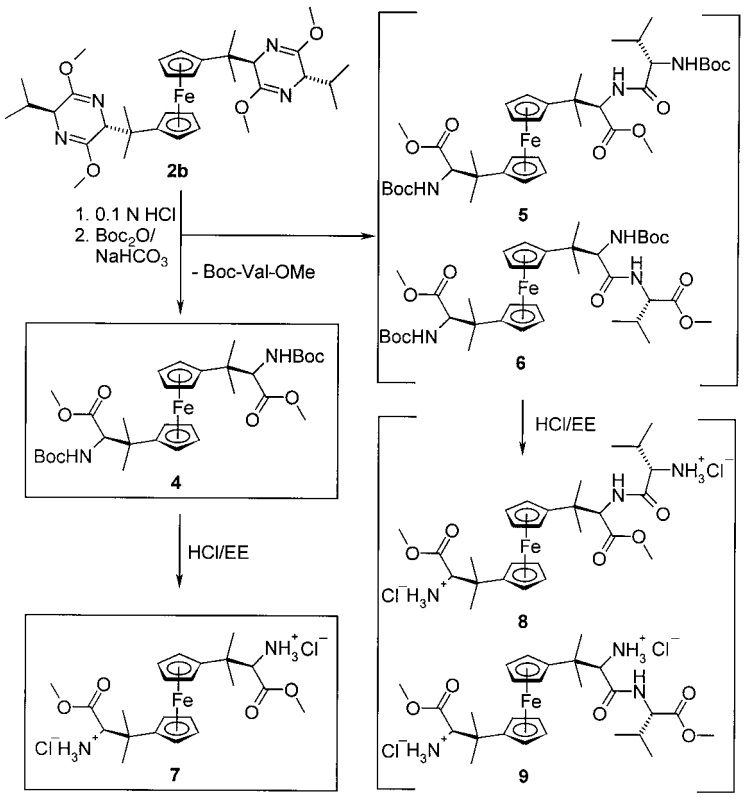
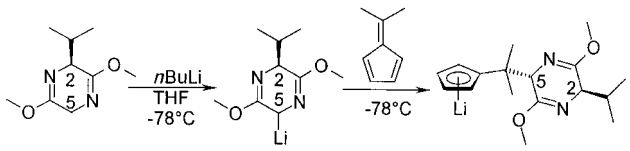
$(dmso)_4$] the bis(aminoacid) derivatives **2** and **3** in high (M = Fe) to good (M = Ru) yields (Scheme 1; **2a**: M = Fe C2/C2′ *R*, C5/C5′ *S*; **2b**: M = Fe C2/C2′ *S*, C5/C5′ *R*; **3a**: M = Ru C2/C2′ *R*, C5/C5′ *S*; **3b**: M = Ru C2/C2′ *S*, C5/C5′ *R*). As confirmed by ^{1}H NMR spectroscopy only one diastereoisomer of **2** and **3** is formed (*de* > 99%). For the diastereotopic protons of the Cp groups in **3** a lowfield shift of 0.4 ppm compared to that of **2** is observed. In the ^{13}C NMR spectra of **2** and **3** a lowfield shift by 28 ppm for the *ipso*-carbon atom of the Cp ligand is noteworthy.

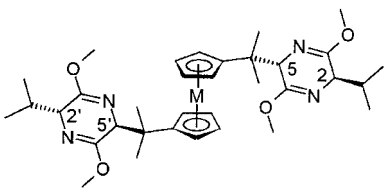
Complexes **2a** and **2b** were characterized by X-ray diffraction (see Figure 1) . The expected absolute configurations at C2 and C5 were confirmed by the experiment. As an example **2b** was hydrolyzed with 0.1 N HCl (CH_3CN/H_2O), and by *tert*-butyloxycarbonyl (Boc) protection of the amino groups and chromatographic separation the bis(valine ester) complex **4** was isolated along with a mixture of the isomers **5** and **6** which contain an amino acid and a dipeptide residue (Scheme 2). Further hydrolysis gave the 1,1′-bis(valine ester) ferrocene **7** as well as **8** and **9**. The ^{1}H NMR spectra show the expected signals and reveal that no racemization of **2b** occurred during hydrolysis.



Scheme 2. Synthesis of **4**–**9**.



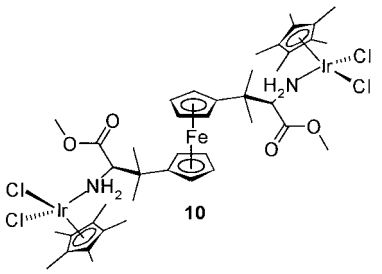
1a,b



2a,b (M= Fe); **3a,b** (M= Ru)

Scheme 1. Synthesis of compounds **1**–**3**.

substituents. Complex **7** can be used as ligand and was treated with [{Cp*$IrCl_2$}$_2$] to give the heterotrimetallic compound **10**. In spite of the diastereotopic protons of the Cp residue only two multiplets were observed in the ^{1}H NMR spectrum of **10**. Similarly, from **1a** and $CoCl_2$ with subsequent oxidation by iodine the cobaltocinium complex **11** was obtained as a single diastereoisomer in high yield (80%). Its absolute structure was confirmed by an X-ray structure determination (see Figure 2). The *S* configuration of C5 and the *R* configuration



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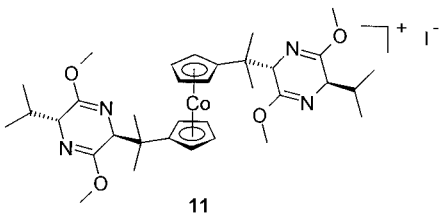

11

Cyclovoltammetric studies on **7** reveal a completely reversible oxidation to the monocationic species with a redox potential (252 mV), 135 mV less than that of ferrocene. This is due to the electron-donating effect of the amino acid

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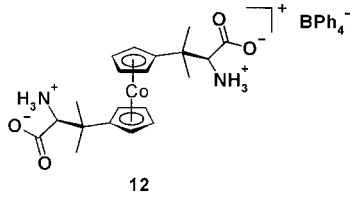
of C2 in **1a** are retained at the corresponding carbon atoms C3/C24 and C9/C26 of **11**, respectively.

As expected, complex **11** is very stable and can even be hydrolyzed with aqueous 6N HCl to give analytically and again optically pure **12** after neutralization and precipitation with $NaBPh_4$.



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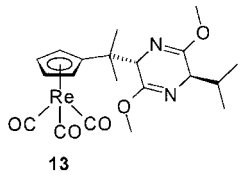

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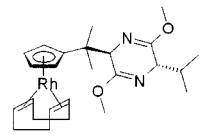

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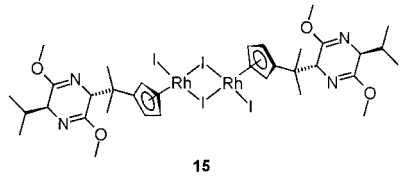

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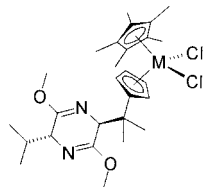


16 (M= Ti), **17** (M= Zr)

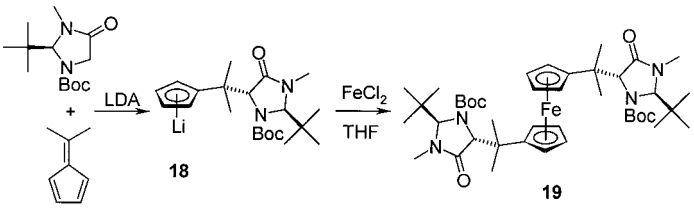
From **1** and $[Re(CO)_5Br]$, $[(cod)RhCl]_2$ or $[Cp^*MCl_3]$ (M = Ti, Zr), the optically active complexes **13**–**17** were obtained. Complex **15** is formed by oxidation of **14** with iodine.

Bioligands that contain metal carbonyls as in **13** could be used for the carbonyl metalloimmunoassay which was introduced by Jaouen[24a] or as radiopharmaceuticals.[24b] Recently the $[(C_5H_4)Re(CO)_3]$ fragment was attached to a steroid using Pauson's fulvene method.[25]

Halide-bridged rhodium complexes are important precursors for homogeneous catalysts.[26] Complex **15** contains an asymmetric residue as well as a donor function and could therefore be useful as chiral catalyst. Cyclopentadienylrhodium complexes with tethered donor functions are rare.[27] The X-ray structure determination of **15** (see Figure 3) again confirmed the expected absolute configurations of the 2- and 5-positions: *S* for C9/C26 and *R* for C7/C24.

The titanium and zirconium complexes **16** and **17** are new chiral candidates for application as catalysts in olefin polymerization.[28] Recently a highly enantioselective electron-transfer reaction of oxiranes catalyzed by a titanocene dichloride with chiral Cp ligands was reported.[29] The crystal of **16** contains two independent molecules of a single diastereoisomer with the expected absolute configurations (see Figure 4). The *R* configuration of C2 and *S* configuration of C5 in **1b** are retained at the corresponding carbon atoms C19/C19A and C17/C17A of **16**, respectively.

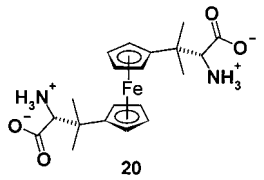
The addition of the deprotonated Seebach reagent (*tert*-butyl 2-(*tert*-butyl)-3-methyl-4-oxo-1-imidazolidinecarboxylate; (*R*)-Boc-BMI)[22] to 6,6-dimethylfulvene gave the lithium cyclopentadienide **18** with a $de > 99\,\%$ from which the ferrocene derivative **19** could be prepared (Scheme 3). In



18 **19**

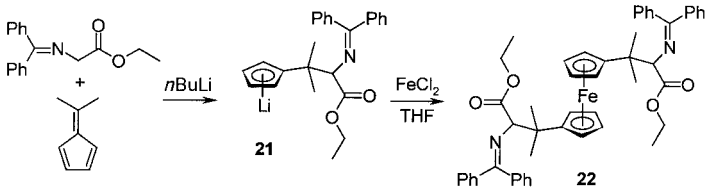
Scheme 3. Synthesis of compounds **18** and **19**.

the ^1H NMR spectrum of **19** only one diastereoisomer can be detected. Following Seebach's procedure[22] 1,1′-ferrocenylene-bis(valine) **20** was accessible. In the IR spectrum of **20** the typical NH_3^+ absorption at 3091 cm^{-1} for the zwitterionic form is observed.



20

In an analogous manner the O′Donnell reagent[23] could be successfully added to 6,6-dimethylfulvene to give **21** and finally the ferrocene derivative **22** (Scheme 4). The latter is formed as a 1:1 mixture of diastereoisomers (*RR*/*SS* and *RS*), as expected. From an ethylacetate/*n*-hexane solution of **22** only one diastereoisomer crystallized, as ascertained by ^1H NMR spectroscopy.



21 **22**

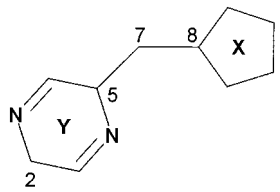
Scheme 4. Synthesis of compounds **21** and **22**.

Discussion of the molecular structures of 2a, 2b, 11, 15, and 16[30]

The experimental details of the crystal structure determinations are collected in Table 1, while the most important structural features (Scheme 5) of these complexes are summarized in Table 2. As mentioned before, all structure determinations confirmed the postulated absolute structures: at least for the isolated and examined crystals, any racemization can be excluded.

Table 1. Crystallographic data of **2a**, **b**, **11**, **15**, and **16**.[39]

	2a	**2b**	**11**	**15**	**16**
molecular formula	$C_{34}H_{50}N_4O_4Fe$	$C_{34}H_{50}N_4O_4Fe$	$C_{34}H_{51}N_4O_{4.5}CoI$	$C_{34}H_{50}N_4O_4I_4Rh_2$	$C_{27}H_{40}N_2O_2Cl_2Ti$
formula weight	634.63	634.63	773.61	1292.20	543.41
a [Å]	21.425(4)	21.422(2)	7.566(3)	8.4626(13)	12.037(3)
b [Å]	7.297(2)	7.2985(12)	15.1355(16)	8.6919(13)	15.598(3)
c [Å]	14.972(2)	14.9671(10)	32.245(4)	14.472(3)	15.500(4)
α [°]	90	90	90	79.286(14)	90
β [°]	133.434(11)	133.419(7)	90	84.859(14)	101.25(2)
γ [°]	90	90	90	85.905(13)	90
V [Å^3]	1699.9(5)	1699.7(3)	3692.4(16)	1040.1 (3)	2854.3(12)
Z	2	2	4	1	4
crystal system	monoclinic	monoclinic	orthorhombic	triclinic	monoclinic
space group	$C2$	$C2$	$P2_12_12_1$	$P1$	$P2_1$
μ [mm^{-1}]	0.485	0.485	1.342	3.801	0.512
ρ [g cm^{-3}]	1.240	1.240	1.390	2.063	1.265
crystal Size [mm]	$0.53 \times 0.40 \times 0.20$	0.53x0.43x0.10	$0.38 \times 0.38 \times 0.38$	$0.43 \times 0.40 \times 0.23$	$0.53 \times 0.40 \times 0.13$
diffractometer	Enraf Nonius CAD 4	Enraf Nonius CAD 4	Siemens Syntex P4	Enraf Nonius CAD4	Enraf Nonius CAD4
temperature [K]	294(2)	295(2)	293(2)	295(2)	295(2)
2Θ scan range [°]	5.24 to 47.94	5.24 to 47.94	3.70 to 50.02	6.00 to 47.94	4.72 to 47.94
reflections collected	2757	2984	4747	6633	9712
indep. refl. [R_{int}]	2658 (0.0134)	2658 (0.0098)	4495 (0.0259)	6506 (0.0144)	8922 (0.0166)
absorption correction	Ψ scans	Ψ scans	Ψ scans	Ψ scans	Ψ scans
max./min. transmission	0.999/0.941	0.998/0.941	0.922/0.904	0.999/0.599	0.999/0.959
data/restraints/param.	2658/1/201	2658/1/201	4495/0/418	6506/3/445	8922/1/635
goodness-of-fit on F^2	1.059	1.073	1.058	1.129	1.055
R_1 [$F > 4\sigma(F)$]	0.0245	0.0225	0.0505	0.0260	0.0392
wR_2 (all data)	0.0646	0.0586	0.1371	0.0678	0.0973
Largest difference peak and hole [e Å^{-3}]	0.153 and −0.240	0.132 and −0.145	0.454 and −0.967	0.887 and −0.618	0.429 and −0.286



Scheme 5. Numbering scheme for discussion of structures.

Table 2. Comparison of important structural features of **2a, 2b, 11, 15**, and **16**.[a]

	2a	**2b**	**11**	**15**	**16**
Sigpln (Cp)	0.004	0.002	0.008/0.013	0.026/0.023	0.016/0.014
Sigpln (Het)	0.122	0.121	0.033/0.071	0.140/0.132	0.147/0.144
[Cp, Het] [°]	42.2	42.2	45.6/43.5	37.4/33.8	31.5/32.5
[Cp, Cp′] [°]	2.7	2.6	4.8	–	(55.8/55.8)
[Cp, C_{578}] [°]	96.1	96.0	78.6/91.8	101.7/106.7	80.2/82.6
d (M−Cp) [Å]	1.659	1.659	1.644/1.645	1.769/1.797	2.100/2.104
d (M−X) [Å]	1.659	1.659	1.644/1.646	1.770/1.797	2.118/2.120
$(r_{CC}\ (Cp))_{av}$ [Å]	1.409	1.408	1.405/1.424	1.394/1.418	1.401/1.397
d (X−Y) [Å]	3.44	3.44	3.45/3.49	4.41/4.58	3.24/3.24
τ [°]	133.1	133.1	143.2	–	–
C_2-C_5-C_7 [°]	118.3	118.6	124.6/126.5	116.2/114.7	115.8/115.6
C_8-C_7-C_5-C_2 [°]	0.9	−1.2	−10.1/7.1	−102.7/117.6	5.4/5.8

[a] The symbols for the carbon atoms (C_i) and the ring centroids (X, Y) correspond to those given in Scheme 5. Cp, Cp′, Het, and C_{578} represent the planes defined by both cyclopentadienyl rings, the heterocycle and the three carbon atoms C_5-C_7-C_8. d stands for distance and $r_{CC}\ (Cp)_{av}$ for the average C−C bond lengths within the cyclopentadienyl rings. The ring-planarity parameter Sigpln is defined in the program package WINGX] as Sqrt(Sum($j = 1{:}n$) (D_j^2/($n-3$)) and the conformational angle τ is defined in the paper by Herberhold et al. as the torsional angle C_8-X-X′-C_8′.

The metric parameters of the two enantiomeric ferrocenes **2a** and **2b** (Figure 1) are as expected identical. Both compounds crystallize in the acentric monoclinic space group $C2$, with the iron atom on the crystallographic C_2 axis. The cyclopentadienyl rings are essentially planar, nearly eclipsed (ca 11.4° stagger) with their planes inclined by about 2.6°. The dihedral angle between the Cp substituent bonds, C1−C6 and C1A−C6A, is about 120.5°.

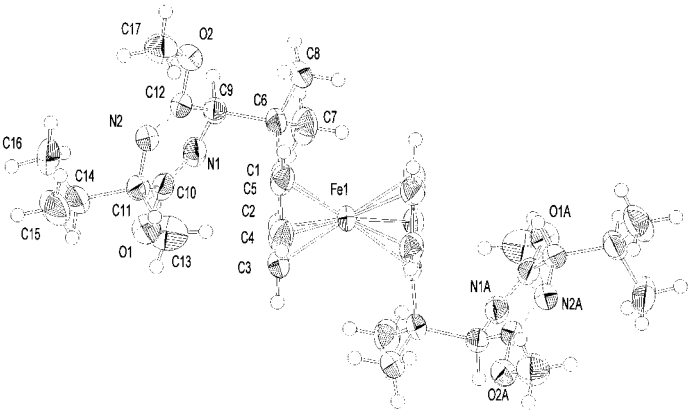


Figure 1. Molecular structure of **2b**.

It appears interesting to take a closer look at the relative orientations of the cyclopentadienyl ring and the heterocyclic substituent. The angle between their "best planes" is 42.2°,while the plane of the connecting carbon atoms 5-7-8 (Scheme 5) is nearly orthogonal to the Cp ring. This allows

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the heterocycle to bend towards the π system of the cyclopentadienyl ring, which is indeed the case, as can be seen from the dihedral angle between the carbon atoms 8–7 and 5–2, and the distance of 3.44 Å between their ring centroids.

Most likely due to its ionic character the isoelectronic cobalticinium salt **11** (Figure 2) crystallizes in a different space group, the orthorhombic $P2_12_12_1$, with half a water molecule of crystallization. The crystal contains neither crystallographic nor molecular symmetry, which means that both Cp rings have to be treated independently. The cyclopentadienyl rings are essentially planar, fully eclipsed (1.6° stagger) and their planes inclined by 4.8°. These parameters are very similar to the ones observed for $[\{Co(C_5H_4tBu)_2\}_2][CoCl_4]$.[31]

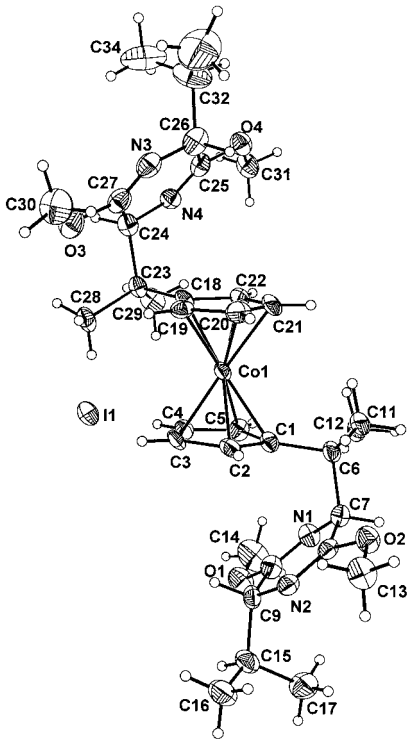

Figure 2. Molecular structure of **11**.

While the interplanar angles between the Cp rings and the attached heterocycles are very similar for both rings and also to the ones found in the ferrocenes **2a** and **2b**, there is a significant difference in the relative orientations of the connecting units at carbon atoms 5-7-8: the plane defined by C24-C23-C18 is nearly orthogonal to the cyclopentadienyl ring, as is observed in the ferrocenes described above, while the plane defined by C1-C6-C7 is inclined by about 12° from orthogonality. While both heterocycles are still bent towards the π systems of their cyclopentadienyl ring neighbors, the distance between the ring centroids is longer by about 4 pm in the second case.

The titanocene dichloride complex **16** crystallizes in the monoclinic space group $P2_1$ with two independent molecules (Figure 4). However, as can be seen from the data in Table 2, there are only minor differences in the general structural features of these molecules. Despite the principal distinctions between bent metallocenes and „parallel“ metallocenes on one hand, and symmetrical (with two identical Cp rings) and

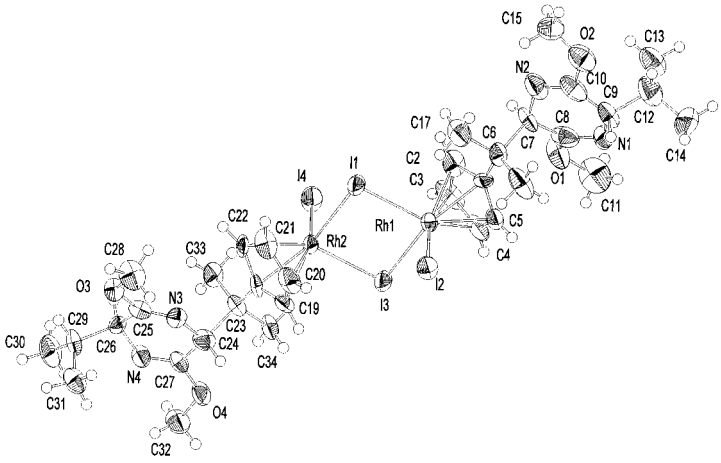

Figure 3. Molecular structure of **15**.

unsymmetrical metallocenes on the other hand, the geometrical parameters around the connection of cyclopentadienyl ring and heterocyclic substituent are very similar to the ones found for the above-mentioned ferrocenes and the cobalticinium compound. The major difference in this part of the molecule is the much smaller angle between the planes of the cyclopentadienyl ring and the heterocycle, which leads to a significantly closer approach of the corresponding ring centroids. The most striking difference, however, to the other cyclopentadienyl complexes described herein, is the observation of significant ring slippage for the monosubstituted cyclopentadienyl ring. The Ti–C bond lengths for this ring vary between 2.31 and 2.58 Å, with the largest distances observed for the substituted carbon atoms. Although ring slippage has been observed before for mono-substituted titanocene dichlorides, for example $[(C_5H_4tBu)_2TiCl_2]$,[32] or $[(C_5H_4CMe_2C_{13}H_9)_2TiCl_2]$,[33] such a long Ti–$C_{Cp}$ bond has never been reported.

The dimeric doubly iodide-bridged rhodium complex **15** crystallizes in the triclinic space group $P\bar{1}$. Besides the lack of crystallographic symmetry there is also no molecular symmetry in the crystal, that is both cyclopentadienylrhodium units are independent (Figure 3). The central Rh_2I_2 unit is planar, as usual for complexes of the type $[\{CpRhI_2\}_2]$[34] or generally doubly halide- bridged d^8 complexes,[35] and forms a nearly ideal square with Rh-I-Rh angles of about 92° and I-Rh-I angles of about 88° (Rh–Rh distance ca. 3.89 Å). The geometry around Rh is best described as distorted octahedral.

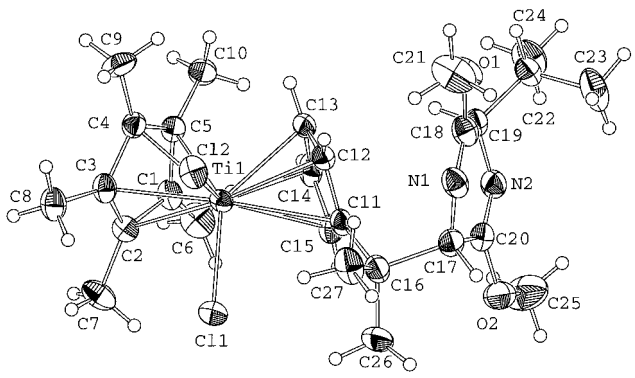

Figure 4. Molecular structure of **16**.

While in the four other complexes described before the heterocycle was bent towards the π system of the cyclopentadienyl ring, it is rotated away in this rhodium complex. The large torsional angles around the C–C linkages 8–7 and 5–2, particularly in the Rh2-"half" of the molecule, lead to distances between the centroids of the five- and six-membered rings that are more than 1 Å larger than in the other complexes. Although this fact is obvious from the data, we cannot give an explanation for this difference, as there seem to be no special intermolecular forces in the crystal packing.

Conclusion

The procedure described herein is a straightforward method for the synthesis of optically active bis(valine) metallocenes from Schöllkopf or Seebach reagents and 6,6-dimethylfulvene. Only a few steps are necessary and the bis(amino acid) metallocenes are formed in good yields and with excellent diastereoselectivites. The novel compounds may be of use for asymmetric reactions.

Experimental Section

All experiments were carried out in Schlenk tubes under argon. Precipitates were separated by centrifugation with a Kryofuge 6000 i (Heraeus). Silica gel (0.063–0.200 mm, Merck) was used for chromatography. IR: Nicolet 520 FT-IR and Perkin-Elmer Modell 841. NMR: Jeol GSX270 and Jeol EX400. Elemental analyses: Analytical laboratory of the Department Chemie.

$[RuCl_2(dmso)_4]$,[36] $[Rh(cod)Cl]_2$[37] and $[\{Cp^*IrCl_2\}_2]$[38] were prepared as described. The other starting materials were used as purchased.

General method for 1a and 1b: A 1.6 M solution of *n*BuLi (1.25 mL, 2.0 mmol) in *n*-hexane was added dropwise at −78 °C to a solution of (2*R*)- or (2*S*)-2,5-dihydro-3,6-dimethoxy-2-isopropylpyrazine (Schöllkopf reagent) (2.0 mmol) in THF (10 mL). After stirring for 15 min a cooled solution of 6,6-dimethylfulvene (2.0 mmol) in THF (5 mL) was added dropwise over 30 min. After stirring for 2 h at −78 °C, the solution was allowed to warm up to room temperature. This solution was used for the preparation of the cyclopentadienyl complexes. For the characterization of **1** the solvent was removed from a small amount of the solution; the residue was dried in vacuo. ^{1}H NMR (270 MHz, C_6D_6): $\delta = 0.21$ (s, 3H; $(CH_3)_2CH$), 0.65 (s, br, 3H; $(CH_3)_2CH$), 1.21 (s, br, 3H; $(CH_3)_2C_q$), 1.28 (s, br, 3H; $(CH_3)_2C_q$), 1.80 (s, br, 1H; $(CH_3)_2CH$), 2.51 (s, br, 1H; C(2)-*H*), 3.27 (s, br, 3H; OCH_3), 3.34 (s, br, 3H; OCH_3), 3.59 (m, 1H; C(5)-*H*), 5.56 (s, br, 2H; Cp), 5.91 (s, br, 2H; Cp).

[Fe{C_5H_4-CMe_2-[$C_4H_2N_2$(OMe)$_2$*i*Pr]}$_2$] (2a): $FeCl_2$ (300 mg, 2.39 mmol), was added at room temperature to a solution of **1a** from (2*R*)-Schöllkopf reagent (884 mg, 4.80 mmol), a solution of *n*BuLi (3,0 mL, 4.80 mmol), and 6,6-dimethylfulvene (509 mg, 4.80 mmol) in THF (30 mL). After the mixture had been stirred for 15 h, the solvent was removed in vacuo and the residue was purified by column chromatography (silica gel, *n*-hexane/ethyl acetate 4/1). Crystals were obtained from a solution in diethyl ether at +4 °C. Orange crystals. Yield 1380 mg (91 %). IR (KBr): $\tilde{\nu} = 3109$ m, 2979 s, 2967 s, 2883 s, 1691 vs (C=N), 1432 s, 1382 s, 1298 s, 1241 vs (C–O), 1193 s, 1100 s, 1014 vs, 824 vs, 773 s cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.47$ (d, $^3J = 7.0$ Hz, 6H; $(CH_3)_2CH$), 0.86 (d, $^3J = 7.0$ Hz, 6H; $(CH_3)_2CH$), 1.40 (s, 6H; $(CH_3)_2C_q$), 1.44 (s, 6H; $(CH_3)_2C_q$), 2.06 (dsept, $^3J = 3.2$ Hz, 2H; $(CH_3)_2CH$), 2.61 (t, $^3J = 3.1$ Hz, 2H; C(2)-*H*), 3.59 (s, 6H; OCH_3), 3.63 (s, 6H; OCH_3), 3.80 (m, 2H; Cp), 3.85 (m, 2H; Cp), 3.86 (m, 2H; Cp), 3.96 (m, 2H; Cp), 3.99 (m, 2H; Cp); ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta =$ 16.23 ($(CH_3)_2CH$), 19.18 ($(CH_3)_2CH$), 26.48 ($(CH_3)_2C_q$), 27.05 ($(CH_3)_2C_q$), 29.92 ($(CH_3)_2CH$), 40.42 ($(CH_3)_2C_q$), 51.88 (OCH_3), 52.38 (OCH_3), 59.61 (C(2)), 65.73 (C(5)), 67.49, 67.88, 68.01, 68.17, 94.13 (Cp), 162.60 (C=N), 164.92 (C=N); elemental analysis (%) calcd for $C_{34}H_{50}N_4FeO_4$ (634.64): C 64.35, H 7.94, N 8.83; found: C 64.43, H 7.74, N 8.81.

[Fe{C_5H_4-CMe_2-[$C_4H_2N_2$(OMe)$_2$*i*Pr]}$_2$] (2b): The compound **2b** was obtained as described for **2a** using (2*S*)-Schöllkopf reagent (858 mg, 4.66 mmol), a 1.6 M solution of *n*BuLi (2.9 mL, 4.66 mmol), 6,6-dimethylfulvene (561 μL, 4.66 mmol), and $FeCl_2$ (295 mg, 2.39 mmol). Orange crystals. Yield 1316 mg (89 %). IR (KBr): $\tilde{\nu} = 3109$ m, 2979 s, 2967 s, 2883 s, 1691 vs (C=N), 1432 s, 1382 s, 1298 s, 1241 vs (C–O), 1193 s, 1100 s, 1014 vs, 824 vs, 773 s cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.47$ (d, $^3J = 7.0$ Hz, 6H; $(CH_3)_2CH$), 0.86 (d, $^3J = 7.0$ Hz, 6H; $(CH_3)_2CH$), 1.41 (s, 6H; $(CH_3)_2C_q$), 1.44 (s, 6H; $(CH_3)_2C_q$), 2.06 (dsept, $^3J = 3.2$ Hz, 2H; $(CH_3)_2CH$), 2.61 (t, $^3J = 3.1$ Hz, 2H; C(2)-*H*), 3.59 (s, 6H; OCH_3), 3.63 (s, 6H; OCH_3), 3.80 (m, 2H; Cp), 3.85 (m, 2H; Cp), 3.86 (m, 2H; C(5)-*H*), 3.97 (m, 2H; Cp), 4.00 (m, 2H; Cp); ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta = 16.23$ ($(CH_3)_2CH$), 19.18 ($(CH_3)_2CH$), 26.48 ($(CH_3)_2C_q$), 27.05 ($(CH_3)_2C_q$), 29.92 ($(CH_3)_2CH$), 40.42 ($(CH_3)_2C_q$), 51.88 (OCH_3), 52.38 (OCH_3), 59.61 (C(2)), 65.73 (C(5)), 67.49, 67.88, 68.01, 68.17, 94.13 (Cp), 162.60 (C=N), 164.92 (C=N); elemental analysis (%) calcd for $C_{34}H_{50}N_4FeO_4$ (634.64): C 64.35, H 7.94, N 8.83; found: C 64.47, H 7.84, N 8.89.

[Ru{C_5H_4-CMe_2-[$C_4H_2N_2$(OMe)$_2$*i*Pr]}$_2$] (3a): $[RuCl_2(dmso)_4]$ (264 mg, 0.55 mmol) was added at room temperature to a solution of **1a** from (2*R*)-Schöllkopf reagent (201 mg, 1.09 mmol), a solution of *n*BuLi (0.68 mL, 1.09 mmol), and 6,6-dimethylfulvene (131 μL, 1.09 mmol) in THF (10 mL). After the mixture had been stirred for 15 h, the solvent was removed in vacuo and the residue was purified by column chromatography (silica gel, *n*-hexane/ethyl acetate 4/1). Analytically pure material was obtained from a solution in diethyl ether at −30 °C. Slightly yellow crystals. Yield 267 mg (72 %). IR (KBr): $\tilde{\nu} = 3106$ m, 2967 s, 2872 m, 1690 vs (C=N), 1434 s, 1381 m, 1301 s, 1238 vs (C–O), 1194 s, 1100 m, 1016 s, 827 m, 776 s cm^{-1}; ^{1}H NMR (270 MHz, CD_2Cl_2): $\delta = 0.53$ (d, $^3J = 6.7$ Hz, 6H; $(CH_3)_2CH$), 0.94 (d, $^3J = 6.7$ Hz, 6H; $(CH_3)_2CH$), 1.19 (s, 6H; (CH_3C_q), 1.21 (s, 6H; $(CH_3)_2C_q$), 2.16 (dsept, $^3J = 3.3$ Hz, 2H; $(CH_3)_2CH$), 2.99 (t, $^3J = 3.1$ Hz, 2H; C(2)-*H*), 3.62 (s, 6H; OCH_3), 3.66 (s, 6H; OCH_3), 3.93 (d, $^3J = 3.2$ Hz, 2H; C(5)-*H*), 4.28–4.36 (m, 8H; Cp); ^{13}C NMR (100.5 MHz, CD_2Cl_2): $\delta = 15.97$ ($(CH_3)_2CH$), 19.08 ($(CH_3)_2CH$), 26.98 ($(CH_3)_2C_q$), 27.43 ($(CH_3)_2C_q$), 29.97 ($(CH_3)_2CH$), 40.10 ($(CH_3)_2C_q$), 51.79 (OCH_3), 52.36 (OCH_3), 59.83 (C(2)), 64.99 (C(5)), 70.39, 70.44, 70.59, 70.93, 98.94 (Cp), 162.99 (C=N), 164.67 (C=N); elemental analysis (%) calcd for $C_{34}H_{50}N_4O_4Ru$ (679.86): C 60.07, H 7.41, N 8.24; found: C 60.38, H 7.54, N 8.16.

[Ru{C_5H_4-CMe_2-[$C_4H_2N_2$(OMe)$_2$*i*Pr]}$_2$] (3b): The complex **3b** was obtained as described for **3a**. (2*S*)-Schöllkopf reagent (188 mg, 1.02 mmol), a solution of *n*BuLi (0.64 mL, 1.02 mmol), 6,6-dimethylfulvene (123 μL, 1.02 mmol), and $[RuCl_2(dmso)_4]$ (247 mg, 0.51 mmol) were used. Slightly yellow crystals. Yield 112 mg (69 %). IR (KBr): $\tilde{\nu} = 3106$ m, 2967 s, 2872 m, 1690 vs (C=N), 1434 s, 1381 m, 1301 s, 1238 vs (C–O), 1194 s, 1100 m, 1016 s, 827 m, 776 s cm^{-1}; ^{1}H NMR (270 MHz, CD_2Cl_2): $\delta = 0.53$ (d, $^3J = 6.7$ Hz, 6H; $(CH_3)_2CH$), 0.94 (d, $^3J = 6.7$ Hz, 6H; $(CH_3)_2CH$), 1.19 (s, 6H; $(CH_3)_2C_q$), 1.21 (s, 6H; $(CH_3)_2C_q$), 2.16 (dsept, $^3J = 3.3$ Hz, 2H; $(CH_3)_2CH$), 2.99 (t, $^3J = 3.1$ Hz, 2H; C(2)-*H*), 3.62 (s, 6H; OCH_3), 3.66 (s, 6H; OCH_3), 3.93 (d, $^3J = 3.2$ Hz, 2H; C(5)-*H*), 4.28–4.36 (m, 8H; Cp); ^{13}C NMR (100.5 MHz, CD_2Cl_2): $\delta = 15.97$ ($(CH_3)_2CH$), 19.08 ($(CH_3)_2CH$), 26.98 ($(CH_3)_2C_q$), 27.43 ($(CH_3)_2C_q$), 29.97 ($(CH_3)_2CH$), 40.10 ($(CH_3)_2C_q$), 51.79 (OCH_3), 52.36 (OCH_3), 59.83 (C(2)), 64.99 (C(5)), 70.39, 70.44, 70.59, 70.93, 98.94 (Cp), 162.99 (C=N), 164.67 (C=N); elemental analysis (%) calcd for $C_{34}H_{50}N_4O_4Ru$ (679.86): C 60.07, H 7.41, N 8.24; found: C 59.43, H 7.46, N 8.02.

4 and 5/6: Acetonitrile (20 mL) and 0.2 N hydrochloric acid (20.0 mL, 4.00 mmol) were added to **2b** (634 mg, 1.00 mmol). Gas was removed from the suspension using vacuum and argon (3 ×). After the mixture had been stirred for 15 h a clear orange solution was obtained. The solvent was removed in vacuo, and $CHCl_3$ (15 mL) and water (10 mL) were added to the residue. The two-phase mixture was cooled at 0 °C and $NaHCO_3$ (336 mg, 4.00 mmol) and Boc_2O (873 mg; 4.00 mmol) were added. After the mixture had been stirred for 14 h the aqueous phase was extracted with $CHCl_3$ (2 × 10 mL). The organic solution was dried over Na_2SO_4 and the solvent was removed in vacuo under stirring. The residue was purified by column chromatography (*n*-hexane/ethyl acetate 3/1). The first yellow fraction gave compound **4**, and the second yellow fraction contained a mixture of **5** and **6**.

[Fe{C_5H_4-CMe_2-CH(NHBoc)COOMe}$_2$] (4): Yellow powder. Yield 406 mg (63 %). IR (KBr): $\tilde{\nu} = 3055$ vs, 2986 vs, 2833 w, 1739 vs, 1715 vs, 1500 s (CO_2, NCO), 1392 s, 1368 s, 1208 m, 1161 s, 1054 m, 1022 m, 897 m, 829 w cm^{-1};

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^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 1.33$ (s, 6H; $(CH_3)_2C_q$), 1.35 (s, 18H; $(CH_3)_3C$), 1.38 (s, 6H; $(CH_3)_2C_q$), 3.49 (s, 6H; OCH_3), 3.98 (m, 2H; Cp), 4.01 (m, 2H; Cp), 4.04–4.07 (m, 2H; α-H), 4.11 (m, 2H; Cp), 4.13 (m, 2H; Cp), 4.94 (d, $^3J = 9.4$ Hz, 2H; NH); ^{13}C NMR (100.5 MHz, CD_2Cl_2): $\delta =$ 24.86 ($(CH_3)_2C_q$), 25.52 ($(CH_3)_2C_q$), 28.04 ($(CH_3)_3C$), 37.97 ($(CH_3)_2C_q$), 49.38 (CH), 51.40 (OCH_3), 66.52, 66.89, 68.49, 68.58 (Cp), 79.39 ($(CH_3)_3C$), 95.15 (*ipso*-Cp), 155.28 (CON), 171.56 (CO_2); elemental analysis (%) calcd for $C_{32}H_{48}N_2O_8Fe$ (644.58): C 59.63, H 7.51, N 4.35; found: C 59.49, H 7.78, N 4.67.

[Fe{C_5H_4-CMe_2-CH[NHCOCH(NHBoc)(*i*Pr)]COOMe} {$C_5H_4CMe_2$CH-(NHBoc)COOMe}]; mixture of isomers 5 and 6: Yellow powder. Yield 156 mg (21%). IR (KBr): $\tilde{\nu} = 3099$ m, 2974 s, 2931 m, 2842 w, 1742 vs, 1719 vs, 1679 vs, 1502 s (CO_2, NCO), 1392 s, 1366 s, 1298 s, 1248 m, 1172 s, 1052 m, 1025 m, 906 w, 874 w, 825 w, 772 w cm^{-1}; ^{1}H NMR (270 MHz, CD_2Cl_2): $\delta =$ 0.79 (pt, $^3J = 6.6$ Hz, 6H; $(CH_3)_2CH$), 1.33 (s, 3H; $(CH_3)_2C_q$), 1.34 (s, 3H; $(CH_3)_2C_q$), 1.36 (s, 9H; $C(CH_3)_3$), 1.37 (s, 9H; $C(CH_3)_3$), 1.39 (s, 3H; $(CH_3)_2C_q$), 1.40 (s, 3H; $(CH_3)_2C_q$), 1.90 (m, 1H; $(CH_3)_2CH$), 3.49 (s, 3H; OCH_3), 3.64 (s, 3H; OCH_3), 3.81 (d, $^3J = 8.8$ Hz, 1H; CH), 3.99–4.22 (m, 10H; CH und Cp), 4.93 (d, $^3J = 9.6$ Hz, 1H; NH), 5.11 (d, $^3J = 7.0$ Hz, 1H; NH), 5.60 (d, $^3J = 7.8$ Hz, 1H; NH); ^{13}C NMR (67.9 MHz, CD_2Cl_2): $\delta =$ 18.14 ($(CH_3)_2CH$), 18.53 ($(CH_3)_2CH$), 24.21, 24.82 ($(CH_3)_2C_q$), 25.55, 26.02 ($(CH_3)_2C_q$), 28.04 ($(CH_3)_3C$), 31.04 ($(CH_3)_2CH$), 37.66, 37.96 ($(CH_3)_2C_q$), 51.42 (OCH_3), 51.85 (OCH_3), 57.40 ($CHCH(CH_3)_2$), 62.46 (CH), 63.66 (CH), 66.64, 66.92, 67.01, 67.07, 68.43, 68.51, 68.61, 68.81 (Cp), 79.42, 79.44 ($(CH_3)_3C$), 95.22, 96.34 (*ipso*-C, Cp), 155.18, 155.21 (CON), 171.55, 171.72 (CO_2); MS(FAB): 743 (100) $[M]^+$, 687 (5), 644 (12), 588 (7), 544 (3), 449 (11); elemental analysis (%) calcd for $C_{37}H_{57}N_3O_9Fe$ (743.71): C 59.75, H 7.72, N 5.64; found: C 59.65, H 7.92, N 5.47.

[{Fe[C_5H_4-CMe_2-CH(NH_3^+)$COOMe]_2$}$^{2+}$(Cl^-)$_2$] (7): A 2M solution of hydrogen chloride in ethyl acetate (15 mL) was added at 0°C to **4** (200 mg, 0.31 mmol) and the mixture was stirred for 15 h under argon. The yellow precipitate was centrifuged off from the colorless solution and dried in vacuo. Ochre yellow powder. Yield 157 mg (98%). IR (KBr): $\tilde{\nu} = 2960$ s, 2872 s, 1745 vs (C=O), 1508 m, 1374 m, 1315 m, 1268 m, 1241 m, 1160 w, 1034 m, 830 w cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD): $\delta = 1.51$ (s, 6H; $(CH_3)_2C_q$), 1.55 (s, 6H; $(CH_3)_2C_q$), 3.66 (s, 6H; OCH_3), 3.73 (s, 2H; α-H), 4.20 (m, 2H; Cp); 4.22 (m, 2H; Cp), 4.31 (m, 4H; Cp); ^{13}C NMR (100.5 MHz, CD_3OD): $\delta = 23.84$ ($(CH_3)_2C_q$), 24.27 ($(CH_3)_2C_q$), 36.62 ($(CH_3)_2C_q$), 51.81 (OCH_3), 62.43 (CH), 66.81, 67.03, 69.30, 69.43 (Cp), 94.39 (*ipso*-C, Cp), 168.48 (CO_2); elemental analysis (%) calcd for $C_{22}H_{34}N_2Cl_2FeO_4$ (517.27): C 51.08, H 6.62, N 5.42; found: C 50.79, H 6.90, N 5.16.

[{Fe[C_5H_4-CMe_2-CH[NHCOCH(NH_3^+)(*i*Pr)] COOMe]{C_5H_4-CMe_2CH-(NH_3^+)COOMe}}$^{2+}$(Cl^-)$_2$]; mixture of isomers 8 and 9: A 2M solution of HCl in ethyl acetate (15 mL) was added at 0°C to the mixture of **5** and **6** (102 mg, 0.14 mmol) and the mixture was stirred for 15 h under an atmosphere of argon. The yellow precipitate was centrifuged off from the colorless solution and dried in vacuo. Yellow powder. Yield 81 mg (96%). IR (KBr): $\tilde{\nu} = 3048$ m, 2967 s, 2886 s, 1742 vs (CO_2), 1679 vs, 1585 m, 1510 s, 1374 s, 1268 s, 1239 m, 1159 m, 1034 m, 830 w, 511 w cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD): $\delta = 0.92$ (d, $^3J = 6.7$ Hz, 3H; $(CH_3)_2CH$), 0.95 (d, $^3J =$ 6.7 Hz, 3H; $(CH_3)_2CH$), 1.49 (s, 3H; $(CH_3)_2C_q$), 1.51 (s, 3H; $(CH_3)_2C_q$), 1.56 (s, 3H; $(CH_3)_2C_q$), 1.58 (s, 3H; $(CH_3)_2C_q$), 2.05 (m, 1H; $(CH_3)_2CH$), 3.66 (s, 3H; OCH_3), 3.68 (s, 1H; CH), 3.70 (s, 3H; OCH_3), 3.72 (s, 1H; CH), 4.17 (d, $^3J = 6.0$ Hz, 1H; $CHCH(CH_3)_2$), 4.19–4.31 (m, 8H; Cp); ^{13}C NMR (100.5 MHz, CD_3OD): $\delta = 17.73$ ($(CH_3)_2CH$), 18.22 ($(CH_3)_2CH$), 23.26, 23.84, 24.29, 24.48 ($(CH_3)_2C_q$), 30.19 ($(CH_3)_2CH$), 36.39, 36.63 ($(CH_3)_2C_q$), 51.28 (OCH_3), 51.80 (OCH_3), 58.52 ($CHCH(CH_3)_2$), 62.04 (CH), 62.45 (CH), 66.82, 66.92, 67.04, 67.40, 69.14, 69.33, 69.45, 69.55 (Cp), 94.39, 95.31 (*ipso*-C, Cp), 152.52 (CON), 172.26 (CO_2); MS(FAB): 544 (42) $[M - 2Cl]^+$, 349 (25), 307 (30), 289 (16); elemental analysis (%) calcd for $C_{27}H_{43}N_3Cl_2FeO_5$ (616.40): C 52.60, H 7.03, N 6.81; found: C 52.09, H 7.25, N 6.41.

[Fe{C_5H_4-CMe_2-CH(COOMe)(NH_2-IrCp*Cl_2)}$_2$] (10): Compound **7** (29 mg, 0.055 mmol) in methanol (10 mL) was deprotonated with a 1.5M solution of NaOMe in methanol (74 μL, 0.11 mmol). [{Cp*$IrCl_2$}$_2$] (44 mg, 0.055 mmol) was added to the resulting yellow solution and the mixture was stirred for 15 h. The solvent was removed in vacuo and dichloromethane (5 mL) was added to the residue. After filtration over celite *n*-hexane (20 mL) was added to the filtrate. The precipitate was centrifuged off and dried in vacuo. Orange powder. Yield 62 mg (92%); IR (KBr): $\tilde{\nu} = 2975$ m, 2916 m, 1732 vs (C=O), 1630 w, 1564 m, 1453 s, 1381 s, 1248 s, 1163 s, 1123 m, 1059 s, 1033 s, 837 m cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 1.35$ (s, 6H; $(CH_3)_2C_q$), 1.37 (s, 6H; $(CH_3)_2C_q$), 1.46 (s, 30H; $C_5(CH_3)_5$), 3.59 (s, 6H; OCH_3), 3.83 (s, br, 2H; α-H), 4.02 (m, 4H; Cp), 4.19 (m, 2H; Cp); ^{13}C NMR (100.5 MHz, CD_2Cl_2): $\delta = 8.72$ ($C_5(CH_3)_5$), 24.76 ($(CH_3)_2C_q$), 25.51 ($(CH_3)_2C_q$), 38.72 ($(CH_3)_2C_q$), 51.96 (OCH_3), 65.39 (CH), 66.84, 67.10, 69.09, 69.22 (Cp), 85.02 ($C_5(CH_3)_5$), 95.01 (*ipso*-C, Cp), 171.43 (CO_2); elemental analysis (%) calcd for $C_{42}H_{62}N_2Cl_4FeIr_2O_4$ (1241.06): C 40.64, H 5.04, N 2.26; found: C 40.38, H 4.96, N 2.18.

[{Co{C_5H_4-CMe_2-[$C_4H_2N_2(OMe)_2$*i*Pr]}$_2$}$^+$$I^-$] (11): $CoCl_2$ (280 mg, 2.16 mmol) was added to a solution of **1a** in THF (30 mL) which was obtained from (2*R*)-Schöllkopf reagent (795 mg, 4.31 mmol), a solution of *n*BuLi (2.70 mL, 4.31 mmol), and 6,6-dimethylfulvene. After stirring for 1 h a solution of iodine (285 mg, 1.12 mmol) in THF (10 mL) was added dropwise whereby the mixture became solid. After addition of methanol (10 mL) and stirring for a few minutes the solvent was removed in vacuo. The residue was dissolved in dichloromethane (20 mL), LiCl was centrifuged off, and the product was precipitated with *n*-pentane and purified by column chromatography (silica gel, $CHCl_3$/MeOH 20/1). Crystals were obtained by evaporation of a solution of **11** in CH_3OH/THF on air. Yellow thin plates. Yield 1321 mg (80%). IR (KBr): $\tilde{\nu} = 3055$ w, 2975 m, 2938 m, 2872 w, 1691 vs (C=N), 1437 m, 1383 m, 1332 w, 1240 vs (C–O), 1195 m, 1005 m, 873 w, 777 s cm^{-1}; ^{1}H NMR (270 MHz, CD_3OD): $\delta = 0.54$ (d, $^3J =$ 7.0 Hz, 6H; $(CH_3)_2CH$), 0.98 (d, $^3J = 7.0$ Hz, 6H; $(CH_3)_2CH$), 1.50 (s, 12H; $(CH_3)_2C_q$), 2.23 (dsept. $^3J = 3.3$ Hz, 2H; $(CH_3)_2CH$), 3.35 (t, $^3J = 3.3$ Hz, 2H; C(2)-*H*), 3.62 (s, 6H; OCH_3), 3.66 (s, 6H; OCH_3), 3.95 (d, $^3J = 3.7$ Hz, 2H; C(5)-*H*), 5.70 (m, 4H; Cp), 5.76 (m, 4H; Cp); ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta = 15.14$ ($(CH_3)_2CH$), 18.22 ($(CH_3)_2CH$), 24.98 ($(CH_3)_2C_q$), 25.09 ($(CH_3)_2C_q$), 30.41 ($(CH_3)_2CH$), 40.37 ($(CH_3)_2C_q$), 51.46 (OCH_3), 52.03 (OCH_3), 60.08 (C(2), 64.55 (C(5)), 82.54, 82.63, 83.03, 83.07 (Cp), 117.22 (*ipso*-C, Cp), 161.59 (C=N), 165.09 (C=N); elemental analysis (%) calcd for $C_{34}H_{50}N_4CoIO_4$ (764.62): C 53.41, H 6.59, N 7.33; found: C 53.25, H 6.57, N 7.33.

[{Co[C_5H_4-CMe_2-CH(NH_3^+)COO^-]$_2$}$^+$$BPh_4^-$] (12): 6N hydrochloric acid (10 mL) was added to **11** (200 mg, 0.26 mmol) at 0°C and the mixture was stirred for 2 h. Then, concentrated hydrochloric acid (5 mL) was added dropwise to the solution. After the mixture had been stirred for 15 h the solution was concentrated to 3 mL in vacuo under stirring and neutralized with 6N NaOH to pH 6.5 using a potentiometer. Compound **12** was precipitated by addition of a solution of $NaBPh_4$ in methanol, washed with water and dried in vacuo. Yellow powder. Yield 112 mg (80%). IR (KBr): $\tilde{\nu} = 3055$ m (br, NH_3^+), 2967 m, 2872 w, 1674 s (CO_2), 1600 s, 1582 m, 1508 m, 1471 m, 1440 s, 1397 s, 1339 s, 1275 s, 1242 s, 1028 m, 869 m, 740 m, 705 vs (Ph) cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD): $\delta = 1.39$ (s, br, 6H; $(CH_3)_2C_q$), 1.44 (s, br, 6H; $(CH_3)_2C_q$), 4.18 (m, 2H; α-H), 5.53–5.64 (m, 8H; Cp), 7.28–7.37 (m, 12H; *m*- und *p*-C_6H_5), 7.53–7.58 (m, 8H; *o*-C_6H_5), ^{13}C NMR (100.5 MHz, CD_3OD): $\delta = 23.57$ ($(CH_3)_2C_q$), 24.96 ($(CH_3)_2C_q$), 38.43 ($(CH_3)_2C_q$), 57.13 (CH), 82.17, 82.59, 83.27, 83.34 (Cp), 115.02 (ipso-C, Cp), 122.15, 125.07, 127.11, 127.35, 128.01, 128.13, 133.76, 135.89 (Ph), 174.22 (CO_2); elemental analysis (%) calcd for $C_{44}H_{48}N_2BCoO_4$ (738.17): C 71.55, H 6.55, N 3.79; found: C 71.35, H 6.71, N 3.52.

[Re{C_5H_4-CMe_2-[$C_4H_2N_2(OMe)_2$*i*Pr]}(CO)$_3$] (13): [Re(CO)$_5$Br] 1062 mg, 261 mmol) was added at room temperature to a solution of **1a** in THF (30 mL) which was obtained from (2*R*)-Schöllkopf reagent (482 mg, 2.61 mmol), a solution of *n*BuLi (1.64 mL, 2.61 mmol), and 6,6-dimethylfulvene (315 μL, 2.61 mmol). The suspension was refluxed for 16 h and the solvent was removed in vacuo. The residue was chromatographed on silica gel with *n*-hexane/ethyl acetate 4/1). Slightly yellow oil. Yield 394 mg (27%). IR (KBr): $\tilde{\nu} = 3121$ w, 2974 m, 2938 w, 2872 w, 2022 vs (C≡O), 1917 (C≡O), 1690 vs (C=N), 1435 s, 1382 w, 1303 m, 1238 (C–O) vs, 1194 m, 1106 m, 1016 s, 827 m, 776 m cm^{-1}; IR (CH_2Cl_2): $\tilde{\nu} = 2022$ vs (C≡O), 1925 vs (C≡O), 1754 s, 1693 vs (C=N) cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 0.57$ (d, $^3J = 6.9$ Hz, 3H; $(CH_3)_2CH$), 1.00 (d, $^3J = 6.9$ Hz, 3H; $(CH_3)_2CH$), 1.26 (s, 3H; $(CH_3)_2C_q$), 1.29 (s, 3H; $(CH_3)_2C_q$), 2.25 (dsept, $^3J = 3.3$ Hz, 1H; $(CH_3)_2CH$), 3.31 (t, $^3J = 3.3$ Hz, 1H; C(2)-*H*), 3.65 (s, 3H; OCH_3), 3.68 (s, 3H; OCH_3), 4.01 (d, $^3J = 3.7$ Hz, 1H; C(5)-*H*), 5.19 (m, 2H; Cp), 5.26 (m, 1H; Cp), 5.31 (m, 1H; Cp); ^{13}C NMR (100.5 MHz, CD_2Cl_2): $\delta = 15.93$ ($(CH_3)_2CH$), 19.02 ($(CH_3)_2CH$), 27.12 ($(CH_3)_2C_q$), 27.60 ($(CH_3)_2C_q$), 30.48 ($(CH_3)_2CH$), 40.57 ($(CH_3)_2C_q$), 52.05 (OCH_3), 52.52 (OCH_3), 60.22 (C(2)), 64.80 (C(5)), 82.13, 82.23, 86.07, 86.26, 115.43 (Cp), 162.06 (C=N), 164.74

(C=N), 194.78 (C≡O); elemental analysis (%) calcd for $C_{20}H_{25}N_2O_5Re$ (559.63): C 42.93, H 4.50, N 5.01; found: C 43.63, H 4.69, N 4.95.

[(C_8H_{12})Rh{C_5H_4-CMe_2-[$C_4H_2N_2(OMe)_2$(*i*Pr)]}] (14): A solution of [{(cod)RhCl}$_2$] (423 mg, 0.86 mmol) in THF (20 mL) was added by a syringe to a solution of **1b** in THF (20 mL) which was obtained from (2*S*)-Schöllkopf reagent (316 mg, 1.72 mmol), a solution of *n*BuLi (1.07 mL, 1.72 mmol), and 6,6-dimethylfulvene (207 μL, 1.72 mmol). After the mixture had been stirred for 15 h, the solvent was removed in vacuo and the residue was chromatographed on silica gel with *n*-hexane/ethyl acetate 15/1. Yellow crystals were obtained from a solution in *n*-pentane at −30 °C. Yield 294 mg (34 %). IR (KBr): $\tilde{\nu}$ = 2969 s, 2938 s, 2872 m, 2828 s, 1691 vs (C=N), 1433 s, 1380 s, 1299 s, 1239 vs (C−O), 1192 s, 1016 s, 892 m, 776 s cm^{-1}; ^{1}H NMR (270 MHz, C_6D_6): δ = 0.82 (d, ^3J = 6.8 Hz, 3H; (CH_3)$_2$CH)), 1.19 (d, ^3J = 6.9 Hz, 3H; (CH_3)$_2$CH), 1.59 (s, 3H; (CH_3)$_2$C$_q$), 1.63 (s, 3H; (CH_3)$_2$C$_q$), 1.94 (m, 4H; H$_{aliph}$-COD), 2.22 (m, 4H; H$_{aliph}$-COD), 2.44 – 2.58 (m, 1H; (CH_3)$_2$C*H*), 3.12 (t, ^3J = 3.3 Hz, 1H; C(2)-*H*), 3.57 (s, 3H; OCH_3), 3.63 (s, 3H; OCH_3), 3.97 (s, br, 4H; H$_{olef}$-COD), 4.26 (d, ^3J = 3.3 Hz, 1H; C(5)-*H*), 4.50 (m, 2H; Cp), 4.95 (m, 2H; Cp); ^{13}C NMR (67.9 MHz, C_6D_6): δ = 16.66 ((CH_3)$_2$CH), 19.81 ((CH_3)$_2$CH), 27.76 ((CH_3)$_2$C$_q$), 28.38 ((CH_3)$_2$C$_q$), 30.27 ((CH_3)$_2$C*H*), 32.73 (C$_{aliph}$-COD), 32.93 (C$_{aliph}$-COD), 41.17 ((CH_3)$_2$C$_q$), 51.90 (OCH$_3$), 52.52 (OCH$_3$), 60.03 (C(2)), 63.12 (d, $J_{Rh,C}$ = 4.2 Hz, C$_{olef}$-COD), 63.33 (d, $J_{Rh,C}$ = 4.2 Hz, C$_{olef}$-COD), 66.25 (C(5)), 85.24 (d, $J_{Rh,C}$ = 3.5 Hz, Cp), 85.93 (d, $J_{Rh,C}$ = 3.6 Hz, Cp), 86.36 (d, $J_{Rh,C}$ = 3.9 Hz, Cp), 86.72 (d, $J_{Rh,C}$ = 4.0 Hz, Cp), 113.80 (d, $J_{Rh,C}$ = 4.7 Hz, *ipso*-C, Cp), 163.42 (C=N), 165.04 (C=N); elemental analysis (%) calcd for $C_{25}H_{37}N_2O_2Rh$ (500.48): C 59.99, H 7.45, N 5.60; found: C 59.79, H 7.51, N 5.49.

[{Rh{C_5H_4-CMe_2-[$C_4H_2N_2(OMe)_2$(*i*Pr)]}I}$_2$(μ-I)$_2$] (15): A solution of **14** (180 mg, 0.36 mmol) in diethyl ether (7 mL) was cooled to −10 °C and a solution of iodine (91 mg, 0.36 mmol) in Et_2O (5 mL) was added dropwise. The mixture was allowed to warm up to room temperature over 1 h. Then, the solvent was removed in vacuo. The residue was dissolved in dichloromethane and layered with *n*-hexane to give dark violet crystals of **15**. Yield 252 mg (93 %). IR (KBr): $\tilde{\nu}$ = 2967 m, 2938 w, 2872 w, 1690 vs (C=N), 1467 m, 1435 m, 1304 w, 1239 vs (C−O), 1196 w, 1007 m, 775 s cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.54 (d, ^3J = 7.1 Hz, 3H; (CH_3)$_2$CH), 0.55 (d, ^3J = 6.5 Hz, 3H; (CH_3)$_2$CH), 0.99 (d, ^3J = 6.5 Hz, 3H; (CH_3)$_2$CH), 1.00 (d, ^3J = 7.0 Hz, 3H; (CH_3)$_2$CH), 1.41 (s, 3H; (CH_3)$_2$C$_q$), 1.42 (s, 3H; (CH_3)$_2$C$_q$), 1.45 (s, 3H; (CH_3)$_2$C$_q$), 1.46 (s, 3H; (CH_3)$_2$C$_q$), 2.19 – 2.28 (m, 2H; (CH_3)$_2$C*H*), 3.56 (s, 3H; OCH_3), 3.57 (s, 3H; OCH_3), 3.58 (s, 3H; OCH_3), 3.59 (s, 3H; OCH_3), 3.62 (t, br, ^3J = 3.0 Hz, 2H; C(2)-*H*), 3.85 (s, br, ^3J = 3.3 Hz, 2H; C(5)-*H*), 5.40 – 5.46 (m, 4H; Cp), 5.58 – 5.61 (m, 4H; Cp); ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ = 15.93 ((CH_3)$_2$CH), 18.95 ((CH_3)$_2$CH), 25.37 ((CH_3)$_2$C$_q$), 30.86 ((CH_3)$_2$C*H*), 41.18 ((CH_3)$_2$C$_q$), 52.07 (OCH$_3$), 52.60 (OCH$_3$), 60.28 (C(2)), 65.23 (C(5)), 81.29 (d, $J_{Rh,C}$ = 7.9 Hz, Cp), 81.42 (d, $J_{Rh,C}$ = 7.6 Hz, Cp), 85.49 (d, $J_{Rh,C}$ = 5.2 Hz, Cp), 85.88 (d, $J_{Rh,C}$ = 5.3 Hz, Cp), 113.27 (d, $J_{Rh,C}$ = 8.4 Hz, *ipso*-C, Cp), 161.10 (C=N), 164.67 (C=N); elemental analysis (%) calcd for $C_{34}H_{50}N_4I_4O_4Rh_2$ (1292.20): C 31.60, H 3.89, N 4.34; found: C 31.29, H 3.53, N 4.22.

[Cp*Cl_2Ti{C_5H_4-CMe_2-[$C_4H_2N_2(OMe)_2$(*i*Pr)]}] (16): [Cp*$TiCl_3$] (1038 mg, 3.59 mmol) was added at −78 °C to a solution of **1a** in THF (30 mL) which was obtained from (2*R*)-Schöllkopf reagent (661 mg, 3.59 mmol), a solution of *n*BuLi (2.25 mL, 3.59 mmol), and 6,6-dimethylfulvene (432 μL, 3.59 mmol). The mixture was allowed to warm up over 15 h and then the solvent was removed in vacuo. The residue was dissolved in dichloromethane (10 mL) and filtered through a column of silica gel (3 cm). The solvent of the filtrate was removed in vacuo and the residue was recrystallized from warm *n*-octane to give dark red crystals of **16**. Yield 897 mg (46 %). IR (KBr): $\tilde{\nu}$ = 2975 m, 2938 m, 2872 w, 1688 vs (C=N), 1435 m, 1379 m, 1302 m, 1237 vs (C−O), 1194 m, 1009 m, 827 m, 776 m cm^{-1}; ^{1}H NMR (270 MHz, CD_2Cl_2): δ = 0.52 (d, ^3J = 6.7 Hz, 3H; (CH_3)$_2$CH), 0.96 (d, ^3J = 6.8 Hz, 3H; (CH_3)$_2$CH), 1.57 (s, 6H; (CH_3)$_2$C$_q$), 1.98 (s, 15H; Cp*), 2.11 – 2.22 (m, 1H; (CH_3)$_2$C*H*), 3.09 (t, ^3J = 3.3 Hz, 1H; C(2)-*H*), 3.58 (s, 3H; OCH_3), 3.63 (s, 3H; OCH_3), 3.85 (d, ^3J = 3.4 Hz, 1H; C(5)-*H*), 5.84 (m, 1H; Cp), 5.88 (m, 1H; Cp), 6.04 (m, 1H; Cp), 6.11 (m, 1H; Cp); ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ = 13.26 (*C*H$_3$-Cp*), 15.89 ((CH_3)$_2$CH), 19.03 ((CH_3)$_2$CH), 23.78 ((CH_3)$_2$C$_q$), 24.20 ((CH_3)$_2$C$_q$), 30.32 ((CH_3)$_2$CH), 43.94 ((CH_3)$_2$C$_q$), 51.90 (OCH$_3$), 52.46 (OCH$_3$), 59.71 (C(6)), 67.66 (C(3)), 113.21, 113.47, 122.93, 123.56 (Cp), 129.68 (Cp*), 142.91 (*ipso*-C, Cp), 162.38 (C=N), 164.26 (C=N); elemental analysis (%) calcd for $C_{27}H_{40}N_2Cl_2O_2Ti$ (543.41): C 59.68, H 7.42, N 5.15; found: C 59.65, H 7.53, N 5.13.

[Cp*Cl_2Zr{C_5H_4-CMe_2-[$C_4H_2N_2(OMe)_2$(*i*Pr)]}] (17): This complex was obtained as described for **16**: (2*R*)-Schöllkopf reagent (598 mg, 3.25 mmol), a solution of *n*BuLi (2.03 mL), 6,6-dimethylfulvene (391 μL, 3.25 mmol), and [Cp*$ZrCl_3$] (1080 mg, 3.25 mmol) were used. Colorless crystals. Yield 1009 mg (53 %). IR (KBr): $\tilde{\nu}$ = 2974 m, 2938 m, 2872 w, 1688 vs (C=N), 1433 m, 1366 m, 1301 m, 1237 vs (C−O), 1194 m, 1010 s, 813 s, 776 m cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.53 (d, ^3J = 6.9 Hz, 3H; (CH_3)$_2$CH), 0.96 (d, ^3J = 6.9 Hz, 3H; (CH_3)$_2$CH), 1.57 (s, 3H; (CH_3)$_2$C$_q$), 1.58 (s, 3H; (CH_3)$_2$C$_q$), 1.99 (s, 15H; Cp*), 2.17 (dsept, ^3J = 3.2 Hz, 1H; (CH_3)$_2$C*H*), 2.96 (t, ^3J = 3.4 Hz, 1H; C(2)-*H*), 3.60 (s, 3H; OCH_3), 3.65 (s, 3H; OCH_3), 3.87 (d, ^3J = 3.4 Hz, 1H; C(5)-*H*), 5.86 (m, 1H; Cp), 5.89 (m, 1H; Cp), 6.08 (m, 1H; Cp), 6.13 (m, 1H; Cp); ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ = 12.07 (*C*H$_3$-Cp*), 15.68 ((CH_3)$_2$CH), 18.86 ((CH_3)$_2$CH), 24.14 ((CH_3)$_2$C$_q$), 24.63 ((CH_3)$_2$C$_q$), 30.05 ((CH_3)$_2$CH), 42.99 ((CH_3)$_2$C$_q$), 51.70 (OCH$_3$), 52.23 (OCH$_3$), 59.38 (C(2)), 67.22 (C(5)), 110.73, 110,98, 117.83, 118.06 (Cp), 124.12 (Cp*), 138.99 (Cp), 162.17 (C=N), 164.13 (C=N); elemental analysis (%) calcd for $C_{27}H_{40}N_2Cl_2O_2Zr$ (586.75): C 55.27, H 6.87, N 4.77; found: C 55.20, H 6.95, N 4.71.

Li[C_5H_4-CMe_2-{C_3H_2(*t*Bu)(N-Boc)(NMe)O}] (18) and [Fe{C_5H_4-CMe_2-[C_3H_2(*t*Bu)(N-Boc)(NMe)O]}$_2$] (19): A solution of *n*BuLi (2,6 mL, 4.08 mmol) in *n*-hexane was slowly added at −78 °C to diisopropylamine (414 mg, 4.09 mmol) in THF (10 mL). After 30 min a solution of Seebach reagent ((*R*)-Boc-BMI) (950 mg, 3.71 mmol) in THF (10 mL) was added dropwise and the mixture was stirred for 2 h at −78 °C. Then 6,6-dimethylfulvene (496 μL, 3.89 mmol) was added and the slightly yellow solution was stirred for 1 h at −78 °C. From a small amount of this solution the solvent was removed in vacuo and the ^{1}H NMR spectrum of the lithium cyclopentadienide **18** was recorded. ^{1}H NMR (270 MHz, C_6D_6): δ (Cp) = 5.49 (s, br, 2H), 5.87 (s, br, 2H). $FeCl_2$ (236 mg, 1.85 mmol) was added to the solution of **18** and the mixture was allowed to warm up to room temperature over 15 h. The solvent was removed in vacuo and the residue was extracted with diethyl ether (30 mL). The solution was concentrated and purified on silica gel (*n*-hexane/ethyl acetate 4/1). Orange crystals of **19** were obtained from a solution in diethyl ether at −30 °C. Yield 782 mg (54 %). IR (KBr): $\tilde{\nu}$ = 3109 m, 2975 s, 2930 m, 1702 vs (C=O), 1680 s (C=O), 1480 s, 1398 s, 1365 s, 1352 s, 1255 m, 1164 s, 1106 s, 921 m, 786 m cm^{-1}; ^{1}H NMR (270 MHz, CD_2Cl_2): δ = 0.79 (s, 18H; C(CH_3)$_3$), 1.39 (s, 6H; (CH_3)$_2$C$_q$), 1.48 (s, 18H; O-C(CH_3)$_3$), 1.53 (s, 6H; (CH_3)$_2$C$_q$), 2.24 (s, 6H; *N*-CH_3), 3.90 (m, 2H; Cp), 3.97 (m, 2H; Cp), 3.99 (d, ^3J = 2.1 Hz, 2H; C(5)-*H*), 4.03 (m, 4H; Cp), 4.32 (d, ^3J = 1.8 Hz, 2H; C(2)-*H*); ^{13}C NMR (67.9 MHz, CD_2Cl_2): δ = 24.88 (C(*C*H$_3$)$_3$), 26.97 ((CH_3)$_2$C$_q$), 27.80 ((CH_3)$_2$C$_q$), 29.92 (O-C(*C*H$_3$)$_3$), 32.53 (N-CH_3), 41.91 (*C*(CH$_3$)$_3$), 42.99 ((CH_3)$_2$C$_q$), 67.39 (C(5)), 67.46, 67.58, 67.82, 68.14 (Cp), 80.56 (O-*C*(CH$_3$)$_3$), 81.42 (C(2)), 93.92 (*ipso*-C, Cp), 154.87 (C=O$_{Boc}$), 170.04 (C=O$_{Amid}$); elemental analysis (%) calcd for $C_{42}H_{66}N_4FeO_6$ (778.85): C 64.77, H 8.54, N 7.19; found: C 64.51, H 7.98, N 6.74.

[Fe{C_5H_4-CMe_2-CH(NH_3^+)(COO^-)}$_2$] (20): Trifluoroacetic acid (2.17 mL, 28.11 mmol) was added at 0 °C to a solution of **19** (782 mg, 1.00 mmol) in dichloromethane (10 mL). After the mixture had been stirred for 15 h the solvent was removed in vacuo. The residue was dissolved in 0.75 M HCl (20 mL) and brought into an ace pressure tube. DOWEX 50-WX 8 with 0.75 M HCl (10 mL) and toluene (2 mL) were added and the mixture was degassed by bubbling argon for 10 min through the mixture. Then, the pressure tube was heated for three days at 105 °C. The solution was decanted and the ion exchange resin was washed with methanol and then with water to pH 7. In a short column the product was eluted from the resin with aqueous NH_3 solution (10 %). The fractions which gave a positive test with ninhydrin were combined and concentrated in vacuo. The product **20** was purified by recrystallization from methanol/acetone. Orange-brown powder. Yield 128 mg (31 %). IR (KBr): $\tilde{\nu}$ = 2974 m, 2938 m, 2872 m, 1655 s, 1605 m, 1530, 1469 m, 1366 m, 1172 w, 1041 w, 826 m cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD): δ = 1.31 (s, br, 6H; (CH_3)$_2$C$_q$), 1.41 (s, br, 6H; (CH_3)$_2$C$_q$), 4.09 – 4.22 (m, 10H; Cp and CH); elemental analysis (%) calcd for $C_{20}H_{28}N_2FeO_4$ (416.30); MS(FAB): 416 (4) $[M]^+$, 372 (18) $[M - CO_2]^+$.

Li[C_5H_4-CMe_2-CH($NCPh_2$)($COOEt$)] (21) and [Fe{C_5H_4-CMe_2-CH($NCPh_2$)($COOEt$)}$_2$] (22): A solution of *n*BuLi (2.44 mL, 3.90 mmol) in hexane was added dropwise at −78 °C to *N*-diphenylmethylene glycine ethyl ester (1042 mg, 3.90 mmol) in THF (25 mL). The mixture was stirred for 1 h at −78 °C. Then 6,6-dimethylfulvene (470 μL, 3.90 mmol) in cooled THF (7 mL) was added dropwise to the solution and the mixture was again stirred for 2 h. From a small amount of the solution the solvent was

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removed and the ^{1}H NMR spectrum of the lithium cyclopentadienide **21** was recorded (^{1}H NMR (270 MHz, C_6D_6): δ (Cp) = 5.56 (s, br, 2H), 5.94 (s, br, 2H)). $FeCl_2$ (247 mg, 1.95 mmol) was added to the solution of **21**, and the mixture was allowed to warm up to room temperature over 15 h. The solvent was removed under reduced pressure and the residue was crystallized from hot *n*-hexane/ethyl acetate (4/1). The precipitate was centrifuged off and crystals were obtained by layering a solution in ethyl acetate with *n*-hexane. Yellow powder. Yield 1420 mg (91%). IR (KBr): $\tilde{\nu}$ = 3091 w, 2982 s, 2938 m, 1739 vs (C=O), 1625 s (C=N), 1447 s, 1178 vs, 1365 w, 1030 s, 781 m (Ph), 696 vs (Ph) cm^{-1}; ^{1}H NMR (270 MHz, CD_2Cl_2): δ = 1.09 (t, ^3J = 7.1 Hz, 6H; CH_3CH_2), 1.41 (s, 6H; $(CH_3)_2C_q$), 1.44 (s, 6H; $(CH_3)_2C_q$), 3.59 (s, 2H; α-H), 3.92 (q, ^3J = 7.1 Hz, 2H; CH_3CH_2), 3.96 (q, ^3J = 7.1 Hz, 2H; CH_3CH_2), 3.83–4.01 (m, 8H; Cp), 6.74–6.79 (m, 4H; Ph), 7.26–7.37 (m, 12H; Ph), 7.51–7.56 (m, 4H; Ph); ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ = 13.95 (CH_3CH_2), 24.24 ($(CH_3)_2C_q$), 24.81 ($(CH_3)_2C_q$), 39.25 ($(CH_3)_2C_q$), 60.12 (CH_3CH_2), 66.61, 67.36, 67.84, 68.06 (Cp), 75.75 (α-C), 97.53 (*ipso*-C, Cp), 127.91, 127.95, 128.09, 128.32, 128.68, 130.12 (Ph), 136.28, 139.79 (*ipso*-C, Ph), 169.50 (C=N), 170.78 (C=O); MS(FAB): 801 (22) $[M]^+$, 428 (100), 354 (9), 278 (26), 267 (12), 73 (2); elemental analysis (%) calcd for $C_{50}H_{52}N_2FeO_4$ (800.82): C 75.00, H 6.54, N 3.50; found: C 75.46, H 6.64, N 3.33.

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