Electronic Interactions in Ferrocene- and Ruthenocene-Functionalized Tetraazamacrcocyclic Ligand Complexes of $Fe^{II/III}$, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}

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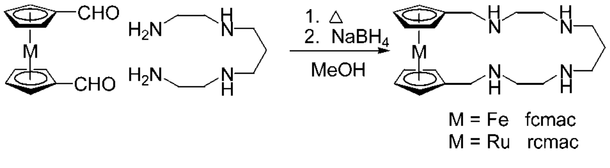
The syntheses of ferrocene- and ruthenocene-functionalized tetraazamacrocyclic ligands and their corresponding transition metal complexes are described. Reaction of *N*,*N'*-bis(2-aminoethyl)-1,3-propanediamine (2,3,2-tet) with 1,1'-diformylferrocene and 1,1'-diformylruthenocene produces the ligands fcmac and rcmac in 81–85% yield. Examination of their Cu^{II}, Ni^{II}, Co^{II}, Zn^{II} and $Fe^{II/III}$ complexes by IR, UV/Vis, EPR and Mössbauer spectroscopy as well as by electrochemical studies suggests electronic communication between the two metal centers of each complex. The molecular structure of $[Cu^{II}(fcmac)(FBF_3)]BF_4$, determined by X-ray structure analysis, is reported and shows that the distance between the two metals is 4.54 Å. Stability constants, determined by potentiometric titration, indicate that the copper(II) complexes are of similar stability as those with unfunctionalized tetraazamacrocyclic ligands (e.g. cyclam = 1,4,8,11-tetraazacyclotetradecane); stability constants of cobalt(II) complexes are about 2 log units smaller, those of nickel(II) and zinc(II) complexes are reduced by more than 10 log units. This selectivity is discussed on the basis of the structural studies.

Introduction

A large variety of metallocene-functionalized macrocyclic ligands have been reported, including crown ethers as well as polyaza- and polythiamacrocycles, Schiff-base and mixed-donor ligand systems, with various binding motifs of the metallocene functional groups.[1–11] With metal ions coordinated to the macrocyclic ligands, tunable energy- and electron transfer processes have been suggested, observed and studied,[12] and molecular switches as well as artificial regulatory systems have been designed.[4] The majority of applications, however, have used the macrocyclic ligands or the macrocyclic ligand complexes as selective receptors for cations or anions, and the metallocene (usually ferrocene) substituents as electrochemical probes, in order to construct highly selective electrochemical sensors.[2,5,9,10] An important feature in these applications is the interaction between the metallocene site and the metal ion coordinated to the macrocyclic donor set, and this has been studied by a variety of electrochemical and spectroscopic techniques.[2,4,5,11]

We report here the synthesis and the structural, electrochemical, and spectroscopic characterization of cyclam-derived ferrocene- and ruthenocene-containing macrocycles, based on a Schiff-base condensation of 2,3,2-tet [2,3,2-tet = *N*,*N'*-bis(2-aminoethyl)-1,3-propanediamine] with 1,1'-diformylmetallocene, and their iron(II)/(III), cobalt(II), nickel(II), copper(II), and zinc(II) complexes. The structural and electrochemical data together with the stability constants, determined by pH titrations, suggest that these ligands may be used as electrochemical sensors for specific metal ions (Cu^{II}), and preliminary Mössbauer spectra of the iron complexes indicate that optical as well as thermal switching between different electronic states is possible; this latter application is currently under further investigation. Here, we report the preparative and structural data as well as stability constants, the spectroscopic and electrochemical characterization of the ligands and their complexes.



Results and Discussion

Syntheses and Structures

The synthesis of the ferrocene- and ruthenocene-substituted ligands fcmac and rcmac is a simple [1+1] Schiff-base condensation, followed by $NaBH_4$ reduction of the imines, which proceeds, as in published examples of similar ligands,[9] in high over-all yield (over 80%). Complexation

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to iron(II)/(III), cobalt(II), nickel(II), copper(II), and zinc(II) results in dinuclear complexes in respectable yields.

The single crystal structure of [Cu(fcmac)(FBF$_3$)]BF$_4$ was solved by X-ray crystallography. A plot of the molecular structure is given in Figure 1 (a), and selected structural parameters are presented in Table 1. Crystals of [Ni(fcmac)(NCCH$_3$)$_2$](BF$_4$)$_2$ and [Ni(rcmac)(NCCH$_3$)$_2$](BF$_4$)$_2$ were also isolated but were not of high enough quality for a full structural analysis and submission of the data to CCDC. However, plots of these two structures also appear in Figure 1, and the determined approximate structural parameters are tabulated for comparison. The macrocycles are in the unusual *trans*-II (*S*,*S*,*R*,S; pseudo-*R*,S,*R*,*R*) configuration. This must be due to the unusually large and rigid ferrocene-appended chelate ring. However, the fact that all Cu−N distances (and the Ni−N distances) are in the expected ranges[13] indicates that little strain is imposed by the ferrocene or ruthenocene group on the macrocyclic ligand complex. This also follows from the other structural parameters; only the N1−M−N4 angles are slightly larger than usual. Another indication for the fairly strain-free geometry of the macrocyclic ligand copper(II) complex are the spectroscopic and electrochemical parameters and stability constants, which are all as expected for cyclam-type tetraazamacrocyclic ligand copper(II) complexes (see Tables 2 and 3 below; note, however, the stability constants of the other transition metal complexes and the relevant discussion). With respect to the geometry of the substituted metallocene group, the three structures are very similar to each other. The two Cp rings are staggered, and the only significant distortion is a small tilt of the two Cp planes by 5−7°, because of the coordination of the copper(II) or nickel(II) centers to the methylamine substituents at the Cp rings. The angles between the averaged Cp and the macrocycle planes are around 35°. The fact that, in terms of spectroscopic and electrochemical properties, all other macrocyclic ligand complexes show similar trends suggests that the structures of the complexes for which no structural data are available are also similar to those reported here.

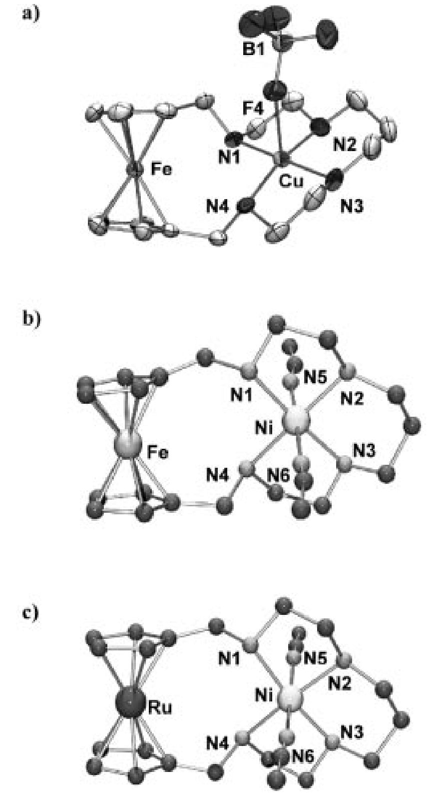

Figure 1. Structural plots of the molecular cations of [Cu(fcmac)(FBF$_3$)]BF$_4$, [Ni(fcmac)(NCCH$_3$)$_2$](BF$_4$)$_2$, and [Ni(rcmac)(NCCH$_3$)$_2$](BF$_4$)$_2$ (the structures of the two nickel complexes are of low quality and appear only for comparison (see text)

Complex Stabilities

Because of problems with the solubility of the ferrocene- and ruthenocene-appended macrocycles, the protonation constants and complex stabilities were determined in 1,4-dioxane/water mixtures. Similar solvent mixtures have been used for other ferrocene-functionalized macrocycles,[11] and those for cyclam (1,4,8,11-tetraazacyclotetradecane) have also been determined here under the same conditions for comparison (see Table 2). The two new ligands fcmac and rcmac have similar protonation constants, and these are also similar to those of another published ferrocene-functionalized cyclam ligand, FcCyclam, which is the 1,1′-ferrocenebis(methyl)-bridged 1,8-substituted cyclam ligand, bridged at 1,8-positions,[11] but the amine donors are significantly less basic than those of the unfunctionalized cyclam macrocycle. For the discussion of the complex stabilities we will concentrate here primarily on the complex formation constants of [M(L)]$^{2+}$, with L = fcmac, rcmac, FcCyclam and cyclam, and M = Cu^{2+}, as well as Co^{2+}, Ni^{2+}, and Zn^{2+}. The complex stabilities with fcmac and rcmac are nearly identical, and, as seen in the Cu^{2+} systems, they are significantly larger than those for the FcCyclam ligand system ($\Delta \log K \approx 10$). Note that the difference in solvent (water/dioxane, 3:7 vs. 7:3) probably does not lead to these large differences {[Cu(cyclam)]$^{2+}$ in H$_2$O: $\log K = 27.2$;[14] in water/dioxane, 3:7: $\log K = 23.5$} and the stability is smaller than that for cyclam ($\Delta \log K \approx 3$). The reduced stability (vs. cyclam) is due to a distortion from planarity of the CuN$_4$ chromophore (see below) and the interaction with the metallocene site. The difference between the fcmac/rcmac systems on one hand and FcCyclam on the other, which is also obvious from the protonation constants, must partially be due to the significantly different Fe···M (Cu) distances (4.5 Å, see Table 1, vs. 3.8 Å).[11]

More interesting is the variation of stabilities along the transition metal series. This usually follows the Irving−Williams series,[15] and for cyclam the corresponding logK values (measured in water)[16] for nickel(II), copper(II), and zinc(II) are 19.4, 27.2, and 15.5, respectively. It appears that fcmac and rcmac stabilize in particular copper(II); cobalt(II) and zinc(II) have stabilities which are a little lower than expected (see above), but nickel(II) is strongly destabilized. We attribute this behavior to the enforced *trans*-II configuration, which must be a result of the large and rather rigid ferrocene-appended chelate ring,

Table 1. Selected structural parameters of $[Cu(fcmac)(FBF_3)]BF_4$, $[Ni(fcmac)(NCCH_3)_2](BF_4)_2$, and $[Ni(rcmac)(NCCH_3)_2](BF_4)_2$ (the data of the two nickel complexes are of low quality and appear only for comparison, see text)

	$[Cu(fcmac)(FBF_3)]BF_4$ M′ = Fe, M = Cu	$[Ni(fcmac)(NCCH_3)_2](BF_4)_2$ M′ = Fe, M = Ni	$[Ni(rcmac)(NCCH_3)_2](BF_4)_2$ M′ = Ru, M = Ni
Distances [Å]			
M−N1	2.062(3)	2.09(3)	2.140(9)
M−N2	2.016(3)	2.05(3)	2.10(1)
M−N3	2.032(3)	2.16(3)	2.083(9)
M−N4	2.039(3)	2.16(3)	2.134(9)
M−X	2.428(4)(F4)	2.14(3)(N5) 2.01(3)(N6)	2.09 (1)(N5) 2.16(1)(N6)
M′−Cp[a]	1.63, 1.64	1.63, 1.64	1.88
N_4-plane (rms)	0.16	0.01	0.01
M-plane	0.12	0.05	0.05
M′···M	4.54	4.88	4.88
Angles [°]			
N1−M−N4	96.8(1)	98(1)	101.4(4)
N1−M−N2	86.5(1)	84(1)	84.1(4)
N4−M−N3	85.1(1)	85(1)	84.3(4)
N3−M−N2	91.2(1)	92(1)	90.0(4)
Φ [b]	37.1	10.7	10.6
θ [c]	6.9	6.6	5.4
τ [d]	34.5	33.2	30.0
α [e]	11.6°	3.9	5.1°

[a] Distance to the centroid of the Cp ring (Fe−Cp: 1.641).[27] [b] Torsional angle between the two Cp rings (amine substituents). [c] Tilt angle between the two Cp planes. [d] Angle between the average of the two Cp planes and the N_4 best plane. [e] Averaged tetrahedral twist of the MN_4 chromophores.

Table 2. Potentiometrically determined protonation and complex stability constants (log K values) of fcmac, rcmac and other tetraazamacrocyclic ligands [water/dioxane, 30:70, T = 25 °C, μ = 0.1 M (KCl)]

Protonation constants	fcmac	rcmac	FcCyclam[11] [a]	cyclam
$L + H^+ \rightleftarrows [LH]^+$	9.77	10.05	9.21	11.10
$L + 2H^+ \rightleftarrows [LH_2]^{2+}$	17.75	18.10	15.27	21.80
$L + 3H^+ \rightleftarrows [LH_3]^{3+}$	23.35	23.2	18.46	24.70
$L + 4H^+ \rightleftarrows [LH_4]^{4+}$	27.40	26.0	−	26.00

Stability constants	Cu/Fcmac	Cu/rcmac	Cu/FcCyclam	Cu/Cyclam	Co/fcmac	Co/rcmac	Ni/fcmac	Ni/rcmac	Zn/fcmac	Zn/rcmac
$M^{2+} + L + 2H^+ \rightleftarrows [MLH_2]^{4+}$	26.50	26.00	−	−	26.0	26.0	21.3	−	20.5	20.0
$M^{2+} + L + H^+ \rightleftarrows [MLH]^{3+}$	24.00	23.00	13.9	29.0	23.0	23.0	15.8	15.5	15.6	15.1
$M^{2+} + L \rightleftarrows [ML]^{2+}$	20.40	20.50	9.3	23.5	18.0	18.0	9.6	9.6	8.5	10.2
$M^{2+} + L + OH^- \rightleftarrows [ML(OH)]^+$	6.80	7.30	−3.3	9.5	12.0	12.0	0.7	1.8	0.2	2.1
$M^{2+} + L + 2OH^- \rightleftarrows [ML(OH)_2]$	−	−	−	−	4.1	6.3	−	−	−	−

[a] In water/dioxane, 30:70.

which enforces a considerable tetrahedral twist. The tetrahedral twist angles (angle between the planes N2/N3/Cu and N1/N4/Cu) for Cu(fcmac), Ni(fcmac), and Cu(cyclam) are 12°, 4°, and 0°, respectively. A deformation from planarity of the $M(N_4)$ chromophore is more destabilizing for nickel(II) than for copper(II), and the result in the present case (see structural parameters above) leads both to a substantial electronic destabilization and an increase in ligand strain for nickel(II). Probably, it is primarily ligand strain which leads to the relatively low stability of the nickel(II) complex. The result is a strong preference for copper(II), and this selectivity is an important prerequisite for efficient copper-selective sensors, based on fcmac, rcmac, and corresponding derivatives.

Spectroscopy and Electrochemistry

The guest-dependent shift of the Fc/Fc^+ couple in ferrocene-substituted host molecules has often been used to analyze the interaction between the ferrocene iron center and a guest molecule. With cationic guests (metal ions) the reduced form is generally stabilized (shifts towards more positive potentials by a few hundred millivolts).[6,17−20] Primarily, this is due to electrostatic effects, but direct electronic interactions might also contribute (see data in Table 3, see also below).[21] Similar shifts were also observed for the Rc/Rc^+ couple in complexes with rcmac ($[Cu(rcmac)](BF_4)_2$ 834 mV, $[Ni(rcmac)(NCCH_3)_2](BF_4)_2$ 716 mV, measured vs. $Ag/AgNO_3$ under the same conditions). The ligand rcmac

Table 3. Electrochemical and spectroscopic data of fcmac and the corresponding complexes

Compound	E_p (ΔE_p)[a] [mV]	IR C−H out-of-plane[c] [cm^{-1}]	Mössbauer[b] δ_{IS} [mm/s]	ΔE_Q [mm/s]
Ferrocene	87	815	0.416	2.370
fcmac	109 (47)	840[d]	–[e]	–
fcmac·HCl	–[f]	–	0.392	2.350
[Cu(fcmac)(FBF$_3$)]BF$_4$	308 (50)	820	0.423	2.410
[Ni(fcmac)(NCCH$_3$)$_2$](BF$_4$)$_2$	233 (87)	816	0.403; 0.384	2.390; 2.254
[Zn(fcmac)](ClO$_4$)$_2$	264 (82)	–	0.380; 0.407	2.231; 2.368
[Co(fcmac)](BF$_4$)$_2$	–[g]	812	0.387; 0.404	2.201; 2.374
[Fe(fcmac)](SCN)$_3$	–[h]	809	0.397; 0.250	2.323; 0.515
[Fe(fcmac)]Fe(SO$_4$)$_2$	–[h]	809	–	–
[Cu(fcmac)(BF$_4$)$_2$]PF$_6$	–[f]	834	0.394; 0.405	2.250; 0.435

[a] CH_3CN, 0.1 M Bu_4NPF_6, 298 K, Fc/Fc$^+$-centered process. [b] Relative to Co in Rh, 10 K. [c] KBr pellets. [d] Fcmac$^+$PF$_6^-$. [e] Ligand is a liquid. [f] Decomposition during measurement. [g] Irreversible oxidation. [h] Insoluble in all common solvents.

itself decomposes under the measurement conditions and therefore gives no interpretable voltammogram.

Another efficient tool to analyze metal···metal interactions in ferrocene-appended host molecules is the C−H out-of-plane bending vibration in ferrocene (815 cm^{-1}), shifted to higher energies (840 cm^{-1}) in the ferrocenium ion. The comparably small shifts[6] observed in the present examples indicate that the distance between the ferrocene (or ruthenocene) subunits and the guest metal ion is large, and that the metal···metal interaction is relatively weak. The fact that the shift with Cu^{2+} is largest correlates well with the observed reduction potentials, and this indicates that some electron transfer is involved.

Both the UV/Vis and the EPR spectra of [Cu(fcmac)]$^{2+}$ indicate that the CuN$_4$ plane is significantly distorted ($g_{x,y}$ = 2.06, g_z = 2.20, $A_{x,y}$ = 18 × 10^{-4} cm^{-1}, A_z = 197 × 10^{-4} cm^{-1}, λ_{max} = 557 nm; the corresponding data for a 15-membered N$_4$ macrocycle {[Cu[15]ane N$_4$]$^{2+}$; [15]ane N$_4$] = 1,4,8,12-tetraazacyclopentadecane, which is known to have a tetrahedral distortion similar to that of [Cu(fcmac)]$^{2+}$, with a twist angle of 16°},[22] are 2.05, 2.19, 24 × 10^{-4}, 194 × 10^{-4}, 582, respectively). This is as expected from the solid state structural data.

The isomer shifts δ_{IS} and quadrupole splitting values ΔE_Q in the ^{57}Fe Mössbauer spectra (10 K) of the fcmac complexes are also summarized in Table 3, where the corresponding values of ferrocene and fcmac·HCl appear for comparison. The parameters for fcmac·HCl (δ_{IS} = 0.392 mm s^{-1}, ΔE_Q = 2.350 mm s^{-1}) are typical for low-spin Fe^{II} in a metallocene coordination sphere and indicate, in comparison with ferrocene (δ_{IS} = 0.416 mm s^{-1}, ΔE_Q = 2.370 mm s^{-1}), a reduced electron density at the nucleus and an increased distortion of the iron center. The linear correlation of the reduction potentials with the isomer shifts[23] (see Figure 2) is significant and reflects primarily the electrostatic perturbation of the electronic properties of the ferrocene iron centers. For the Ni^{II}, Zn^{II}, and Co^{II} complexes of fcmac two slightly different doublets were observed, and upon irradiation (Ar laser, 514.5 nm) the relative populations were altered.[24] Preliminary results suggest that the corresponding Fe^{II} and Fe^{III} complexes, [Fe(fcmac)]Fe(SO$_4$)$_2$ and [Fe(fcmac)](SCN)$_3$, appear as thermally and optically induced switches. These features are currently under thorough investigation and will be published in due course.

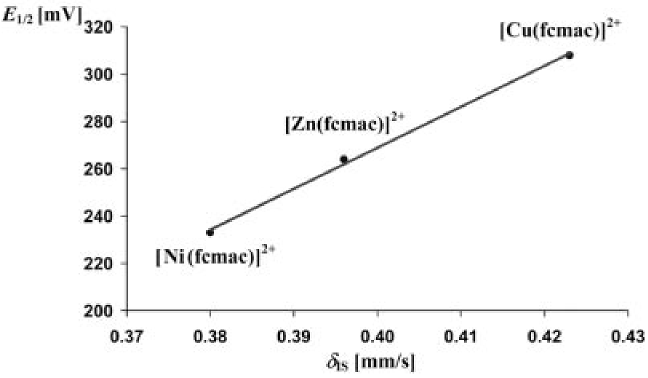

Figure 2. Correlation of the reduction potentials of [Cu(fcmac)]$^{2+}$, [Ni(fcmac)]$^{2+}$, and [Zn(fcmac)]$^{2+}$ with the corresponding Mössbauer isomer shifts

Conclusion

Two novel tetraazamacrocyclic ligands with metallocene (Fe, Ru) bridges and their heterodinuclear transition metal complexes [iron(II)/(III), cobalt(II), nickel(II), copper(II), and zinc(II)] have been prepared and fully characterized. The two main features are (i) that there is significant electronic communication between the metal centers, and this is due to a relatively short metal···metal distance {4.54 Å in the structurally characterized [Cu(fcmac)(FBF$_3$)]BF$_4$ complex}, and (ii) that the complex stabilities with the two macrocycles do not follow the usual Irving−Williams-type behavior; the copper(II) complexes have stabilities which are, as expected, similar to those with tetraazamacrocycles with the usual alkyl bridges; the nickel(II) complexes are unusually unstable. This is probably due to the uncommon *trans*-II configuration of the metallocene-substituted macrocycle, which induces considerable strain on and a distortion from planarity of the macrocycle.

Experimental Section

Measurements and Materials: Commercially available solvents and reagents were used without further purification. The syntheses of the ligands were carried out under argon. 1,1′-Diformylferrocene and 1,1′-diformylruthenocene were prepared as described in the literature.[25] NMR spectra were recorded with a Bruker AS 200 (^{1}H NMR 200.13 MHz, ^{13}C NMR 50.33 MHz) spectrometer. The spectra were referenced to the solvent signals. Mass spectra were recorded with a Finnigan 8400 instrument. IR spectra were recorded with a Perkin−Elmer 16C spectrometer as KBr pellets. UV/Vis spectra were measured with a Varian Cary 1E spectrometer in MeOH or MeCN. Potentiometric titrations were carried out in 1,4-dioxane/water (30:70 v/v, 0.1 M KCl) using a reaction vessel thermostatted at 25.0 ± 0.1 °C under nitrogen. The computer program HYPERQUAD[14,26] was used to calculate the protonation and stability constants. The concentrations of the ligands were 0.05 mmol/L; 0.8 equiv. of metal salts were used. Electrochemical measurements were obtained with a BAS100 W electrochemical analysis instrument. A glassy carbon working electrode and a platinum auxiliary electrode were used; 2×10^{-3} M solutions in CH_3CN with tetrabutylammonium hexafluorophosphate (0.1 M). Potentials were measured relative to $Ag/AgNO_3$ (0.01 M $AgNO_3$). The scan rate was varied from 10 to 100 mV s^{-1}. EPR spectra were recorded with a Bruker ELEXSYS E500 spectrometer (X band) as approximately 10^{-3} mol L^{-1} frozen solutions (liquid N_2) in DMF/water, 2:1. XSophe, version 1.0.2β, on a Linux workstation was used for the simulation of the spectra. A standard transmission Mössbauer spectrometer was used. The ^{57}Co source was kept at room temperature and the isomeric shifts are relative to Co in Rh. An argon ion laser was used for the irradiation at 514.5 nm and 35 mW/cm^2. The Mössbauer spectra were fitted with the software MOSFUN and RECOIL.

Syntheses of the Ligands

fcmac: A solution of 1,1′-diformylferrocene (1.00 g, 4.13 mmol) and 2.3.2-tet (0.66 g, 4.13 mmol) in absolute methanol (40 mL) was refluxed for 4 h. After cooling to room temperature, $NaBH_4$ (0.48 g, 12.69 mmol) in degassed water (10 mL) was added, and the reaction mixture was stirred overnight. The solvent was evaporated, and the water phase was extracted with CH_2Cl_2 (3 × 20 mL). The collected organic extracts were filtered through Celite, and the solvent was evaporated, yielding 1.24 g (3.35 mmol, 81%) of a brown and highly viscous oil. ^{1}H NMR (CD_2Cl_2, 200.13 MHz): δ = 1.49−1.79 (m, 2 H, CH_2), 2.10 (br. s, 4 H, NH), 2.37−2.84 (m, 12 H, CH_2), 3.39 (s, 4 H, Cp−CH_2), 4.00−4.30 (m, 8 H, Cp−H) ppm. ^{13}C NMR (CD_2Cl_2, 50.33 MHz): δ = 28.7 (1 C, CH_2), 48.1 (2 C, CH_2), 49.1 (2 C, CH_2), 49.4 (2 C, Cp−CH_2), 67.3 (4 C, Cp), 67.8 (4 C, Cp), 88.5 (2 C, Cq, Cp) ppm. UV/Vis (MeOH): λ = 309 (ε = 733 $\text{M}^{-1}\text{cm}^{-1}$), 436 ($\varepsilon$ = 251 $\text{M}^{-1}\text{cm}^{-1}$) nm. MS-FAB (NBA): *m*/*z* = 371.1 [M + H]$^+$.

rcmac: As described for fcmac, the reaction of 1,1′-diformylruthenocene (0.50 g, 1.74 mmol) with 2.3.2-tet (0.28 g, 1.74 mmol) in absolute methanol (20 mL), followed by reduction with $NaBH_4$ (0.20 g, 5.29 mmol) in degassed water (5 mL) yielded 0.61 g (1.48 mmol, 85%) of rcmac as a yellow and highly viscous oil. ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 1.42−1.98 (m, 6 H, CH_2 and NH), 2.49−2.77 (m, 12 H, CH_2), 3.21 (s, 4 H, Cp−CH_2), 4.38 (m, 4 H, Cp−H), 4.54 (m, 4 H, Cp−H) ppm. ^{13}C NMR (CD_2Cl_2): 28.0 (1 C, CH_2), 49.7 (2 C, CH_2), 50.2 (4 C, CH_2), 50.3 (2 C, Cp-CH_2), 70.2 (4 C, Cp-C), 71.5 (4 C, Cp−C), 94.0 (2 C, C$_q$, Cp−C) ppm. MS-FAB (NBA): *m*/*z* = 417.2 [M + H]$^+$.

fcmac$^+$PF$_6$: A solution of fcmac (478 mg, 1.29 mmol) and ferrocenyl hexafluorophosphate (427 mg, 1.29 mmol) in abs. CH_2Cl_2 (20 mL) was stirred at room temperature for 2.5 h. It was filtered, and the solvent was evaporated. The resulting brown solid was washed with Et_2O until washings were colorless. Drying in vacuo yielded 371 mg (0.72 mmol, 56%) of a brown powder. MS-FAB (NBA): *m*/*z* = 514.3 [M]$^+$, 371.3 [M − PF$_6$]$^+$. UV/Vis (MeOH): λ = 317 (ε = 353 $\text{M}^{-1}\text{cm}^{-1}$), 440 ($\varepsilon$ = 197 $\text{M}^{-1}\text{cm}^{-1}$) nm. IR: $\tilde{\nu}$ = 3235 (w), 3078 (w), 2932 (w), 2833 (w), 2358 (w), 1457 (m), 1106 (w), 1040 (w), 840 (s), 557 (m) cm^{-1}.

Metal Complexes of fcmac and rcmac: Complexes of fcmac and rcmac were obtained by reaction of equal amounts of ligand and metal salt in methanol (0.5 mmol in 5 mL) at room temperature and stirring overnight. The resulting precipitate was filtered off, washed with methanol, and dried in vacuo. If necessary the compounds were recrystallized from acetonitrile. Single crystals for X-ray diffraction were obtained by ether diffusion into complex solutions in acetonitrile.

[Cu(fcmac)(FBF$_3$)]BF$_4$: Yield 46% of a pink solid. $C_{19}H_{30}B_2CuF_8FeN_4$ (607.38): calcd. C 37.57, H 4.98, N 9.22; found C 37.67, H 5.19, N 8.95. MS-FAB (NBA): *m*/*z* = 607.1 [Cu(fcmac)(BF$_4$)$_2$]$^+$, 520.1 [Cu(fcmac)(BF$_4$)]$^+$, 433.1 [Cu(fcmac)]$^+$. UV/Vis (MeCN): λ = 411 (ε = 302 $\text{M}^{-1}\text{cm}^{-1}$), 557 ($\varepsilon$ = 150 $\text{M}^{-1}\text{cm}^{-1}$) nm. IR: $\tilde{\nu}$ = 3252 (m), 2922 (w), 2870 (w), 2358 (m), 2336 (w), 1636 (w), 1456 (w), 1420 (w), 1082 (s), 880 (w), 820 (w), 522 (w), 478 (w) cm^{-1}. Single crystals were obtained by ether diffusion into an acetonitrile solution.

[Ni(fcmac)(NCCH$_3$)$_2$](BF$_4$)$_2$: Yield 23% of a brown solid. $C_{19}H_{30}B_2F_8FeN_4Ni$ (602.62): calcd. C 37.87, H 5.02, N 9.30; found C 38.72, H 5.37, N 8.92. UV/Vis (MeCN): λ = 310 (ε = 223 $\text{M}^{-1}\text{cm}^{-1}$), 436 ($\varepsilon$ = 84 $\text{M}^{-1}\text{cm}^{-1}$) nm. IR: $\tilde{\nu}$ = 3534 (s), 3232 (s), 2942 (m), 2876 (m), 2358 (w), 1636 (m), 1462 (m), 1430 (m), 1058 (s), 816 (m), 764 (w), 520 (m), 484 (w) cm^{-1}.

[Zn(fcmac)](ClO$_4$)$_2$×MeOH: Yield 21% of a brown solid. $C_{20}H_{34}Cl_2FeN_4O_9Zn$ (666.65): calcd. C 36.03, H 5.14, N 8.40; found C 36.47, H 5.24, N 8.59.

[Fe(fcmac)](SCN)$_3$: Yield 47% of a brown solid. MS-FAB (NBA): *m*/*z* = 542.1 [Fe(fcmac)(SCN)$_2$]$^+$, 484.1 [Fe(fcmac)(SCN)]$^+$. IR: $\tilde{\nu}$ = 3391 (m), 3068 (w), 2939 (w), 2042 (s, SCN), 1647 (m), 1443 (w), 1238 (w), 1039 (w), 828 (w), 478 (w) cm^{-1}.

[Fe(fcmac)]Fe(SO$_4$)$_2$×3MeOH: Yield 51% of a brown solid. $C_{22}H_{44}Fe_3N_4O_{11}S_2$ (772.27): calcd. C 34.22, H 5.74, N 7.25; found C 34.63, H 5.51, N 6.73. IR: $\tilde{\nu}$ = 3386 (s), 3217 (m), 3080 (m), 2923 (m), 2358 (m), 2343 (w), 1635 (m), 1458 (m), 1109 (s, SO$_4$), 1026 (s), 966 (w), 809 (w), 602 (w), 484 (w) cm^{-1}.

[Cu(rcmac)](BF$_4$)$_2$: Yield 64% of a violet solid. $C_{19}H_{30}B_2CuF_8N_4Ru$ (652.69): calcd. C 34.96, H 4.63, N 8.58; found C 35.02, H 4.74, N 8.33. MS-FAB (NBA): *m*/*z* = 479.4 [Cu(rcmac)]$^+$. UV/Vis (MeCN): λ = 532 (ε = 120 $\text{M}^{-1}\text{cm}^{-1}$) nm. IR: $\tilde{\nu}$ = 3251 (m), 3103 (w), 2930 (w), 2886 (w), 1418 (m), 1069 (s), 812 (m), 519 (w), 429 (w) cm^{-1}.

[Ni(rcmac)(NCCH$_3$)$_2$]](BF$_4$)$_2$: Yield 52% of a yellow solid. $C_{19}H_{30}B_2F_8N_4NiRu$ (647.84): calcd. C 35.23, H 4.67, N 8.65; found C 35.29, H 4.73, N 8.55. MS-FAB (NBA): *m*/*z* = 561.5 [Ni(rcmac)(BF$_4$)]$^+$. UV/Vis (MeCN): λ = 309 (ε = 201 $\text{M}^{-1}\text{cm}^{-1}$), 400 ($\varepsilon$ = 36 $\text{M}^{-1}\text{cm}^{-1}$) nm. IR: $\tilde{\nu}$ = 3262 (m), 3228 (m), 2949 (w), 2879 (w), 1460 (m), 1420 (m), 1034 (s), 819 (w), 518 (w) cm^{-1}. Single crystals were obtained by ether diffusion into an acetonitrile solution.

$[Cu(fcmac^+)](BF_4)_2PF_6$: A solution of $fcmac^+PF_6^-$ (116 mg, 0.23 mmol) and $Cu(BF_4)_2\cdot 6H_2O$ (78 mg, 0.23 mmol) in absolute methanol (7 mL) was stirred at room temperature overnight. The solution was filtered, and the solvent was evaporated. The resulting violet solid was dried in vacuo. Yield 98 mg (0.11 mmol, 49%). MS-ESI (MeOH): m/z = 502.6 $[Cu(fcmac_{ox})BF_4]^+$, 434.6 $[Cu(fcmac_{ox})]^+$. UV/Vis (MeOH): λ = 353 (ε = 1243 $M^{-1}cm^{-1}$), 489 (ε = 376 $M^{-1}cm^{-1}$), 609 (ε = 191 $M^{-1}cm^{-1}$) nm. IR: $\tilde{\nu}$ = 3419 (w), 3262 (w), 3114 (w), 2949 (w), 2921 (w), 1050 (s), 834 (s), 558 (m) cm^{-1}.

Crystal Structure Determinations: Crystal data and details of the structure determinations are listed in Table 4. Intensity data were collected at low temperature with a Stoe IPDS image plate (Mo-K_α radiation, λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least squares, based on F^2 with all reflections using the SHELXTL programs (G. M. Sheldrick, *SHELXTL NT*, v5.10, Bruker AXS, Madison, Wisconsin, USA, **1998**). CCDC-218906 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html [or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail:deposit@ccdc.cam.ac.uk].

Table 4. Crystallographic data and data collection parameters for $[Cu(fcmac)(FBF_3)]BF_4$

Empirical formula	$C_{19}H_{30}B_2CuF_8FeN_4$
M_r	607.48
T [K]	203(2)
λ [Å]	0.71073
Crystal system, space group	orthorhombic, $P2_12_12_1$
Unit cell dimensions	a = 8.094 (2) Å b = 14.352 (3) Å c = 4.0611 (8) Å
Crystal size [mm]	0.30 × 0.30 × 0.05
Volume [nm³]	4.717(2)
Z	8
Density (calculated) [g/cm³]	1.711
Absorption coefficient [mm⁻¹]	1.596
F(000)	2472
Goodness-of-fit on F^2	0.961
Final R indices {$R1$ [$I > 2\sigma(I)$]; $wR2$ (all data)}	$R1$ = 0.0300; $wR2$ = 0.0713
Largest diff. peak/hole [e·Å⁻³]	0.313/−0.391

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[1] P. D. Beer, *Chem. Soc., Rev.* **1989**, *18*, 409.
[2] P. D. Beer, *Acc. Chem. Res.* **1998**, *31*, 71.
[3] J. M. Lloris, R. Martinez-Manez, M. Padialla-Tasta, T. Pardo, J. Soto, M. J. L. Tendero, *J. Chem. Soc., Dalton Trans.* **1998**, 3657.
[4] H. Plenio, C. Aberle, *Angew. Chem.* **1998**, *110*, 1467; *Angew. Chem. Int. Ed.* **1998**, *37*, 1397.
[5] P. D. Beer, P. A. Gale, G. Z. Chen, *J. Chem. Soc., Dalton Trans.* **1999**, 1897.
[6] P. Comba, J. Ensling, P. Gütlich, A. Kühner, A. Peters, H. Pritzkow, *Inorg. Chem.* **1999**, *38*, 3316.
[7] P. Comba, A. Kühner, A. Peters, *J. Chem. Soc., Dalton Trans.* **1999**, 509.
[8] P. D. Beer, D. Hesek, K. C. Nam, M. G. B. Drew, *Organometallics* **1999**, *18*, 3933.
[9] P. D. Beer, J. Cadman, J. M. Lloris, R. Martinez-Manez, M. E. Padilla, T. Pardo, D. K. Smith, J. Soto, *J. Chem. Soc., Dalton Trans.* **1999**, 127.
[10] P. D. Beer, P. V. Bernhardt, *J. Chem. Soc., Dalton Trans.* **2001**, 1428.
[11] H. Plenio, C. Aberle, Y. Al Shihadd, J. M. Lloris, R. Matinez-Manez, T. Pardo, J. Soto, *Chem. Eur. J.* **2001**, *7*, 2848.
[12] D. Astruc, *New. J. Chem.* **1992**, *16*, 305.
[13] J. C. A. Boeyens, S. M. Dobson, in *Stereochemical and Stereophysical Behaviour of Macrocycles* (Ed.: I. Bernal), Elsevier, Amsterdam, New York, **1987**, p. 1.
[14] L. Alderighi, P. Gans, A. Ienco, D. Peters, A. Sabbatini, A. Vacca, *Coord. Chem. Rev.* **1999**, *148*, 311.
[15] H. Irving, R. J. P. Williams, *Nature* **1948**, *162*, 746.
[16] R. C. Luckay, R. D. Hancock, *J. Chem. Soc., Dalton Trans.* **1991**, 1491.
[17] A. Togni, T. Hayashi, in *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science* (Eds.: A. Togni, T. Hayashi), VCH, Weinheim, New York, **1995**.
[18] P. D. Beer, J. N. Nation, S. L. W. Mcwhinnie, M. E. Harman, M. B. Hursthouse, M. I. Ogden, A. H. White, *J. Chem. Soc., Dalton Trans.* **1991**, 2485.
[19] P. D. Beer, Z. Cheng, M. G. B. Drew, J. Kingston, M. Ogden, P. Spencer, *J. Chem. Soc., Chem. Commun.* **1993**, 1046.
[20] U. Siemeling, *J. Chem. Soc., Dalton Trans.* **1997**, 4705.
[21] A. J. Evans, S. E. Watkins, D. C. Craig, S. B. Colbran, *J. Chem. Soc., Dalton Trans.* **2002**, 983.
[22] P. Comba, T. W. Hambley, M. A. Hitchman, H. Stratemeier, *Inorg. Chem.* **1995**, *34*, 3903.
[23] P. Gütlich, R. Link, A. Trautwein, *Mössbauer Spectroscopy and Transition Metal Chemistry*, Springer-Verlag, Berlin, New York, **1978**.
[24] P. Comba, K. Merz, F. Renz, manuscript in preparation.
[25] G. G. A. Balavoine, G. Doisenau, T. Fillebeen-Khan, *J. Organomet. Chem.* **1991**, *412*, 381.
[26] P. Gans, A. Sabatini, A. Vacca, *Talanta* **1996**, *43*, 1739.
[27] J. D. Dunitz, L. E. Orgel, A. Rich, *Actra Crystallogr.* **1956**, *9*, 373.

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