In conclusion, we suggest that DAF-FM is a useful tool for visualizing the temporal and spatial distribution of intracellular NO.

Experimental Section

The synthesis of the indicators is described in the Supporting Information.

Fluorescence spectroscopy: The DAFs were dissolved in DMSO to obtain 10 mM stock solutions. Relative quantum efficiencies of fluorescence of DAFs and DAF-Ts were obtained by comparing the area under the corrected emission spectrum of the test sample upon excitation at 492 nm with that of a solution of fluorescein in 0.1 M sodium hydroxide, which has a quantum efficiency of 0.85.[8] Bleaching of dyes (10 μM) was determined in 0.1 M sodium phosphate buffer (pH 7.4). The solutions in 30-mL vials were placed in full sunlight on a fine day in November in Tokyo and were sampled every 1 h.

Imaging: Primary cultured endothelial cells from bovine aorta were passaged in Dulbecco's modified Eagle's medium containing 10% fetal bovine serum and antibiotics. Cells between the 13th and 16th passages were used for these experiments. The cells were incubated for 1 h at 37 °C in PBS(+) (PBS = phosphate buffered saline) containing 10 μM DAF-FM DA (0.2% DMSO) for loading, and washed with PBS(+). They were mounted on an inverted fluorescence microscope (Olympus IX70, Tokyo, Japan) equipped with an objective lens (×20), an excitation filter (490 nm), a dichroic mirror (505 nm), and a long-pass emission filter (515 nm). The air temperature was maintained at 37 °C with a warming box (IX-IBM, Olympus). Optical signals were recorded with an Argus 50 (Hamamatsu Photonics, Shizuoka, Japan), which is an imaging system including a cooled charge-coupled device (CCD) camera. Bradykinin and L-NAME were purchased from Sigma (St. Louis, MO, USA).

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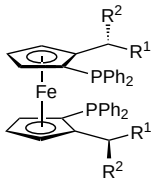
[1] *Methods Enzymol.* **1996**, *269* (the reference refers to the whole issue).
[2] M. Bätz, H. G. Korth, R. Sustmann, *Angew. Chem.* **1997**, *109*, 1555 – 1557; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1501 – 1503.
[3] H. Kojima, N. Nakatsubo, K. Kikuchi, S. Kawahara, Y. Kirino, H. Nagoshi, Y. Hirata, T. Nagano, *Anal. Chem.* **1998**, *70*, 2446 – 2453.
[4] N. Nakatsubo, H. Kojima, K. Kikuchi, H. Nagoshi, Y. Hirata, D. Maeda, Y. Imai, T. Irimura, T. Nagano, *FEBS Lett.* **1998**, *427*, 263 – 266.
[5] I. Fleming, M. Hecker, R. Busse, *Circ. Res.* **1994**, *74*, 1220 – 1226.
[6] NONOate = (*Z*)-1-{*N*-[3-aminopropyl]-*N*-[4-(3-aminopropylammonio)butyl]amino}diazen-1-ium-1,2-diolate; see: J. A. Hrabie, J. R. Klose, D. A. Wink, L. K. Keefer, *J. Org. Chem.* **1993**, *58*, 1472 – 1476.
[7] W. C. Sun, K. R. Gee, D. H. Klaubert, R. P. Haugland, *J. Org. Chem.* **1997**, *62*, 6469 – 6475.
[8] Y. Nishikawa, K. Hiraki, *Analytical Methods of Fluorescence and Phosphorescence*, Kyoritsu Publishing Company, Tokyo, **1984**, pp. 76 – 80.

Ferrocenyl Ligands with Two Phosphanyl Substituents in the α,ε positions for the Transition Metal Catalyzed Asymmetric Hydrogenation of Functionalized Double Bonds**

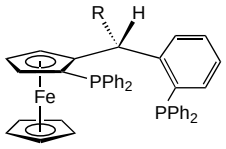
Tania Ireland, Gabriele Grossheimann, Catherine Wieser-Jeunesse, and Paul Knochel*

Dedicated to Professor Armin de Meijere on the occasion of his 60th birthday

Chiral ferrocene ligands have found numerous useful applications in asymmetric catalysis.[1] Recently, we described a new family of C_2-symmetrical ferrocenyl ligands called Ferriphos **1**, which proved to be efficient catalysts for the hydrogenation of α-acetoamidoacrylic acid derivatives.[2, 3] We have now discovered another class of chiral diphosphanylferrocenyl derivatives **2a**–**d** which are excellent ligands for the enantioselective hydrogenation of various functionalized double bonds and carbonyl groups. The relatively broad area



1: Ferriphos



2a : R = NMe_2
2b : R = *N*-pyrrolidyl
2c : R = Me
2d : R = *i*Pr

of application of this new class of α,ε-diphosphanes in asymmetric catalysis as well as their short synthesis makes these ligands especially attractive. The modular approach to their synthesis means that a variety of substituents R (alkyl or amino groups) can be introduced in the benzylic position. As shown later, the nature of R is crucial to the enantioselectivity observed with these ligands.

The ferrocenyl derivatives **2** are readily prepared in five steps starting from ferrocene (Scheme 1). Thus, a Friedel–Crafts acylation of ferrocene with 2-bromobenzoyl chloride furnishes the ferrocenyl ketone **3** in 80% yield. The Corey-Bakshi-Shibata (CBS) reduction[4] of **3** affords the corresponding ferrocenyl alcohol in 95% yield and 96% *ee*. This

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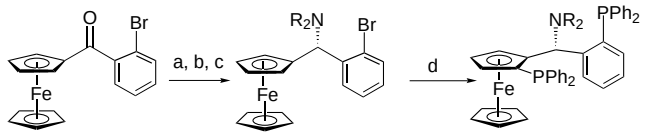
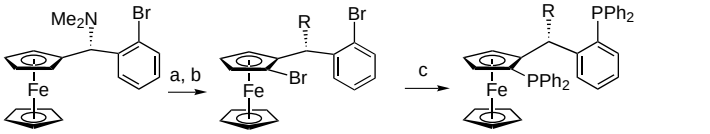


Scheme 1. a) CBS catalyst (0.3 equiv), BH_3-Me_2S, 0 °C, 2 h; b) Ac_2O, pyridine, 12 h; c) HNR_2, CH_3CN, H_2O, 12 h; d) *t*BuLi (3.5 equiv), −78 °C to room temperature (RT), 1 h; then $ClPPh_2$ (2.5 equiv), −78 °C to RT, 1 h.

alcohol is obtained almost enantiomerically pure (99.5 % *ee*) after recrystallization from heptane. Acylation of the alcohol gives the intermediate acetate in a quantitative yield, which is converted into the corresponding amino derivatives **4a** and **4b** by treatment with dimethylamine or pyrrolidine, respectively. These are then converted into **2b** and **2c**, respectively, in approximately 97 % *ee* by the reaction with *t*BuLi followed by the addition of $ClPPh_2$,

Finally, **4a** was dilithiated with *t*BuLi and converted into the corresponding dibromide by reaction with $Cl_4Br_2C_2$ (80 % yield, 97.5 % *ee*; Scheme 2), which can then be directly substituted with various organozinc reagents (Me_2Zn and



Scheme 2. a) *t*BuLi (3.5 equiv), −78 °C to RT, 1 h; then $Cl_4Br_2C_2$ (2.2 equiv), −78 °C to RT, 1 h, 80 % yield, 97.5 % *ee*; b) CH_3COCl (2 equiv), R_2Zn (4 equiv), THF, −78 °C to RT, 12 h; c) *n*BuLi (2.2 equiv), −78 °C, 15 min, then $ClPPh_2$ (2.3 equiv), −78 °C to RT, 1 h.

iPr_2Zn) using acetyl chloride as a promotor. This process leads to the substitution products **5a** and **5b** with high retention of configuration (*d.r.* > 94:6). The diphosphanes **2c** and **2d** were obtained in 92 and 31 % yield, respectively, after exchange of the bromine atoms with lithium and reaction with $ClPPh_2$.

Remarkably, the ligands **2a**–**d** are highly efficient for the asymmetric hydrogenation of various β-ketoesters of type **6** (Table 1).[5, 6] The hydrogenation reactions were performed using the standard conditions of $[Ru(cod)(C_4H_7)_2]/HBr$[7] (0.5 mol %; cod = cycloocta-1,5-diene, C_4H_7 = 2-methylallyl) and ligands **2a**–**d** (0.5 mol %) in EtOH at 50 °C and under H_2 (50 bar).

The same configuration for the hydrogenated products **7** are obtained using the ligands **2a, 2b**, and **2d**, while the β-hydroxyesters having the opposite configuration (*ent*-**7**) result from the use of **2c** (R = Me) (92–96 % *ee*; entries 4, 6, and 9 in Table 1).

The hydrogenation can be applied successfully to cyclic ketoesters such as ethyl 2-oxocyclopentane carboxylate[8] to give (1*R*,2*R*)-ethyl 2-hydroxy-1-cyclopentane carboxylate (**8**) with 98 % *de* and 90.9 % *ee* after complete conversion ("Ru"/**2a** (0.5 mol %), H_2 (50 bar), CH_2Cl_2/EtOH 1/10, 50 °C, 65 h). The enantiomeric product (1*S*,2*S*)-*ent*-**8** is obtained with 90.5 % *de* and 91.6 % *ee* from **2c** ("Ru"/**2c** (0.5 mol %),

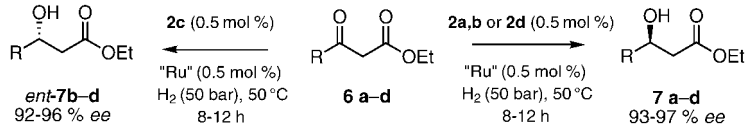
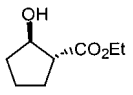
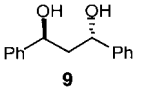
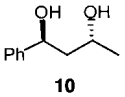


Table 1. Enantioselective hydrogenation of β-ketoesters with the "Ru"[a] chiral ligand catalytic system.

Entry	Substrate	R	Ligand	Product	% *ee*[b]
1	**6a**	Me	**2a**	**7a**	95.5 (93.2)[c]
2	**6a**	Me	**2d**	**7a**	95.9
3	**6b**	*n*Pr	**2a**	**7b**	96.5
4	**6b**	*n*Pr	**2c**	ent-**7b**	92.7
5	**6c**	*i*Pr	**2a**	**7c**	95.9
6	**6c**	*i*Pr	**2c**	ent-**7c**	96.5
7	**6d**	Ph	**2a**	**7d**	95.0
8	**6d**	Ph	**2d**	**7d**	96.0
9	**6d**	Ph	**2c**	ent-**7d**	93.7

[a] $[Ru(cod)(C_4H_7)_2]/HBr$; [b] Determined by GC on a chiral phase (Chirasil-L-Val) or by HPLC on a chiral phase (Daicel Chiralcel OD, OJ, or AD columns). The absolute stereochemistry was established by comparison with the literature. [c] Reaction performed with a substrate to catalyst ratio of 5000 to 1.

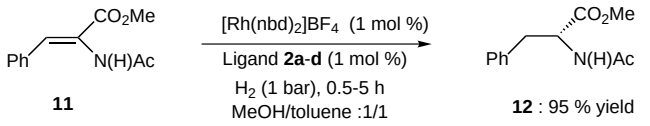
Table 2. Enantioselective hydrogenation of various β-dicarbonyl compounds.

Entry	Product	Ligand	*de* (%)[a]	*ee* (%)[a,b]
1	 **8**	**2a**	98.2	90.9 (1*R*,2*R*)
2	*ent*-**8**	**2c**	90.5	91.6 (1*S*,2*S*)
3	 **9**	**2a**	98.0	98.2 (1*S*,3*S*)
4	*ent*-**9**	**2c**	98.8	98.8 (1*R*,3*R*)
5	 **10**	**2a**	97.2	98.4 (1*S*,3*R*)
6	*ent*-**10**	**2c**	99.4	91.8 (1*R*,3*S*)

[a] Determined after complete conversion. [b] See Table 1.

H_2 (50 bar), EtOH, 25 °C, 21 h; Table 2). Dibenzoylmethane undergoes a double reduction using **2a** ("Ru"/**2a**, H_2 (50 bar), EtOH, 50 °C, 10 h) to produce the C_2-symmetrical 1,3-diol (*S*,*S*)-**9** with 98.2 % *ee*. The opposite enantiomer (*R*,*R*)-*ent*-**9** can be obtained in 98.8 % *ee* using **2c** with the same reaction conditions. Unsymmetrical β-diketones such as 1-phenyl-1,3-butanedione[9] is diastereoselectively reduced to (1*S*,3*R*)-1-phenyl-1,3-butanediol **10** with 98.4 % *ee* using **2a** and (1*R*,3*S*)-1-phenyl-1,3-butanediol (*ent*-**10**) in 91.8 % *ee* using **2c** ("Ru"/**2a** or **c**, H_2 (50 atm), EtOH, 50 °C, 10 h). Thus excellent enantioselectivities are obtained with a broad range of β-dicarbonyl compounds.[11]

We also found in preliminary experiments that (*Z*)-α-methylacetamido cinnamate (**11**) is smoothly hydrogenated[5, 10] in the presence of 1 mol % of catalyst (H_2 (1–5 bar), RT, 0.5–5 h) to give the amino acid derivative **12** with enantioselectivities up to 96.6 % (Scheme 3).[12] Interestingly,

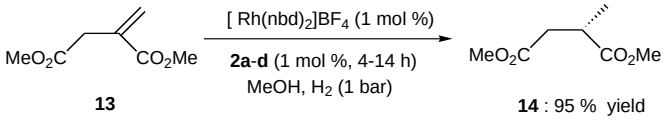


11 **12** : 95 % yield

with **2a** : 95 % *ee (R)* with **2c** : 52 % *ee (S)* [a]
with **2b** : 92 % *ee (R)* [a] with **2d** : 96.6 % *ee (R)*

Scheme 3. Enantioselective reduction of methyl α-acetamido cinnamates (**11**) to the amino acid derivatives **12**. [a] Reaction performed under H_2 (5 bar).

the ligand **2d** also gives the best results for the hydrogenation of dimethyl itaconate (**13**)[5, 10] (H_2 (1 bar), MeOH, 14 h; >95 %; 98 % *ee*; Scheme 4).



13 **14** : 95 % yield

with **2a** : 91 % *ee (S)* with **2c** : 19 % *ee (R)* [a]
with **2b** : 81 % *ee (S)* [a] with **2d** : 98 % *ee (S)*

Scheme 4. Enantioselective reduction of dimethyl itaconate (**13**). [a] Reaction performed in MeOH/toluene (1/1).

The complex [Rh(nbd)**2a**]BF_4 (**15**, nbd = norbornadiene) was isolated and characterized by X-Ray crystallography (Figure 1).[13] Remarkably, the ligand **2a** acts as a tridentate ligand and forms two six-membered metallocycles with an unusual pentacoordinated Rh^I atom. The coordination of the amino group seems not to be important to the catalytic hydrogenation since the ligand **2d** (R = *i*Pr) gives similar enantioselectivities.

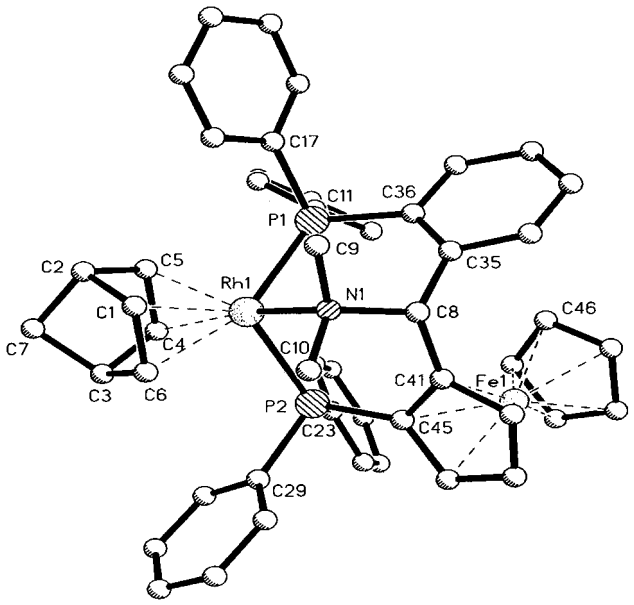


Figure 1. Structure of the complex cation [Rh(nbd)(**2a**)]$^+$ in the crystal (the hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh-P1 2.337(1), Rh-P2 2.433(1), Rh-N1 2.233(4); P1-Rh-P2 107.53(4), N1-Rh-P1 86.86(10), N1-Rh-P2 91.65(9).

It is interesting to note the difference in the enantioselectivity observed in the hydrogenation reactions using **2c**. In an attempt to explain these results, the complexes formed between $[Rh(nbd)_2]BF_4$ and **2a**–**d** were isolated. All these complexes are monomers according to FAB measurements although the ^{31}P NMR spectrum of the [Rh(nbd)**2c**]BF_4 complex shows a smaller Rh,P coupling constant than the other three complexes.[14] It seems that the presence of the α-benzylic methyl group induces a particular space arrangement of the chelating diphosphanes.

In summary, we have developed a new family of ferrocenyl ligands (**2**) with two phosphane substituents. These ligands gave good to excellent enantioselectivities in the reduction of various functionalized double bonds and β-dicarbonyl compounds. Interestingly, the two opposite configurations of the reduced products can be obtained just by modifying the substituent R in the benzylic position. Further ligand modifications and applications in asymmetric catalysis are currently underway.

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[1] a) A. Togni, R. L. Halterman, *Metallocenes*, *Vol. 2*, WILEY-VCH, Weinheim, **1998**, pp. 685–721; b) C. J. Richards, A. J. Locke, *Tetrahedron: Asymmetry* **1998**, *9*, 2377.
[2] a) J. J. Almena Perea, A. Börner, P. Knochel, *Tetrahedron Lett.* **1998**, *39*, 8073; b) J. J. Almena Perea, M. Lotz, P. Knochel, *Tetrahedron: Asymmetry* **1999**, *10*, 375.
[3] J. Kang, J. H. Lee, J. S. Choi, *Tetrahedron Lett.* **1998**, *39*, 5523.
[4] a) L. Schwink, P. Knochel, *Chem. Eur. J.* **1998**, *4*, 950; b) J. Wright, L. Framkes, P. Reeves, *J. Organomet. Chem.* **1994**, *476*, 215.
[5] For reviews, see a) K. E. Koenig in *Asymmetric Synthesis*, *Vol. 5* (Eds.: J. D. Morrison), Academic Press, Orlando, FL, USA, **1985**, p. 71; b) H. Takaya, T. Ohta, R. Noyori in *Catalytic Asymmetric Synthesis* (Ed.: I. Ojima), VCH, New York, **1993**, p. 1; c) R. Noyori, *Asymmetric Catalysis in Organic Synthesis*, Wiley, New York, **1994**, p. 16.
[6] M. J. Burk, M. F. Gross, T. G. Harper, C. S. Kalberg, J. R. Lee, J. P. Martinez, *Pure Appl. Chem.* **1996**, *68*, 37.
[7] a) J. P. Genêt, C. Pinel, S. Mallart, S. Jugé, S. Thorimbert, J. A. Laffitte, *Tetrahedron: Asymmetry* **1991**, *2*, 555; b) J. P. Genêt, C. Pinel, V. Ratovelomanana-Vidal, S. Mallart, X. Pfister, L. Bischoff, S. Darses, C. Galopin, J. A. Laffitte, *Tetrahedron: Asymmetry* **1994**, *5*, 675.
[8] M. Kitamura, H. Ohkuma, M. Tokunaga, R. Noyori, *Tetrahedron: Asymmetry* **1990**, *1*, 1.
[9] M. Kitamura, T. Ohkuma, S. Inoue, N. Sayo, H. Kumobayashi, S. Akutayawa, T. Ohta, H. Takaya, R. Noyori, *J. Am. Chem. Soc.* **1988**, *110*, 629.
[10] a) M. J. Burk, F. Bienewald, M. Harris, A. Zanotti-Gerosa, *Angew. Chem.* **1998**, *110*, 2034; *Angew. Chem. Int. Ed.* **1998**, *37*, 1931; b) A. Togni, C. Breutel, A. Schnyder, F. Spindler, H. Landert, A. Tijani, *J. Am. Chem. Soc.* **1994**, *116*, 4062.
[11] However, preliminary experiments show that 2-substituted β-dicarbonyl compounds give moderate diastereoselectivities but also excellent enantioselectivities under our conditions. Hydrogenation of ethyl 2-methyl-3-oxo-butyrate with ligand **2a** affords ethyl 3-hydroxy-2-methyl-butyrate with 40 % *de*, 91.4 % *ee* (2*R*,3*S*), and 86.0 % *ee* (2*S*,3*S*).
[12] Enantiomeric excesses were determined by GC or HPLC on a chiral phase (Chirasil-L-Val, and Diacel Chiralcel columns OD, OJ, AD).

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[13] Crystal data for **15**: $M_r = 1001.44$, monoclinic, space group $P2_1$, $a = 1073.7(1)$, $b = 2317.0(2)$, $c = 1756.3(1)$ Å, $\beta = 97.03(1)^\circ$, $V = 4336.4(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.534$ Mg m^{-3}, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu = 0.847$ mm^{-1}. Data were collected on a STOE IPDS system at 193 K. The structure was solved by direct methods and refined on F_0^2 by full-matrix least-squares methods (SHELXS-97, SHELXL-97, SHELDRICK, 1997). All non-hydrogen atoms were refined anisotropically. $\omega R2 = 0.0893$ (all unique data), $R1 = 0.0367$ for data with $I > 2\sigma(I)$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-134965. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CD21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[14] Selected ^{31}P NMR data (81 MHz, $CDCl_3$) of the phosphane ligands **2** and their complexes with Rh^{I}: **2a**: $\delta = -16.7$ (d, $J_{P,P} = 19.1$ Hz), -23.2 (d, $J_{P,P} = 19.1$ Hz); [Rh(nbd)(**2a**)]BF_4: $\delta = 23.1$ (dd, $J_{P,P} = 22.0$, $J_{P,Rh} = 129.7$ Hz), 8.6 (dd, $J_{P,P} = 22.0$, $J_{P,Rh} = 117.6$ Hz); **2b**: $\delta = -17.1$ (d, $J_{P,P} = 20.3$ Hz), -22.4 (d, $J_{P,P} = 20.3$ Hz); [Rh(nbd)(**2b**)]BF_4: $\delta = 24.4$ (dd, $J_{P,P} = 30.5$, $J_{P,Rh} = 155.1$ Hz), 5.1 (dd, $J_{P,P} = 30.5$, $J_{P,Rh} = 153.2$ Hz); **2c**: $\delta = -12.9$ (d, $J_{P,P} = 18.4$ Hz), -22.4 (d, $J_{P,P} = 18.4$ Hz); [Rh(nbd)(**2c**)]BF_4: $\delta = 17.9$ (dd, $J_{P,P} = 23.5$, $J_{P,Rh} = 101.9$ Hz), 16.0 (dd, $J_{P,P} = 23.5$, $J_{P,Rh} = 101.9$ Hz); **2d**: $\delta = -17.8$ (d, $J_{P,P} = 26.7$ Hz), -22.8 (d, $J_{P,P} = 26.7$ Hz); [Rh(nbd)(**2d**)]BF_4: $\delta = 24.8$ (dd, $J_{P,P} = 31.1$, $J_{P,Rh} = 155.1$ Hz), 12.3 (dd, $J_{P,P} = 31.1$, $J_{P,Rh} = 155.1$ Hz).

Dendritic Iron Porphyrins with Tethered Axial Ligands: New Model Compounds for Cytochromes**

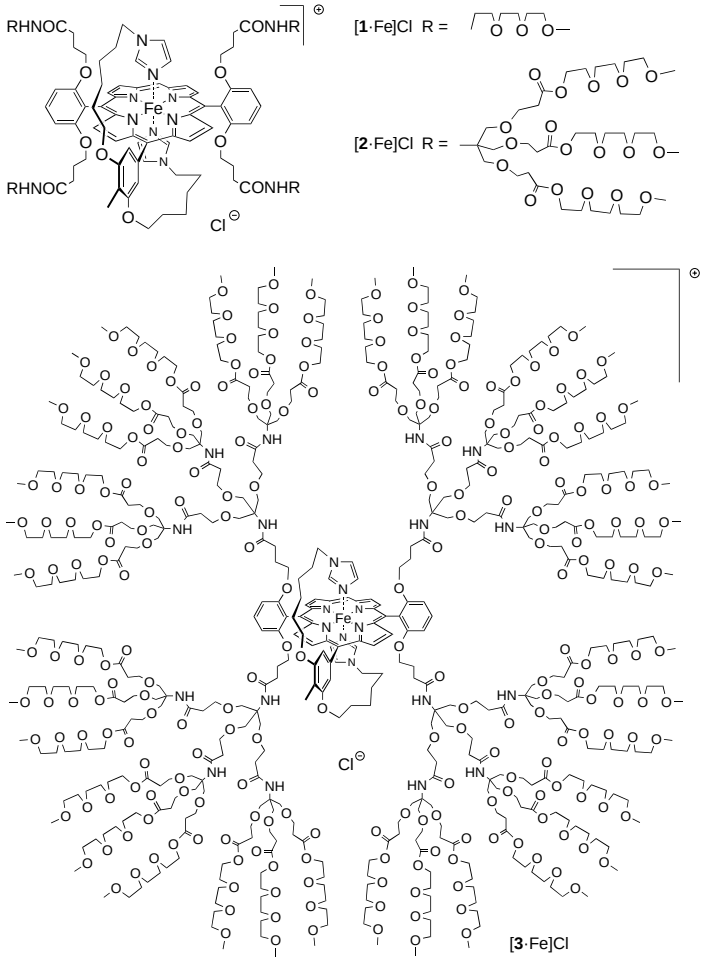
Philipp Weyermann, Jean-Paul Gisselbrecht, Corinne Boudon, François Diederich,* and Maurice Gross

Dedicated to Professor Jean-Marie Lehn on the occasion of his 60th birthday

The most intriguing characteristics of the cytochrome family of electron transfer proteins is the very broad range of redox potentials featured by the Fe^{III}/Fe^{II} couple at the electroactive heme core.[1] A variety of model studies have identified a dependency of this potential from the nature of substituents at the porphyrin ring,[2] axial ligation to the iron center,[3] hydrogen bonding to the axial ligands,[4] and ruffling of the porphyrin macrocycle.[5] In contrast, the influence of environmental effects such as heme solvation,[6] polarity of the heme microenvironment,[7] and the nature of the surrounding protein shell[8] have not been intensively investigated using model compounds and are less well understood.

We have already reported the use of dendritic iron porphyrins[9, 10] as model compounds for cytochromes in which the protein shell around the buried electroactive core is mimicked by the dendritic superstructure. These investigations revealed a strong correlation between the redox potential and the degree of dendritic branching. In these early systems, however, the nature of the axial ligation to the iron center, which is known to have a very strong influence on the redox properties[3] was not controlled. Therefore, the observed shifts in redox potential caused by the dendritic shell could not be quantified independently from axial ligation effects and no general conclusions concerning the effects of the dendritic superstructure could be drawn.

We now present a new series of dendritic cytochrome mimics, which contain a defined and stable axial ligation pattern. This allows, for the first time, a quantitative evaluation of the effect of an insulating dendritic shell on the redox properties of the embedded iron porphyrin core. The three novel dendrimers of generation zero ([**1**·Fe]Cl), one ([**2**·Fe]Cl), and two ([**3**·Fe]Cl) feature controlled axial ligation at the iron center by two imidazoles tethered to the porphyrin core. This stable ligation pattern, which is kinetically inert towards coordinating solvents, is found in the cytochrome b_5 family of electron transfer proteins.[11] The optimal length of the alkyl tethers between the iron-coordi-



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