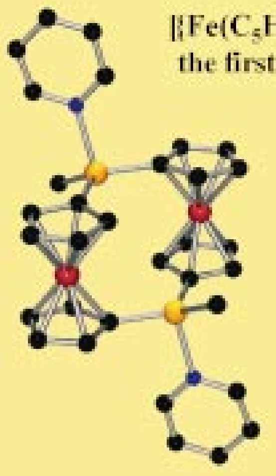
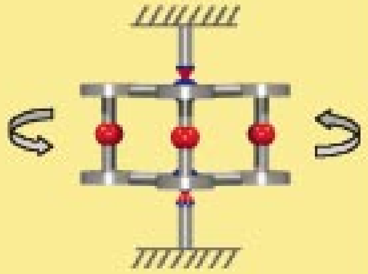
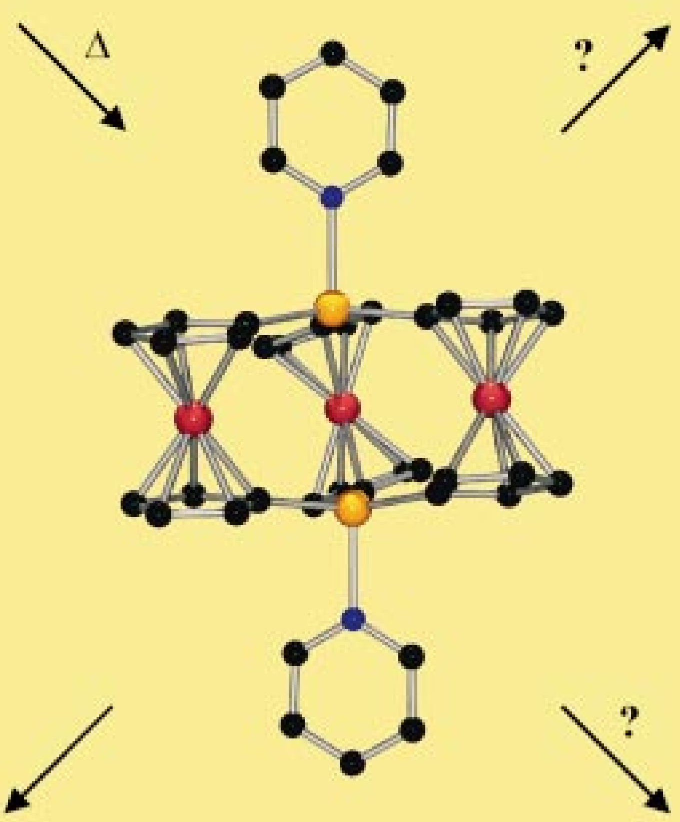
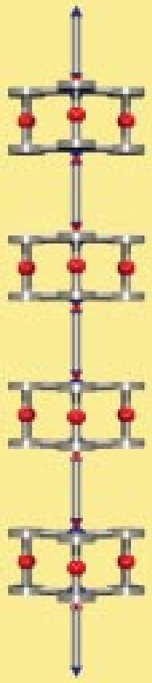


$[\{Fe(C_5H_4)_2\}_2(GaCH_3{\cdot}NC_5H_5)_2]$, the first digallaferrocenophane

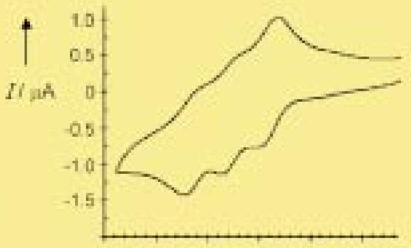


molecular carousel





molecular rod



reversible oxidation upto the trication

$[\{Fe(C_5H_4)_2\}_3(Ga{\cdot}NC_5H_5)_2]$

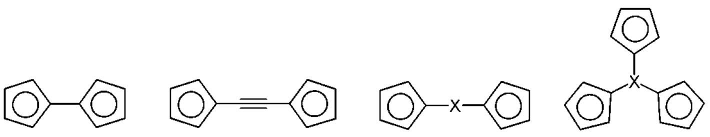
A new type of structure in organometallic chemistry: three ferrocene-1,1'-diyl units are linked by two gallium centers to give a carousel structure. The donor-free skeleton is a potential building block in supramolecular chemistry.
Find out more on the following pages.

[{$Fe(C_5H_4)_2$}$_3${$Ga(C_5H_5N)$}$_2$]: A Trinuclear Gallium-Bridged Ferrocenophane with a Carousel Structure**

Peter Jutzi,* Norman Lenze, Beate Neumann, and
Hans-Georg Stammler

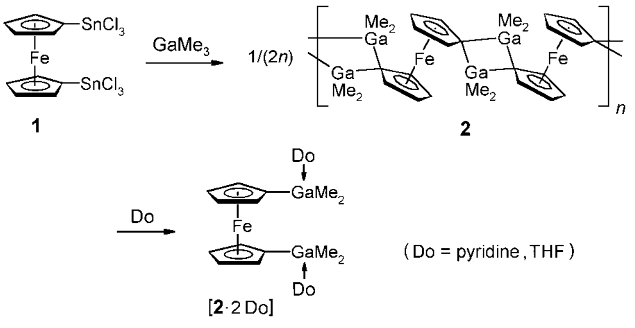
*Dedicated to Professor Hansgeorg Schnöckel
on the occasion of his 60th birthday*

Multinuclear ferrocene systems are important model substances in the study of Fe–Fe interactions, such interactions can result in very different electronic and magnetic effects.[1] Particularly interesting are those compounds in which the ferrrocene units are fixed in a mutually coplanar geometry. This criterion is met ideally by the dinuclear [*m.m*]ferrocenophanes that are derived from the dicyclopentadienyl units of type I and II, and to a lesser extent by the compounds derived from type III.[1, 2] Until now no trinuclear ferrocenophane complexes based on the tricyclopentadienyl system IV were known.[3] Herein we report this new type of linking for the first time and describe a complex in which the three ferrocene-1,1′-diyl units are held together by gallium centers.



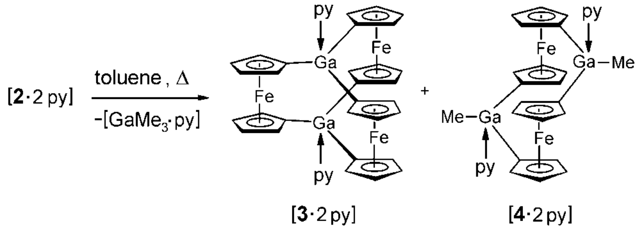
I II III IV

The complex 1,1′-bis(dimethylgallyl)ferrocene[4] (**2**), reported here for the first time, is prepared in good yield from 1,1′-bis(trichlorostannyl)ferrocene (**1**)[5] with an excess of trimethylgallium (Scheme 1) and serves as the starting material. This orange compound, which is sparingly soluble in nondonating solvents and extremely air sensitive, is presumably a coordination polymer made up of [{$Fe(C_5H_4)(\mu_2\text{-}GaMe_2)_2(C_5H_4)$}$_n$] units with bridging $GaMe_2$ units which form four-membered Ga_2C_2 rings (for comparison: dimethylgallylferrocene has a dimeric structure with $GaMe_2$ bridges[6]). The solubility of **2** in donor solvents (Do), for example pyridine and THF, results from the formation of monomeric adducts [**2**·2Do].



Scheme 1. Synthesis of the coordination polymer 1,1′-bis(dimethylgallyl)ferrocene **2** and the formation of the monomeric adduct in donor solvents.

If a solution of **2**, in a mixture of pyridine (py) and, for example, toluene is heated for a short time to a temperature over 100°C, then, on cooling, the title complex [**3**·2py] is formed in good yield as an orange microcrystalline solid (Scheme 2). This product can also include a relatively small amount of the [1.1]digallaferrocenophane [**4**·2py][7]. A further product, the pyridine adduct of trimethylgallium, can be identified in the NMR spectra of the reaction solution.



Scheme 2. Preparation of the ferrocenophanes [**3**·2py] and [**4**·2py].

Dissolving the product mixture in a high-boiling solvent (e.g. toluene or *p*-xylene) and subsequent cooling affords [**3**·2py] in a pure crystalline form. During this process some of the [**4**·2py] is converted into [**3**·2py]. This proposal is confirmed by the conversion of pure [**4**·2py][7] into [**3**·2py] in boiling toluene (Scheme 3). Consequently the prolonged heating of **2** in toluene/pyridine affords exclusively [**3**·2py].

$$3\,[\mathbf{4}\cdot 2\,\mathrm{py}] \xrightarrow{\Delta} 2\,[\mathbf{3}\cdot 2\,\mathrm{py}] + 2\,[\mathrm{GaMe_3}\cdot \mathrm{py}]$$

Scheme 3. The formation of [**3**·2py] from [**4**·2py].

Clearly [**4**·2py] and [**3**·2py] must be formed by highly selective condensation reactions. In understanding the formation of [**3**·2py] it is important to know that the complex [**4**·2py], which in the solid state is found in the *anti*-conformation, is highly dynamic in solution where the *anti*- and *syn*-conformations are in equilibrium. This behavior is demonstrated by NMR spectroscopy which shows only one set of signals arising from the α-CH and one set from the β-CH groups of both ferrocene-1,1′-diyl units.[8]

As a result of their poor solubility analytical data for the compounds [**3**·2py] and [**4**·2py] could only be obtained in [D_6]DMSO. This treatment leads to the complete exchange of the pyridine donors by DMSO donors, as confirmed by a ^{1}H NMR spectrum of a solid which precipitated from a solution of [**3**·2py] in [D_6]DMSO and which no longer displays any signals arising from pyridine. Similar behavior is expected for the compounds [**4**·2py] and [$GaMe_3$·py]. Compound [**3**·2Do] (Do = py or [D_6]DMSO) is fully characterized by NMR spectroscopy, mass spectrometry, crystal-

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[*] Prof. Dr. P. Jutzi, Dipl.-Chem. N. Lenze, B. Neumann,
Dr. H.-G. Stammler
Fakultät für Chemie der Universität
Universitätsstrasse 25
33615 Bielefeld (Germany)
Fax: (+49) 521-106-6026
E-mail: peter.jutzi@uni-bielefeld.de

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structure and elemental analysis, and electrochemical methods.

The crystal structure of [**3**$\cdot$2py][9] shows that three ferrocene-1,1′-diyl units are linked together by two pyridine-stabilized gallium(III) centers to form a "carousel structure"[2] (Figure 1; the disordered toluene molecules found in the crystal lattice are not shown). The Ga–Ga separation is 3.87 Å which is roughly double the van der Waals radius of gallium (1.87 Å[10]); the average nonbonding distance between the Fe centers is 5.46 Å. The gallium center has a slightly distorted trigonal pyramidal coordination geometry (C-Ga-C angle sum: 355°; C-Ga-N angles: 95.0(6), 98.1(7), 98.8(7)°; Ga–C bond (average): 1.97 Å; Ga–N bond: 2.143(14) Å).[11] The pyramidalization of the gallium centers twists the complex and results in a deviation of the Cp(centroid)-C-Ga units from linearity and a distortion of the ferrocene-1,1′-diyl units. The six cyclopentadienyl ligands of the three ferrocene-1,1′-diyl units deviate from a mutually coplanar arrangement in that they are tilted in the same direction relative to the Ga–Ga axis. This results in the complex having a slightly twisted and thus chiral structure; the torsion angles α_T, taken from the Ga–Ga axis and the individual Cp(centroid)–Cp(centroid) axes of the ferrocene-1,1′-diyl units can be used as a measure of the amount of twist ($\alpha_T = 11.3°$ (average)).[12] The C(Cp)–Ga bonds, with reference to the Cp ring plane, are bent away from the iron centers by 4.4° (average). The deviation of the Cp ligands within the ferrocene-1,1′-diyl units from a mutually parallel arrangement is slight (Cp-Cp angle: 3.7° (average)), the average distance between the centers of the Cp rings is 3.3 Å which corresponds to that in ferrocene. A result of the chiral structure is that in the layerlike structure of the crystal lattice two enantiomeric forms, **A** and **B**, of complex [**3**$\cdot$2py] are found. Each layer is made up of only one enantiomer and the layers alternate through the lattice in an AB pattern (Figure 2). The poor solubility of the complex probably arises from π–π interactions between the pair wise, mutually parallel arranged pyridine groups on each pair of molecules (py–py separation: 3.45 Å).

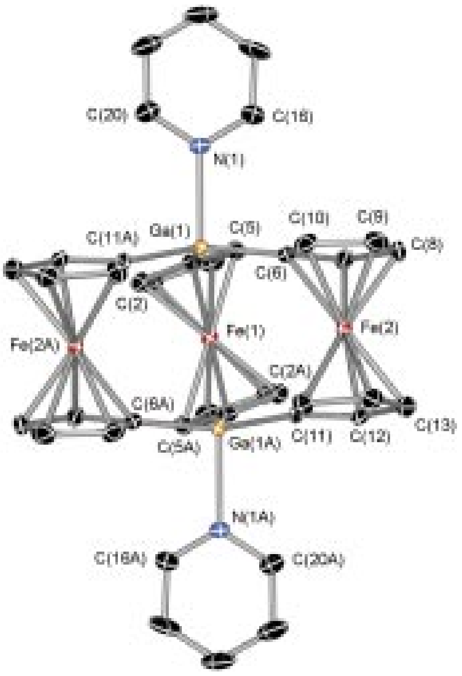

Figure 1. The molecular structure of [**3**$\cdot$2py]. Selected distances [Å] and angles [°]: Ga(1)-C(1) 1.968(19), Ga(1)-C(6) 1.965(17), Ga(1)-C(11A) 1.973(17), Ga(1)-N(1) 2.143(14), Fe-C(Cp) 2.034–2.101, C(Cp)-C(Cp) 1.41–1.44, Ga$\cdots$Ga 3.87, Fe(1)$\cdots$Fe(2) 5.40, Fe(2)$\cdots$Fe(2A) 5.58; C(1)-Ga(1)-C(6) 117.9(8), C(1)-Ga(1)-C(11A) 116.8(7), C(6)-Ga(1)-C(11A) 120.6(8), C(2)-C(1)-Ga(1) 128.3(14), C(5)-C(1)-Ga(1) 126.9(13), C(7)-C(6)-Ga(1) 127.1(14), C(10)-C(6)-Ga(1) 126.4(13), C(12A)-C(11A)-Ga(1) 124.8(14), C(15A)-C(11A)-Ga(1) 129.3(14), C(1)-Ga(1)-N(1) 98.1(7), C(6)-Ga(1)-N(1) 95.0(6), C(11A)-Ga(1)-N(1) 98.8(7).

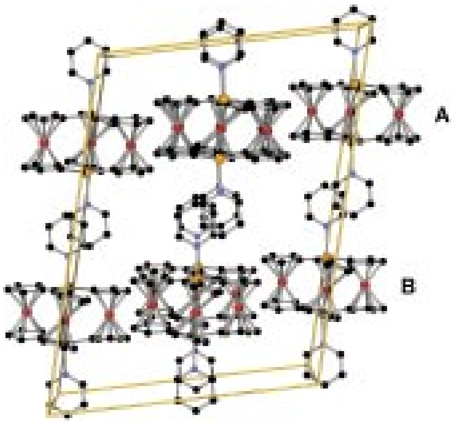

Figure 2. Layered packing of the enantiomers **A** and **B** of [**3**$\cdot$2py] in the crystal lattice (the disordered toluene molecules between the layers are not shown).

Both the ^{1}H and ^{13}C NMR spectra of [**3**$\cdot$2Do] display only one set of signals for the α-CH and one set for the β-CH units of the three ferrocene-1,1′-diyl fragments. This result indicates an averaged, highly symmetrical structure in solution. One can assume that a rapid interconversion of the enantiomers **A** and **B** into their respective mirror-image structures, as well as rapid motion of the donor molecules and the fc$_3$Ga$_2$ fragment (fc = ferrocene-1,1′-diyl) around the Ga–Ga axis occurs.

Figure 3 shows the cyclic and the square-wave voltammogram[13] of [**3**$\cdot$2py] dissolved in DMSO. The voltammograms show three reversible oxidation steps in which the waves corresponding to the oxidation and reduction process are

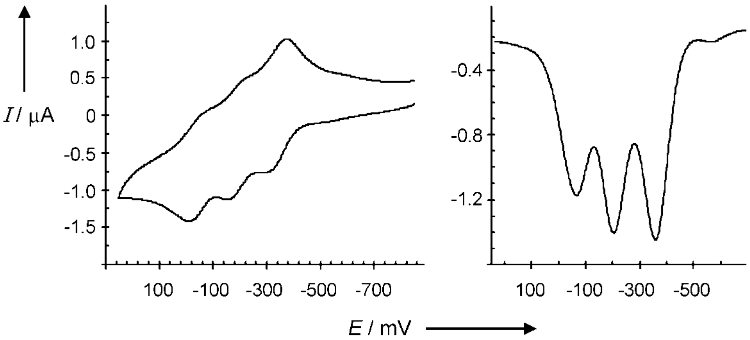

Figure 3. Cyclic and square-wave voltammograms of [**3**$\cdot$2py] dissolved in DMSO (0.1 M NBu$_4$PF$_6$).[13]

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separated by 70 mV in each case. The corresponding half-wave potentials are $E_1 = -360$, $E_2 = -205$, and $E_3 = -65$ mV (vs. the ferrocene/ferrocenium ion couple); thus the complex [**3**·2DMSO] is more easily oxidized than ferrocene. The observed differences in the half-wave potentials of $\Delta E_{2-1} = 155$ mV ($\mathbf{3}^{+}/\mathbf{3}^{2+}$) and $\Delta E_{3-2} = 140$ mV ($\mathbf{3}^{2+}/\mathbf{3}^{3+}$) indicate only a partial delocalization of the unpaired electron(s) in the cationic species (presumably, class II in the Robin and Day classification[14]). To obtain a more detailed description of the electronic properties of [**3**·2Do] further physical measurements are required.

The donor-stabilized ferrocenophanes of the form [**3**·2Do] are the first compounds of a new structural class, they suggest many new avenues of further study. Spectroelectrochemical and magnetic measurements of the cationic species should provide detailed information on the Fe–Fe interactions.[1] The donor-free species **3** has potential as a building block in supramolecular chemistry; through the incorporation of different polyfunctional donor groups the design of oligomeric and polymeric coordination compounds should be possible.[15, 16] The reaction of [**3**·2Do] with electron acceptors should enable the preparation of new charge-transfer complexes.[17] If it were possible to fix the donor molecules then the rotation of the fc_3Ga_2 fragment about the donor-Ga-Ga-donor axis, as in a molecular-level carousel, could be expected; in which case it would be worth investigating whether the rotation of such a molecule or one with a derivatized fc_3Ga_2 fragment could be controlled in a planned way.[18]

Experimental Section

2: Trimethylgallium ((pyrophoric!) 4.17 g, 36.3 mmol) was added to a suspension of 1,1′-bis(trichlorostannyl)ferrocene **1** (2.30 g, 3.63 mmol) in toluene (5 mL) in a 25 mL Schlenk flask. The reaction mixture was heated to 60°C in the tightly closed flask until everything had dissolved. On cooling to room temperature **2** formed as an orange, microcrystalline solid. The supernatant solution was decanted and the solid residue was washed with hexane (or toluene) and dried in vacuum, yield 1.20 g (3.13 mmol; 86%). ^{1}H NMR (500.1 MHz, [D_5]pyridine): $\delta = 0.19$ (12H; CH_3), 4.38 (4H; ring C2/5-H or C3/4-H), 4.58 (4H; ring C2/5-H or C3/4-H); ^{1}H NMR (500.1 MHz, [D_8]THF): $\delta = -0.27$ (12H; CH_3), 3.86 (4H; ring C2/5-H or C3/4-H), 4.08 (4H; ring C2/5-H or C3/4-H); ^{13}C NMR (125.8 MHz, [D_5]pyridine): $\delta = -6.6$ (CH_3), 70.8 (ring C2/5 or C3/4), 75.3 (ring C2/5 or C3/4), 70.8 (C1-$GaMe_2$). Compound **2** is very air sensitive.

[**3**·2py]: **2** (0.30 g, 0.78 mmol) was dissolved in pyridine (0.5 mL) and together with toluene (5 mL) heated to boiling point for 5 min in a closed Schlenk flask. After cooling and decantation of the supernatant reaction solution the residue was washed with hexane to give an orange, microcrystalline solid containing [**3**·2py] and a small amount of [**4**·2py][7]. The product mixture was dissolved in hot toluene and then cooled affording [**3**·2py] as orange, toluene-containing crystals; removal of the toluene under vacuum left [**3**·2py] as a powder which was characterized by NMR spectroscopy and elemental analysis, yield 76 mg (0.11 mmol; 42%). ^{1}H NMR (500.1 MHz, [D_6]DMSO): $\delta = 4.20$ (12H; ring C2/5-H or C3/4-H), 4.30 (12H; ring C2/5-H or C3/4-H), 7.38/7.78/8.55 (free pyridine); ^{13}C NMR (125.8 MHz, [D_6]DMSO): $\delta = 69.2$ (ring C2/5 or C3/4), 74.9 (ring C2/5 or C3/4), 123.9/125.3/150.3 (free pyridine); EI-MS: m/z (%): 692 (29) [$M^+ - 2$py]; elemental analysis (%) calcd for $C_{40}H_{34}Fe_3Ga_2N_2$ (849.71): C 56.54, H 4.03, N 3.30; found: C 56.17, H 3.93, N 3.27. [$GaMe_3$·py] can be identified in the reaction solution by NMR spectroscopy: ^{1}H NMR (500.1 MHz, $CDCl_3$): $\delta = -0.33$ (CH_3).

[**3**·2py] from [**4**·2py]: Several milligrams of [**4**·2py][7] were dissolved in toluene (1 mL) in a tightly closed NMR tube and heated to boiling point for 10 min. On cooling the probe orange crystals formed which, after removal of the solvent, were identified as [**3**·2py] by NMR spectroscopy.

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[7] [**4**·2py], [$\{Fe(C_5H_4)_2\}_2\{GaMe(C_5H_5N)\}_2$], is the first [*m.m*]ferrocenophane to have gallium atoms in the bridges. The compound can be prepared in a planned manner by the reaction of [**2**·2Et_2O] with pyridine at low temperature and can be isolated in a pure form. The synthesis, crystal structure, and dynamic behavior of [**4**·2py] will be reported elsewhere. ^{1}H NMR (500.1 MHz, [D_6]DMSO): $\delta = -0.17$ (6H; CH_3), 4.05 (4H; C_5H_4), 4.18 (4H; C_5H_4), 7.38 (py), 7.78 (py), 8.55 (py); EI-MS: m/z (%): 538 (32) [$M^+ - 2$py], 523 (37) [$M^+ - 2$py $- CH_3$]; elemental analysis (%) calcd for $C_{32}H_{32}Fe_2Ga_2N_2$ (695.76): C 55.24, H 4.64, N 4.03; found: C 55.58, H 4.70, N 4.09.

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[11] The Ga–C and Ga–N bonds of [**3**·2py] deviate, but not significantly, from the corresponding bond lengths in other compounds containing a gallium center in a sterically undemanding environment of the type [$R_3Ga \cdot N$-donor], in this kind of complex the C-Ga-C- angle sum is around 6–8° smaller, see, for example a) H.-S. Sun, X.-M. Wang, X.-Z. You, *Polyhedron* **1995**, *14*, 2159–2163; b) A. M. Bradford, D. C. Bradley, M. B. Hursthouse, M. Motevalli, *Organometallics* **1992**, *11*, 111–115; c) H. Krause, K. Sille, H.-D. Hausen, J. Weidlein, *J. Organomet. Chem.* **1982**, *235*, 253–264.

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[12] An indication that the pyramidalization of the gallium center is the cause of the twisting and other distortions of the fc_3Ga_2 fragment is that in the complex [$\mathbf{3}\cdot 2\,Et_2O$], which we could prepare from **2** and Et_2O, the gallium center is less pyramidalized (C-Ga-C angle sum 357°) and less twisted ($\alpha_T = 4.7°$ (average)). In addition the Ga–Ga separation is shorter (3.73 Å), so it can be assumed that in the donor-free compound **3** there is an even shorter Ga–Ga separation. Because of the poor *R* value of the structure determination the values given should be treated with caution. Whether the $Ga(C_5H_4)_3$ units of this compound are planar and mutually parallel with a Ga–Ga separation of under 3.4 Å (the Cp–Cp separation in ferrocene) should be shown by theoretical calculations (W. W. Schoeller, unpublished results).

[13] The electrochemical experiments were carried out with a Potentiostat/Galvanostat PAR-Model 273A and the corresponding software (Model 270). A three-electrode system was used of which the working electrode was a platinum disc (2 mm diameter), the counter electrode was a platinum wire, and the pseudo reference electrode was a silver wire. By each measurement with an otherwise identical sample decamethylferrocene [$FeCp_2^*$] was added as an internal standard. The measured redox potentials were later converted into ferrocene/ferrocenium ([$FeCp_2$]/[$FeCp_2$]$^+$) potentials (E([$FeCp_2^*$]) $= -480$ mV (in DMSO) vs. [$FeCp_2$]/[$FeCp_2$]$^+$; our own measurement). A 0.1 M solution of the electrolyte NBu_4PF_6 in DMSO was used as solvent. All the potentials given were determined by cyclic (scan rate 100 mV s^{-1}) and by square-wave voltammetry (frequency 5 Hz).

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High-Density Labeling of DNA: Preparation and Characterization of the Target Material for Single-Molecule Sequencing[**]

Susanne Brakmann[*] and Sylvia Löbermann

Single-molecule detection has emerged as the ultimate analytical tool and requires concentrations as low as femto- to zeptomolar (10^{-15} to 10^{-21}). In extreme cases the sensitivity of single-molecule techniques can even reach the yoctomole limit (10^{-24}),[1–5] and, thereby, offer insights into the chemical behavior and fate of individual molecules, as well as reflect subtle changes at the molecular level that might influence chemical reactivities.[6–10] With classic methods these effects have as yet been hidden by ensemble averaging.

Further impetus for research into this field came when it was suggested that sequencing of DNA and RNA might be accelerated by using single-molecule detection and analysis.[3, 11, 12] The sequencing attempts are based on the fact that single fluorescent molecules can be identified within milliseconds,[13] and they combine sequential enzymatic hydrolysis of individual DNA molecules with subsequent identification of released monomers by their fluorescence characteristics, either wavelengths, fluorescence lifetimes, or both.[14, 15] As natural nucleotides exhibit only marginal fluorescence at room temperature, the idea requires complete and faithful labeling of single DNA or RNA molecules with fluorescent dyes, whereby each dye distinctly codes one of the four bases (A, G, C, or T/U). Modification of DNA with fluorophores may be achieved either by enzymatic, or by postsynthetic labeling. As the chemical attachment of even a single dye molecule to oligomeric DNA does not yield 100% modified product, synthetic introduction of dyes would result in unreliable sequencing templates. Instead, fluorophore-labeled DNA may be synthesized enzymatically using polymerase-mediated incorporation of fluorescently tagged nucleotide analogues. Nucleic acid polymerases from a variety of organisms may be used for the synthesis of complementary, fluorescently labeled DNA through nick translation, primer extension, reverse transcription, or a polymerase chain reaction (PCR). However, preliminary experiments performed by us suggested that most natural and commercially available DNA polymerases failed to accept substrates that are heavily modified with fluorescent dyes (unpublished results). Experiments by other groups,[16, 17] as well as suggestions by suppliers of dye-labeled nucleotides,[18] confirmed that a maximum 28% of possible substitution sites could be labeled by PCR, whereas only about 18% exchange were achieved by nick translation.[19]

Using an assay for screening polymerase activity with dye-labeled nucleotides, which was based on fluorescence correlation spectroscopy (FCS),[3] we then observed that the wild-type, as well as the exonuclease-deficient Klenow fragment, of *Escherichia coli* DNA polymerase I is capable of incorporating 55 subsequent, fluorophore-labeled deoxyribonucleotides by extension of a synthetic primer-template (100% incorporation).[20] Although this finding was surprising, it did not contradict the previous results cited above because labeling was achieved by replication in a single round, that is, in the absence of amplification, with an artificial poly(dA) template, and the polymeric product could be detected by the highly sensitive FCS technique. FCS also provided a closer view of the enzymatic fluorophore incorporation because fluorescence intensity and diffusion time of individual molecular species were determined in parallel: Under optimal conditions, that is, in the absence of quenching phenomena and with molecular species of comparable linear shape, FCS yields data on the amount of fluorophores incorporated into a specific molecule, as well as information on the relative length of the polymeric product, which can be clearly distinguished from the length of the respective primer-template.

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[*] Dr. S. Brakmann
Evotec Biosystems AG
Schnackenburgallee 114, 22525 Hamburg (Germany)
Fax: (+49) 551-201-1435
E-mail: sbrakma@gwdg.de

S. Löbermann
Max Planck Institute for Biophysical Chemistry
Am Fassberg, 37077 Göttingen (Germany)

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