Macrocyclic Double Ferrocenes, Their Stereostructure, and an IR and NMR Spectroscopic, X-ray Crystallographic, and Conformational and Dynamic Investigation[‡]

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Condensation reactions of 1,1′-diacetylferrocenes with hydrazine afford a series of novel ferrocenophanes with two incorporated ferrocene units. NMR spectroscopy is used to establish the free rotation of the –CH=N–N=C(R)– bridging chains (R = H, Me, Ph) and the rigidity of the –C(Me)=N–N=C(Me)– chain(s) in these macrocycles. The results of theoretical studies on molecular dynamics of these molecules carried out by density functional calculations are consistent with the spectroscopic observations. The stereostructures of the new compounds were confirmed by IR, ^1H and ^{13}C NMR spectroscopy, including 2D-COSY, 2D-HMQC and 2D-HMBC measurements, and by mass spectrometry.

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Introduction

In the last decades the chemistry of bidentate nitrogen ligands has received considerable attention due to the fascinating structure and promising catalytic activity of their palladium complexes in alkyne oligomerisation[2] and in several kinds of cross-coupling reactions.[3] A series of further rigid 1,4-bidentate ligands,[4] diferrocenyl-substituted 1,5-bidentate ligands[5] and non-rigid 1,4-nitrogen ligands with ferrocenyl Schiff-base units,[6] as well as a few interesting mononuclear zinc, copper,[6] nickel,[7] platinum[8] and binuclear palladium and platinum[9] complexes have also been described. The number of known examples of nitrogen-containing macrocycles with two bridged ferrocene units is, however, limited.[10] These facts prompted us to prepare and characterise such tetradentate ligands in which two azine groups (2,3-diaza-1,3-butadienes) and two ferrocene units are incorporated in a macrocycle potentially capable of coordinating one or two metal atoms to furnish a novel group of complexes expected to have catalytic activity and even some interest in biological applications.[11]

Results and Discussion

1,1′-Diformyl-, 1,1′-diacetyl-, 1-acetyl-1′-formyl- and 1,1′-dibenzoylferrocene (**1a**–**d**, respectively) were condensed with hydrazine hydrate in ethanol (Method A: Scheme 1). Depending on the steric demand of the acyl group and the applied reaction time, **1a**–**c** were converted into three types of products (**4b**, **5c** and **6a**–**d**). In shorter reaction times (0.5–3 h) 1,1′-diformylferrocene (**1a**) directly afforded the poorly soluble dimer **6a**, whereas 1,1′-diacetylferrocene (**1b**) and 1-acetyl-1′-formylferrocene (**1c**) underwent partial condensation to afford bis-hydrazone **4b** and bis-azine **5c**, respectively. Acid-catalysed condensation of **4b** with **1a** (method B) gave macrocycle **6e** in reasonable yield (57%).

Probably due to unfavourable steric conditions **1d** could not be transformed into the tetraphenyl-substituted macrocyclic dimer, but its acid-catalysed condensation with hydrazine hydrate (method C) led to **4d**, treatment of which with **1a** (method B) in situ gave macrocycle **6f**. So far we have not been able to isolate **4d** as the assumed bis-hydrazone intermediate is contaminated by many unidentified impurities. As this mixture was used directly for the condensation with **1a** by method B, the overall yield of **6f** was very low (8%).

Both the prolonged treatment (30 h) of **1b** with an ethanolic solution of hydrazine hydrate (method A) and acid-catalysed self-condensation of bis-hydrazone **4b** in the absence of hydrazine (method D) gave **6b**.

As for the effect of hydrazine hydrate (method A), both **1c** and **5c** were converted into the same mixture (approx. 45–55%) of constitutional isomers **6c** and **6d**. It seems reasonable that condensation of the acetyl groups in **5c** yields macrocycle **6c** directly, whereas the competitive cleavage of the azine moiety regenerates hydrazone **2c**, "head to tail" dimerisation of which gives macrocycle **6d**. Hydrazones **2a** and **2b** can also be considered as intermediates in the reac-

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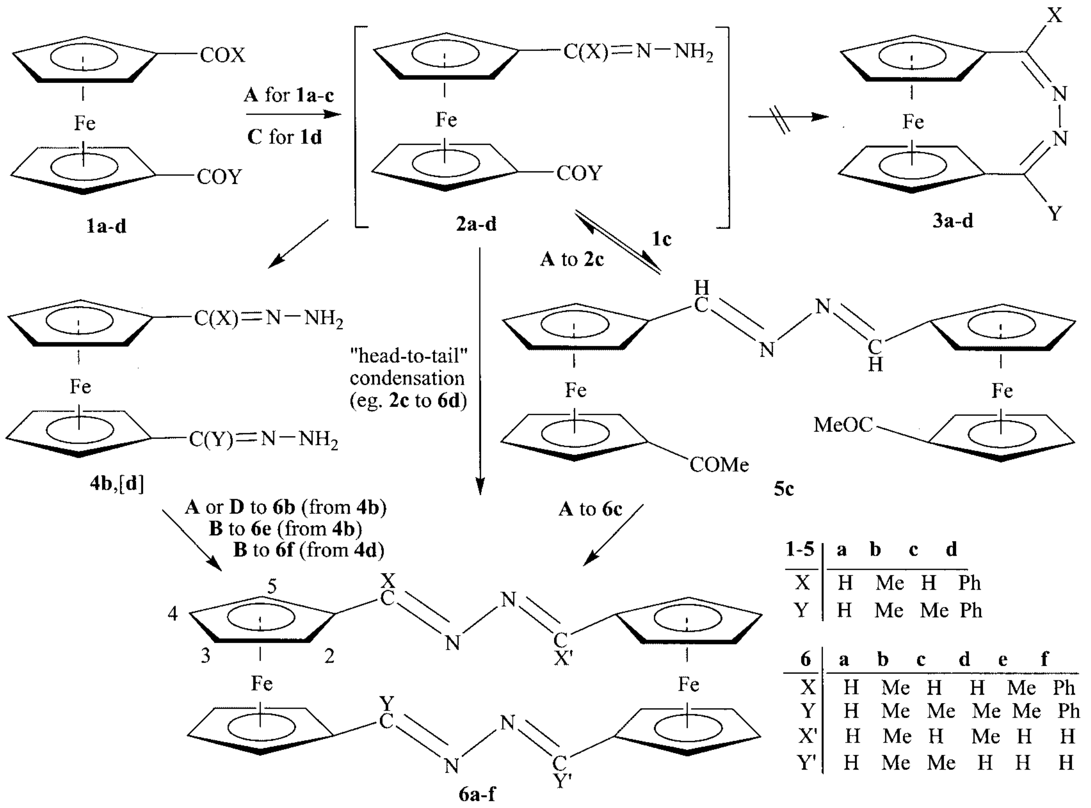

1-5	a	b	c	d
X	H	Me	H	Ph
Y	H	Me	Me	Ph

6	a	b	c	d	e	f
X	H	Me	H	H	Me	Ph
Y	H	Me	Me	Me	Me	Ph
X'	H	Me	H	Me	H	H
Y'	H	Me	Me	H	H	H

Scheme 1. A: $N_2H_4 \cdot H_2O$, reflux, EtOH, 0.5–30 h; B: **1a**, reflux in EtOH/AcOH (100:1), 3 h; C: $N_2H_4 \cdot H_2O$, reflux in EtOH/AcOH (100:1), 5 h; D: reflux in EtOH/AcOH (100:1), 3 h.

tions leading to **6a** and **6b**, respectively. The dimer structure for **6a** and **6b** was confirmed by mass spectrometry.

The formation of diazabutadiene-bridged ferrocenophanes of type **3** was not detected even in traces. In order to get comparable energetic data we carried out density functional calculations at the RB3LYP level of theory using the LANL2DZ basis set and the Gaussian program package[12] for **3a**–**c** and the eclipsed and staggered forms of the corresponding dimers **6a**–**c**. On the basis of the heats of formation obtained after geometry optimisation it is obvious that the monomeric ferrocenophanes have a considerably more-strained structure and, consequently, the dimerisation **2** → **6** generally seems to be a much more favoured process than the cyclisation **2** → **3** (see Table 1). The staggered conformation of **6b** determined by X-ray diffraction (Figure 1) is also in agreement with the results of theoretical calculations [ΔE(**6b**/ecl – **6b**/st) = 5.6 kJ mol^{-1}]. On the basis of this result, a staggered conformation in the solid state can also be predicted for the dimethyl-substituted isomers **6c**–**e** (Table 1).

Table 1. Relative energy [kJ mol^{-1}] of the hypothetical H- and Me-substituted monomers **3a**–**c** and the eclipsed and staggered forms of dimers **6a**–**e**[a,b]

6a/ecl – 2 × **3a**	–198.2
6a/stag – 2 × **3a**	–197.2
6b/ecl – 2 × **3b**	–168.1
6b/stag – 2 × **3b**	–173.7
6c/ecl – 2 × **3c**	–182.7
6c/stag – 2 × **3c**	–185.8
6d/ecl – 2 × **3c**	–181.3
6d/stag – 2 × **3c**	–186.1
2 × **6a**/ecl – **6a**/stag	–1.1
6b/ecl – **6b**/stag	5.6
6c/ecl – **6c**/stag	3.1
6d/ecl – **6d**/stag	4.7

[a] Compound **6e** is not an alternative dimer product of any monomer ferrocenophane. [b] E(**6e**/ecl.) – E(**6e**/stag.) = 2.1 kJ mol^{-1}.

The symmetry properties of macrocycles **6a**–**f** depend on the mutual orientation of the Cp rings and the binding chains, and their flexibility. In rigid structures with coplanar Cp rings and binding chains (C=N double bond) the atomic pairs C/H-2 and C/H-5, and C/H-3 and C/H-4, respectively, are diastereotopic and, consequently, chemically non-equivalent (Table 2 and Table 3). In such conformations one of the H-2 and H-5 signals must be shifted downfield due to anisotropy of the closer lying lone pair on the N atom. In the flexible structures with two freely rotating binding chains the above-mentioned atomic pairs must become isochronous and have identical NMR signals. In fact, in the ^1H and ^{13}C NMR spectra of **6b** and **6c** the C/H-2,5 and C/H-3,4 atomic pairs have separate signals, while in the spectra of our other macrocycles (**6a**,**d**,**e**,**f**) these pairs have identical signals.

In an attempt to clarify the conformational features of the new compounds we carried out NMR measurements at

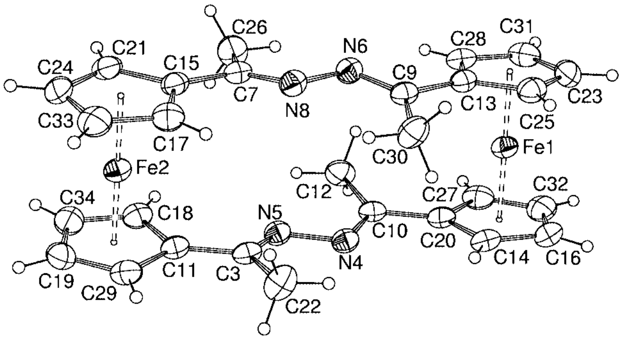

Figure 1. Ortep diagram of **6b**. Only non-hydrogen atoms are labelled. The molecule has three, twofold axes perpendicular to each other (point group D_2). The ellipsoid probability is 30%.

different temperatures. [D$_6$]DMSO solutions of compounds having separated signals was heated to about 430 K, whereas the others with identical signals for atomic pairs C/H-2,5 and C/H-3,4 were cooled (in $CDCl_3$ solution) to about 210 K. All these VT NMR experiments proved negative as no changes, even broadening of the signals, were observed in the spectra recorded at different temperatures. Consequently, **6b** and **6c** must contain Cp rings that are coplanar with the plane of the C=N double bonds. These results are reasonable because the internal rotation of one or both –C(Me)=N–N=C(Me)– binding chain(s) in **6b** and **6c** must be hindered as one of the bulky methyl groups would transitionally have to occupy the sterically unfavourable *endo* position inside the macrocycle.

This assumption was clearly confirmed by theoretical modelling at the RB3LYP/LANL2DZ level of theory. The relative energies of the species involved are listed in Table 4. The computations on the flexible compounds **6a**,**d**,**e** resulted in two, low-energy conformations (eclipsed and staggered, see **6a** in Figure 2) and a high-energy conformation (local minimum **6**/lm) separated by two transition states (saddle points **6**/ts1 and **6**/ts2). The interconversion between the eclipsed and staggered conformations, which results in the chemical equivalence of C/H-2 and C/H-5, and C/H-3 and C/H-4, respectively, can take place by a pathway that avoids the unfavourable inside position of the bulky methyl group. In the first phase of the pseudorotation the half segment of one of the bridging chains (CR=N, R = H or Me) turns out of the plane of the adjacent Cp ring with H or Me in the outside position and, through one of the transition states (**6**/ts1), arrives at the local minimum (**6**/lm). In the second phase the rotation of the other half segment (CH=N) takes place through the other transition state (**6**/ts2), where the H atom gets inside the macrocycle.

The above mode of pseudorotation involves the assumption that the Me group can only exchange its positions by sweeping outside the macrocycle while the azomethine hydrogen can get inside the macrocycle. This was experimentally supported by DIFFNOE measurements detecting the following time-average interactions in **6d**: when irradiating the methyl H's a response of the H-2,5 signal of the Cp rings bonded to C(Me)=N group was observed, while the saturation of the azomethine H signal resulted in responses

Table 2. Characteristic IR frequencies[a] and ^{1}H NMR spectroscopic data[b] of compounds **4b** and **6a**–**f**.[c]

	νC=N band	ν_{as}Cp–Fe–Cp and tilt of Cp bands[13]	CH_3 (s, 3 H)	=CH (s, 1 H)	H-2,5 (2 H)	H-3,4 (2 H)	H-2,5 (2 H)	H-3,4 (2 H)
					Cp ring vicinal to CH=N		Cp ring vicinal to C(CH_3)=N	
4b	1643	525, 512, 488	1.87	–	–	–	4.42	4.18
6a	1624	503, 490	–	8.55	5.15	4.50	–	–
6b	1599	536, 473	2.42	–	–	–	5.04,[d] 4.15	4.48, 4.63
6c	1609	549, 510, 481, 459	2.45	8.40	4.97,[d] 4.86	4.47,[e] 4.32	5.32,[d] 4.84	4.41,[e] 4.22
6d	1611	547, 513, 493, 480, 458	2.46	8.32	4.90	4.36	5.04	4.34
6e	1615	547, 506, 478, 460	2.40	8.16	4.94	4.29	4.88	4.30
6f[f]	1607	539, 503, 473	–	8.53	4.74[f]	≈4.2[g]	4.74[f]	≈4.2[g]

[a] As KBr discs [cm^{-1}]. Further IR bands: νNH_2 (**4b**): 3437, 3354, 3207 cm^{-1}. [b] In $CDCl_3$ solution at 500 MHz. Chemical shifts in ppm (δ_{TMS} = 0 ppm), coupling constants in Hertz. Further ^{1}H NMR signals: $\delta(NH_2)$ (**4b**) = 5.84 ppm (s, 2×2 H); phenyl groups (**6f**): δ = 7.70 (d, (2 H, H-2,6), 7.45 (t, 2 H, H-3,5), 7.40 (t, 1 H, H-4). [c] Assignments were supported by HMQC (**6b**–**e**) and 2D-COSY (**6c**–**e**), and for **6c** also by DIFFNOE measurements. [d] H-2: near (*s-cis*) to the coplanar nitrogen atom. [e] H-3. [f,g] Overlapping signals.

Table 3. ^{13}C NMR chemical shifts[a] of compounds **4b** and **6b**–**f**.[b]

	CH_3	=CH	=CR[c]	C-1	C-2,5	C-3,4	C-1	C-2,5	C-3,4
	Bridging chain			Cp ring vicinal to CH=N			Cp ring vicinal to C(R)=N[c]		
4b	13.5	–	143.8	–	–	–	88.0	67.0	69.8
6b	16.1	–	164.8	–	–	–	86.4	69.0,[d] 69.9	72.6,[e] 71.3
6c	16.5	161.6	163.3	80.5	69.5,[e] 71.2[f]	72.0,[e] 70.8	87.4	67.0,[d] 71.2[f]	71.8,[e] 69.8
6d	16.6	159.3	166.1	82.0	70.4	71.3	86.1	69.2	71.1
6e	16.7	159.7	166.5	82.1	69.8	71.1	85.4	70.1	71.2
6f	–	161.7	168.8	82.0	70.8[f]	71.7[g]	85.4	70.8[f]	71.8[g]

[a] In ppm (δ_{TMS} = 0 ppm) at 125.7 MHz. Solvent: $CDCl_3$. Further lines: phenyl groups (**6f**): δ = 137.3 (C-1), 129.6 (C-2,6), 127.6 (C-3,5), 128.4 (C-4) ppm. [b] Assignments were supported by HMQC (except for **6f**), HMBC (except for **6b**) and for **6b** also by DEPT measurements. [c] R = Me (**6b**–**e**) or Ph (**6f**). [d] C-2: near (*s-cis*) to the coplanar N. [e] C-3. [f] Overlapping signals. [g] Interchangeable assignments.

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Table 4. Calculated energies [kJ mol^{-1}] for the rotamers of **6a**,**c**–**e**.

Rotamer	**6**/ts1 – **6**/ecl	**6**/lm – **6**/ts1	**6**/ts2 – **6**/lm	**6**/stag – **6**/ts2
a	50.9	–14.1	14.3	–50.1
c[a]	37.0	–1.6	518.2[b]	–556.7[b]
d	38.2	–6.5	11.4	–47.8
e	41.1	–8.8	13.0	–47.3

[a] For the rotation of the -C(Me)=N–N=C(Me)- chain. [b] Taking the single-point energy of the ts2-like structure into account.

of both pairs of Cp rings vicinal to C(Me)=N and also to the CH=N groups.

Applying the same calculation for the rotation of the –C(Me)=N–N=C(Me)– binding chain in **6c** it turned out that a saddle-point which would represent a **6**/ts2-like transition state with an endocyclic Me group was not found. The energy obtained for such a highly crowded structure is 556.7 kJ mol^{-1} higher than the energy of **6c**/st (Table 4). This means that, in agreement with our preliminary expectations, the rotation of the –C(Me)=N–N=C(Me)– chain cannot take place in our macrocycles. Due to the presence of the non-rotating dimethyl-substituted chain the rotation of the –CH=N–N=CH– binding chain does not result in chemical equivalence of the C/H-2,5 and C/H-3,4 atomic pairs in **6c**, so they exhibit separate NMR signals. From these studies and the NMR experiments we suppose that this chemical equivalence can only be achieved by the internal rotation of both bridging chains each carrying at least one H atom. This means that this mechanism is applicable even to the molecular dynamics of the diphenyl-substituted macrocycle **6f**, which also exhibits coalesced C/H-2,5 and C/H-3,4 signals. When comparing the theoretical and VT NMR results the following comment is necessary. The calculated energy barriers listed in Table 4 (40–50 kJ mol^{-1}) seem to be high enough to cause separation of the aforementioned signals of **6a**,**d**,**e**,**f** at 210 K. This apparent discrepancy can be resolved as follows. The use of a more extended basis set and solvent model, which unfortunately is prevented by our limited computation capacity, would probably give calculated energy values that are in better agreement with the experiments. However, the results of our calculations carried out for a vacuum model give a definite substituent dependence for the dynamics of the bridging chains, whose tendency is certainly consistent with the experiments.

Finally, we performed a geometry optimisation at the RB3LYP/LANL2DZ level for an input geometry of **6a** in which both chains were set in an *s-cis* arrangement. The calculation converged to a conformer (**6a**/gauche, Figure 3) containing bridging chains twisted to a gauche-like position (dihedral angle found for C=N–N=C sequence: 62.9°), but its energy is higher by 34.9 kJ mol^{-1} than that of **6a**/lm. (This energy is higher than even those of **6a**/ts1 and **6a**/ts2 by 20.8 kJ mol^{-1} and 20.5 kJ mol^{-1}, respectively.) This result

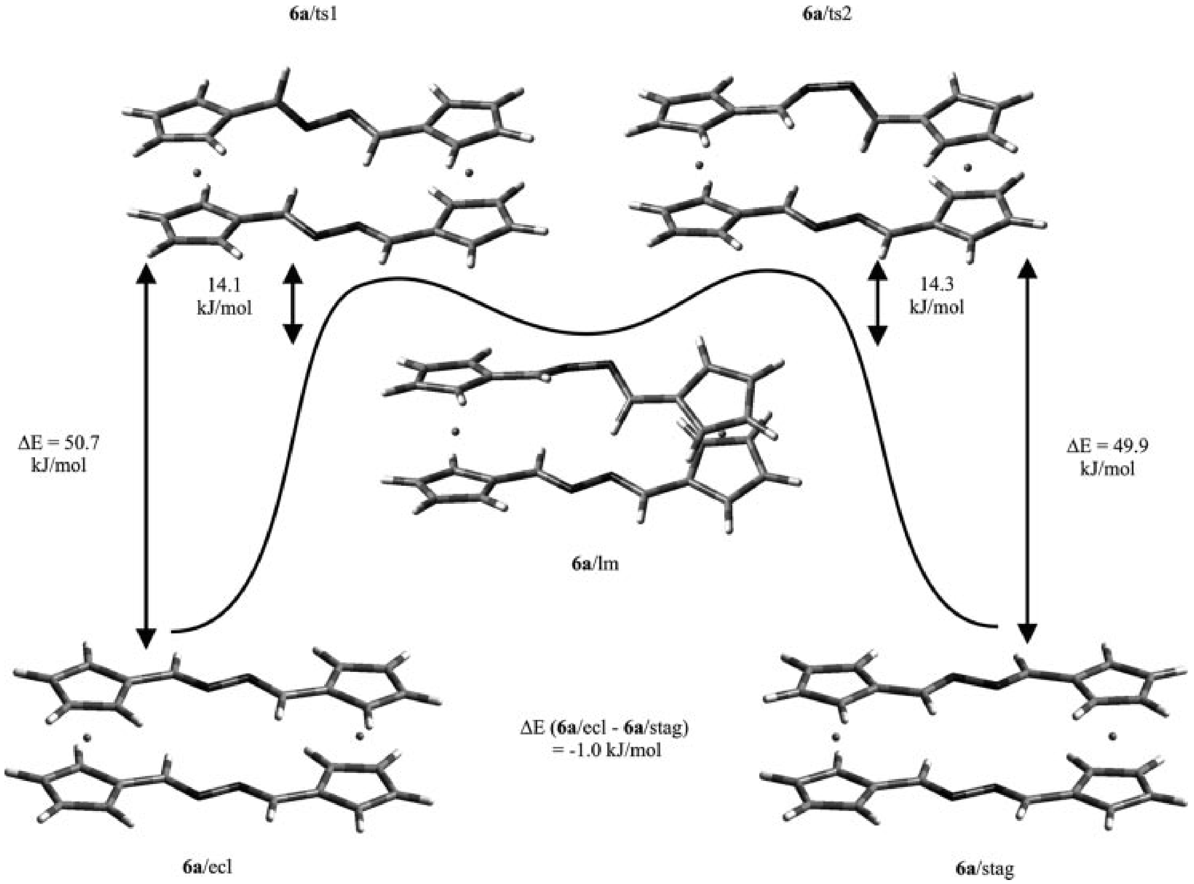
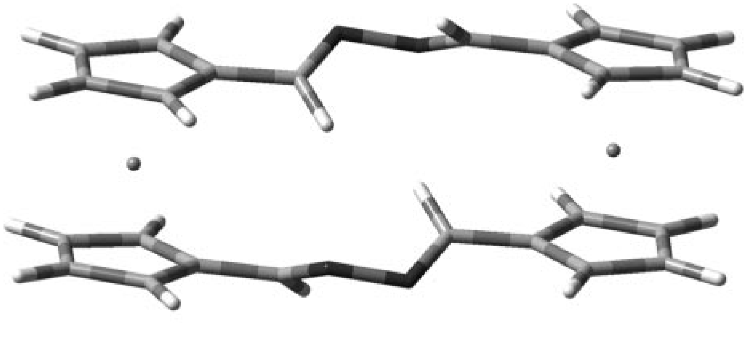


Figure 2.



6a in "gauche" conformation

Figure 3. This structure was optimised at the B3LYP/LANL2DZ level of theory.

suggests that conformations of type **6**/gauche can be ruled out in the molecular dynamics of our macrocycles.

Conclusions

Ferrocenophanes **6a**–**f** are the first representatives of a novel heteromacrocyclic system whose molecular dynamics are controlled by the steric demand of the substituents on the bridging chains. In the light of this a series of further diverse interesting ferrocenophanes with predictable dynamic properties can be prepared and evaluated as potential ligands in homogeneous catalysis.

Experimental Section

General: Melting points (uncorrected) were determined with a Boetius microstage. IR spectra were recorded from KBr pellets with a Bruker IFS 55 FT spectrometer. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution in 5 mm tubes at room temp. on a Bruker DRX 500 spectrometer at 500 (^1H) or 125 (^{13}C) MHz, using TMS as internal reference with the deuterium signal of the solvent as the lock. The standard Bruker microprogram NOEMULT.AU to generate NOEs was used with a selective pre-irradiation time. DEPT spectra were run in a standard manner, using only the Θ = 135° pulse to separate CH/CH_3 and CH_2 lines phased "up" and "down", respectively. 2D-HMQC and 2D-HMBC spectra were obtained by using the standard Bruker pulse programs INV4GS and INV4GSLPLRND, respectively.

The X-ray measurements were made on a Kappa CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The crystals were mounted on a glass fibre and data were collected at a temperature of 293 K.

The mass spectra were recorded with a VG ZAB-2SEQ spectrometer (resolution: 10000) using the electron ionisation method.

1,1′-Diformylferrocene (**1a**) and 1-acetyl-1′-formylferrocene (**1c**) were prepared according to described procedures.[14,15] 1,1′-Diacetylferrocene (**1b**) and 1,1′-dibenzoylferrocene (**1d**) were purchased from Sigma–Aldrich.

Condensation Reactions of 1a–c, 4b and 5c by Method A: Hydrazine hydrate (0.29 mL, 6 mmol) was added to a solution of the carbonyl component **1a**–**c**, **5c** (2 mmol) and anhydrous ethanol (30 mL) and the mixture was heated under reflux. Reaction times: 3 h (for **1a** to give **6a**, for **1b** to give **4b**, for **1c** and **5c** to give a 45:55 mixture of **6c** and **6d**); 0.5 h (for **1c** to give **5c**); 30 h (for **1b** to give **6b**). The reaction mixture was then concentrated to about half its volume and cooled in ice-water. The products separated as a dark-red (**5c**, **6a**,**c**,**d**) precipitate and were filtered off and washed with cold, anhydrous ethanol (5 mL) to obtain analytically pure samples. Dihydrazone **4b** was isolated as follows. After the evaporation of the reaction mixture the oily orange residue was purified by flash column chromatography over silica using CH_2Cl_2/MeOH (10:1) and crystallised with cold ethanol (5 mL) to obtain **4b** in analytically pure form. Macrocycles **6c** and **6d** were obtained as a practically inseparable mixture (45–55% as determined by ^1H NMR spectroscopy) from both the precursors (**1c** and **5c**) used.

4b: Orange powder. Yield 0.54 g (91%). M.p. 153–155 °C. $C_{14}H_{18}FeN_4$ (298.16): calcd. C 56.39, H 6.08, N 18.79; found C 56.43, H 6.11, N 18.55.

5c: Red needles. Yield 0.42 g (83%). M.p. 161–165 °C. $C_{26}H_{24}FeN_2O_2$ (508.17): calcd. C 61.45, H 4.76, N 5.51; found C 61.53, H 4.82, N 5.47.

6a: Deep-red needles. Yield 0.31 g (65%). M.p. 224–227 °C. $C_{24}H_{20}Fe_2N_4$ (476.13): calcd. C 60.54, H 4.23, N 11.77; found C 60.57, H 4.28, N 11.81. MS (EI): calcd. for $C_{24}H_{20}Fe_2N_4$ 476.0387; found 476.0359.

6b: Deep-red powder. Yield 0.33 g (62%). M.p. 198–200 °C. $C_{28}H_{28}Fe_2N_4$ (532.24): calcd. C 63.19, H 5.30, N 10.53; found C 63.23, H 5.34, N 10.58. MS (EI) calcd. for $C_{28}H_{28}Fe_2N_4$ 532.1014; found 532.1020.

An X-ray crystal structure analysis of **6b** revealed the structure depicted in Figure 1. Both the ferrocene units and the dimethyl-substituted chains have a staggered conformation. The point group of the molecule is D_2, as the molecule has three, twofold axes (C_2) perpendicular to each other. The main crystal building force is the interaction between the apolar ferrocene moieties.
CCDC-249559 (for **6b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Preparation and Partial Separation of a Mixture of 6c and 6d: Deep-red powder. Yield 0.35 g (70%; from the reaction of **1c**) and 0.39 g (78%; from the reaction of **5c**). The same composition of the products (45% for **6c** and 55% for **6d**) was obtained by ^1H NMR spectroscopic analysis of both investigated reactions. Analytically pure samples were obtained by chromatography of 0.20 g of this mixture over silica using CH_2Cl_2/MeOH (70:1) as eluent. Due to partial separation, 0.02 g (10%) of **6c** and 0.04 g (20%) of **6d** were isolated in pure form.

6c: Red powder. M.p. 198–202 °C. $C_{26}H_{24}Fe_2N_4$ (504.19): calcd. C 61.94, H 4.80, N 11.11; found C 61.97, H 4.82, N 11.16.

6d: Deep-red powder. M.p. 196–200 °C. $C_{26}H_{24}Fe_2N_4$ (504.19): calcd. C 61.94, H 4.80, N 11.11; found C 61.90, H 4.87, N 11.02.

Preparation of 6e by Method B: Acetic acid (0.30 mL) was added to a solution of **4b** (0.21 g, 0.67 mmol) and **1a** (0.16 g, 0.67 mmol) in anhydrous ethanol (30 mL) and the resulting mixture was refluxed for 3 h. On cooling with ice-water the product separated as a dark-red powder from the reaction mixture. This was filtered off and washed with cold anhydrous ethanol (3 mL) to obtain macrocycle **6e** in a pure form as a deep-red powder. Yield: 0.19 g (57%). M.p. 208–210 °C. $C_{26}H_{24}Fe_2N_4$ (504.19): calcd. C 61.94, H 4.80, N 11.11; found C 61.99, H 4.81, N 11.13.

Preparation of 6f by Method C Followed by Method B: Hydrazine hydrate (0.48 mL, 10 mmol) and acetic acid (0.30 mL) were added to a solution of **1d** (0.39 g, 1 mmol) in anhydrous ethanol (30 mL) and the mixture was heated under reflux. After 5 h **1a** (0.24 g, 1 mmol) was added to the solution which was then boiled for 3 h and concentrated to dryness. The dark, oily residue was purified by chromatography over silica using $CHCl_3$/MeOH (20:1) as eluent. The first, deep-red band was collected. After evaporation of the eluent the oily residue was crystallised with cold ethanol (1.5 mL) to obtain the analytically pure macrocycle **6f** as a deep-red powder. Yield: 0.05 g (8%). M.p. 189–191 °C. $C_{36}H_{28}Fe_2N_4$ (628.32): calcd. C 68.82, H 4.49, N 8.92; found C 68.84, H 4.54, N 8.97.

Acid-Catalysed Dimerisation of 4b by Method D: Acetic acid (0.30 mL) was added to a solution of **4b** (0.30 g, 1 mmol) in anhydrous ethanol (30 mL) and the resulting mixture was heated under reflux for 3 h. After evaporation of the solvent the residue was purified by silica gel flash chromatography using $CHCl_3$/MeOH (20:1) as eluent. The first, deep-red band was collected. After evaporation of the eluent the residue was crystallised from ethanol to obtain macrocycle **6b** in analytically pure form. Yield: 0.16 g (60%).

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[1] A. Csámpai, Á. Abrán, V. Kudar, Gy. Túrós, H. Wamhoff, P. Sohár, *J. Organomet. Chem.* **2005**, *690*, 802–810.

[2] a) K. Moseley, P. M. Maitlis, *J. Chem. Soc., Chem. Commun.* **1971**, 1604; b) T. Ito, Y. Takahashi, Y. Yshi, *J. Chem. Soc., Chem. Commun.* **1972**, 629; c) R. Diercks, L. Stamp, H. tom Dieck, *Chem. Ber.* **1984**, *117*, 1913–1919; d) R. Diercks, H. tom Dieck, *Z. Naturforsch. Teil B* **1984**, *39*, 180–184; e) R. Diercks, H. tom Dieck, *Chem. Ber.* **1985**, *118*, 428–435; f) H. tom Dieck, A. M. Lauer, L. Stamp, R. Diercks, *J. Mol. Catal.* **1986**, *35*, 317–328; g) H. tom Dieck, C. Munz, C. Muller, *J. Organomet. Chem.* **1990**, *384*, 243–255; h) R. van Asselt, C. J. Elsevier, W. J. J. Sweets, A. L. Spek, *Inorg. Chem.* **1994**, *33*, 1521–1531; i) R. van Belzen, H. Hoffmann, C. J. Elsevier, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1743–1745.

[3] a) R. van Belzen, R. A. Klein, H. Koojiman, N. Veldman, A. L. Spek. C. J. Elsevier, *Organometallics* **1998**, *17*, 1812–1825; b) G. A. Grasa, A. C. Hillier, S. P. Nolan, *Org. Lett.* **2001**, *3*, 1077–1080.

[4] R. van Asselt, C. J. Elsevier, C. Amatore, A. Jutand, *Organometallics* **1997**, *16*, 317–328 and references cited therein.

[5] a) I. R. Butler, K. Kalaji, L. Nehrlich, M. Hursthouse, A. J. Karaulov, K. M. A. Malik, *J. Chem. Soc., Chem. Commun.* **1995**, 459–460; b) A. Tárraga, P. Molina, D. Curiel, M. D. Velasco, *Tetrahedron* **2001**, *57*, 6765–6774.

[6] P. Li, I. J. Scoven, J. E. Davies, M. A. Halcrow, *J. Chem. Soc., Dalton Trans.* **1998**, 3791–3799.

[7] R. Diercks, J. Kopf, H. tom Dieck, *Acta Crystallogr. C: Cryst. Struct. Commun.* **1984**, *40*, 363–365.

[8] A. C. Skapski, V. F. Sutcliffe, G. B. Young, *J. Chem. Soc., Chem. Commun.* **1985**, 609–611.

[9] L. K. Thompson, F. L. Lee, E. J. Gabe, *Inorg. Chem.* **1988**, *27*, 39–46.

[10] a) B. Delavaux-Nicot, Y. Guari, B. Dowziech, R. Mathieu, *J. Chem. Soc., Chem. Commun.* **1995**, 585–587; b) M. J. L. Tendero, A. Benito, R. Martinez-Mañez,, J. Soto, J. Payá, A. J. Edwards, P. R. Raithby, *J. Chem. Soc., Dalton Trans.* **1996**, 343–351; c) M. J. L. Tendero, A. Benito, J. Lloris, R. Martinez-Mañez, J. Soto, J. Payá, A. J. Edwards, P. R. Raithby, *Inorg. Chim. Acta* **1996**, *247*, 139–142.

[11] Biological activity of ferrocene derivatives: a) A. Houlton, R. M. G. Roberts, J. Silver, *J. Organomet. Chem.* **1991**, *418*, 107–112 and references cited therein; b) S. Top, J. Tang, A. Vessieres, D. Carrez, C. Prosot, G. Jaouen, *Chem. Commun.* **1996**, 955–956 and references cited therein.

[12] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98* (Revision A.1), Gaussian Inc., Pittsburgh PA, **1998**.

[13] P. Sohár, J. Kuszmann, *J. Mol. Struct.* **1969**, *359*, 3–7.

[14] G. G. A. Balavoine, G. Doisneau, T. J. Fillebeen-Khan, *J. Organomet. Chem.* **1991**, *412*, 381–382.

[15] M. Sato, M. Koga, I. Motoyama, K. Hata, *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1142–1148.

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