

solution was stirred for another 10 min and the solvents were removed on a rotary evaporator. The residue was taken up in water and extracted three times with diethyl ether. The organic phase was dried over sodium sulfate and concentrated. The crude product was purified by column chromatography on silica gel (eluent pentane/diethyl ether 10/1) and the product was obtained as a colorless oil (260 mg, 1.78 mmol, 89% yield).

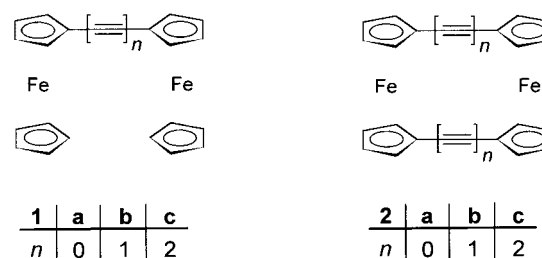
Received: March 7, 2001 [Z16729]

Synthesis and Properties of the First [4.4]Ferrocenophane-1,3,15,17-tetrayne**

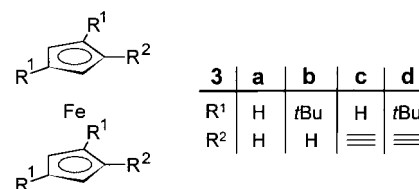
Kai H. H. Fabian, Hans-Jörg Lindner, Norbert Nimmerfroh, and Klaus Hafner*

Dedicated to Professor Siegfried Hünig on the occasion of his 80th birthday

In recent years transition metal complexes of π -conjugated oligomers and polymers have become of increasing interest as potential materials for technical applications.^[1] Studies of novel model compounds such as the bisferrocenes **1a–c** and the ferrocenophanes **2a, b** with defined geometric arrangement of the metal atoms have demonstrated that the physical properties of these complexes are determined predominantly by the extent of delocalization and by the electronic interactions between the metal centers.^[2,3] In this context



the ferrocenophane **2c** with two butadiynyl bridges, homologous with **2a, b**, is of particular interest, yet all attempts to prepare it by the oxidative coupling of 1,1'-diethynylferrocene **3c** have been unsuccessful because of its pronounced tendency towards polymerization.^[4, 5]



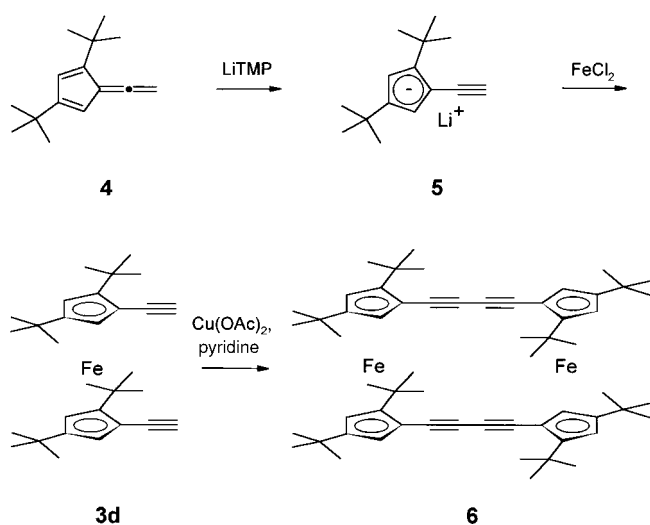
The synthesis of the stable 2,2',4,4'-tetra-*tert*-butyl-1,1'-diethynylferrocene **3d** and its Eglinton coupling^[6] has allowed access to the kinetically stabilized derivative **6** of [4.4]ferrocenophane-1,3,15,17-tetrayne **2c**^[7a] for the first time.

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The 1,1'-diethynylferrocene **3d** is readily prepared by deprotonation of 1,3-di-*tert*-butyl-5-vinylidene-cyclopentadiene (**4**)^[8] with lithium 2,2,6,6-tetramethylpiperidide (LiTMP) and subsequent reaction of the lithium salt **5** with iron(II) chloride (Scheme 1).^[7b] Compound **3d** is obtained as



Scheme 1. Preparation of 1,1'-diethynylferrocene **3d** and [4,4]ferrocenophane-1,3,15,17-tetraene **6**.

red crystals in 26% yield. Since the *tert*-butyl groups inhibit the rotation of the two cyclopentadienyl (Cp) rings the signals of the *tert*-butyl groups and the 3,3' ring protons as well as those of the terminal ethynyl protons of **3d** are broadened in the ¹H NMR spectrum at room temperature. At -40 °C these signals are split into four singlets for the *tert*-butyl groups and two singlets for the ethynyl protons, whereas the signals of each pair of the four ring protons appear as two doublets ($J = 0.8$ Hz). On the basis of this temperature dependency of the ¹H NMR data the energy barrier $\Delta G_{273-293\text{K}}^*$ for the ring rotation in the 1,1'-diethynylferrocene **3d** is calculated to be 58.8 ± 2.2 kJ mol⁻¹.^[9] With selective low-temperature ¹H NMR NOE spectroscopy at 233 K it was possible to establish an achiral *syn* configuration (*meso* form) for **3d**.^[10] The ¹³C NMR signals of the acetylene carbon atoms are located within the characteristic range of $\delta = 76.69-83.83$. The infrared (IR) spectrum exhibits the acetylene stretching frequency at $\tilde{\nu}_{(\text{C}=\text{H})} = 3307$ and $\tilde{\nu}_{(\text{C}=\text{C})} = 2105$ cm⁻¹. The redox potential of **3d**, determined cyclic voltammetrically, at $E_{1/2} = 0.49$ V is higher than that of tetra-*tert*-butylferrocene **3b** ($E_{1/2} = 0.12$ V) as a result of the negative inductive effect of the C-C triple bond (Table 1).^[11]

Compound **3d** can be converted into the ferrocenophane **6** by oxidative Eglinton coupling^[6] with copper(II) acetate in boiling pyridine and is isolated, by chromatography of the reaction mixture, as red needles which do not show any tendency to decompose or melt at up to 230 °C.^[12] In addition, an oligomer mixture was obtained, the separation of which has to-date not been successful.^[13] The ¹H NMR spectrum of **6** with only two singlets for the *tert*-butyl groups and two broad singlets at $\delta = 3.97$ and 4.22 for the ring protons^[14] indicates a symmetrical structure. The IR spectrum shows only weak acetylene stretching bands at $\tilde{\nu}_{(\text{C}=\text{C})} = 2196$ cm⁻¹. The intensity

Table 1. Oxidation potentials of ferrocenes **3a**, **b**, and **d**, bisferrocenes **1a**–**c**, and ferrocenophanes **2a**, **b**, and **6**.

	$E_{1/2}^1$ [V]	$E_{1/2}^2$ [V]	$\Delta E_{1/2}$ [V]	Ref.
3a ^[11]	0.34	–	–	
3b ^[11]	0.12	–	–	
3d ^[11]	0.49	–	–	
1a	0.44	0.79	0.35	[19]
1b	0.63	0.76	0.13	[19]
1c	0.58	0.68	0.10	[19, 20]
2a	0.27	0.86	0.59	[19]
2b	0.62	0.98	0.36	[19]
6 ^[11]	0.35	0.60	0.25	

of the UV/Vis absorption of **6** at $\lambda_{\text{max}} = 232$ nm ($\lg \epsilon = 5.02$), is high in comparison to that of **3d**, and its characteristic ferrocene band, bathochromatically shifted relative to the “monomer” **3d** by $\Delta\lambda = 22$ nm (**3d**: $\lambda_{\text{max}} = 470$ nm ($\lg \epsilon = 2.40$); **6**: $\lambda_{\text{max}} = 492$ nm ($\lg \epsilon = 3.19$)), indicates delocalization through the butadiyne bridges (Figure 1).

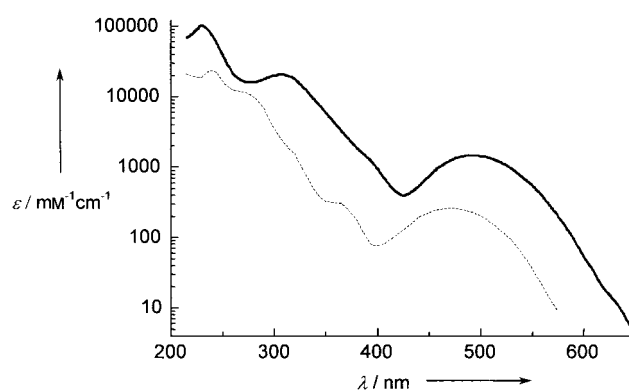


Figure 1. UV/Vis spectra of **3d** (----) and **6** (—) in *n*-hexane.

A single-crystal X-ray structural analysis of the ferrocenophane **6** was performed (Figure 2).^[15] The binuclear complex crystallizes in the space group $P2_1/n$ and has four crystallographically independent molecules per unit cell. The *tert*-butyl groups on the two ferrocene units are in each case situated in the *syn* position. Because of the opposing steric hindrance of the *tert*-butyl groups the two Cp rings lie in an almost perfect

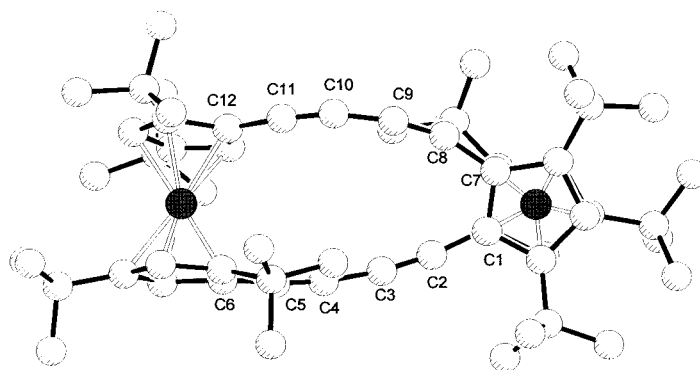


Figure 2. Molecular structure of **6**. The numbering of the atoms does not correspond to the nomenclature. Selected bond lengths [pm] and angles [°]: C1–C2 143.1(5), C2–C3 120.5(5), C3–C4 136.2(6), C4–C5 120.5(5), C5–C6 142.4(5), C7–C8 141.7(5), C8–C9 120.0(5), C9–C10 137.6(6), C10–C11 119.8(5), C11–C12 142.5(6); C1–C2–C3 162.6(4), C2–C3–C4 165.8(4), C3–C4–C5 165.0(4), C4–C5–C6 161.1(4), C7–C8–C9 169.8(4), C8–C9–C10 167.9(4), C9–C10–C11 168.6(4), C10–C11–C12 171.7(4).

antiperiplanar conformation. Consequently the two ethynyl units are twisted relative to each other by an angle of around 45°, and the bond angle along the two butadiynyl bridges deviates considerably from the ideal angle of 180° with values between 161.1–171.7°. Thus the two ferrocene units are twisted by about 82° relative to each other and so are almost orthogonal (“twist” form^[14]) so that the molecule exists in a helical-chiral conformation—as a racemic compound in the crystal.

The lengths of the C–C triple bonds lie within the range of 119.8(5) to 120.5(5) pm and correspond to those of the bisferrocene **1c**.^[3] The Fe–C_{sp} bonds of 203.0(4) to 211.6(3) pm are with an average length of 208 pm longer than in ferrocene (**3a**; 205 pm^[16]) and 1,1',3,3'-tetra-*tert*-butylferrocene (**3b**; 204–206 pm^[17,18]). The distance between the two iron atoms in the ferrocenophane **6** is 802.5(5) pm.

The cyclic voltammogram^[11] of **6** (Figure 3) with two reversible half-wave potentials at $E_{1/2}^1 = 0.35$ V and $E_{1/2}^2 = 0.60$ V suggests a redox interaction between the ferrocene units. The difference between the two half-waves of $\Delta E = 0.25$ V is about twice as large as the value found by Cowan

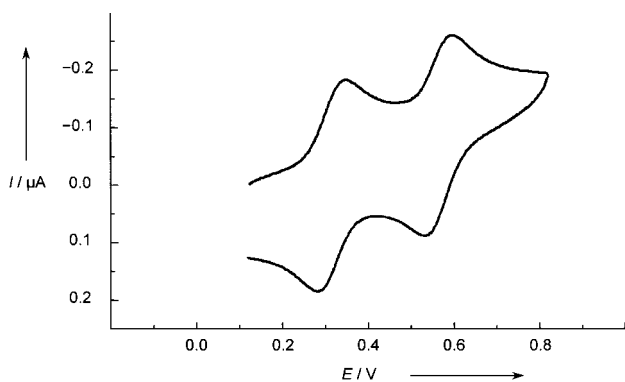


Figure 3. Cyclic voltammogram of **6**.^[11]

et al.^[19] and Hendrickson et al.^[20] for the singly bridged bisferrocenylbutadiyne **1c** ($\Delta E = 0.1$ V). This confirms results according to which in the transformation from “open” bisferrocenophane structures **1** to the “closed” ferrocenophanes **2** the differences between the two half-wave potentials approximately double (Table 1).^[19] A “through-space” interaction between the iron centers in the case of the ferrocenophane **6** can be excluded on account of their large separation.

Experimental Section

2,2',4,4'-tetra-*tert*-butyl-1,1'-diethynylferrocene **3d**: at –90 °C, under purest nitrogen, *n*-butyllithium, (3.3 mL, 5.0 mmol, 1.5 M *n*BuLi solution in *n*-hexane) was added dropwise to a solution of 2,2,6,6-tetramethylpiperidine (0.71 g, 5.0 mmol) in THF (10 mL) and the mixture was allowed to warm to room temperature. The mixture was again cooled to –90 °C, treated dropwise with a solution of **4** (1.01 g, 5.0 mmol) in THF (10 mL), and stirred at room temperature for 2 h. After the addition of FeCl₂ (0.63 g, 5.0 mmol) at –90 °C the reaction mixture was stirred for a further 12 h at room temperature and then treated with water (10 mL) and diethyl ether (20 mL). The aqueous phase was separated, extracted with diethyl ether (20 mL), and the combined organic extracts dried with magnesium sulfate. After filtration and evaporation of the solvent in vacuum the red-brown, oily residue was purified by chromatography on silica gel eluting with *n*-hexane. After removal of the solvent in vacuum **3d** (300 mg, 26%) was

isolated from the orange band as red crystals. M.p. 148–150 °C; IR (KBr): $\bar{\nu} = 3307, 2957, 2926, 2867, 2105$ cm⁻¹; UV/Vis (*n*-hexane): $\lambda_{\text{max}}(\lg \epsilon) = 216$ nm (4.33), 239 (4.41), 266 (4.08) sh, 356 (2.49) sh, 470 (2.40); ¹H NMR (300 MHz, CDCl₃, –40 °C, TMS): $\delta = 1.21$ (s, 9H, C(CH₃)₃), 1.26 (s, 9H, C(CH₃)₃), 1.34 (s, 9H, C(CH₃)₃), 1.45 (s, 9H, C(CH₃)₃), 2.93 (s, 1H, C≡CH), 3.07 (s, 1H, C≡CH), 4.00 (d, $J = 0.8$ Hz, 1H, Cp-H), 4.11 (d, $J = 0.8$ Hz, 1H, Cp-H), 4.15 (d, $J = 0.8$ Hz, 2H, Cp-H); EI-MS (70 eV): m/z (%): 458 (100) [M^+], 57 (35) [C₄H₉⁺]; elemental analysis calcd (%) for C₃₀H₄₂Fe (458.5): C 78.59, H 9.23; found: C 78.51, H 9.42.

6,8,11,13,19,21,24,26-octa-*tert*-butyl-[4.4]ferrocenophane-1,3,15,17-tetrayne **6**: a solution of **3d** (600 mg, 1.3 mmol) in pyridine (10 mL) was added dropwise over 2 h to a suspension of copper(II) acetate (905 mg, 5.0 mmol) in boiling pyridine (70 mL) and the reaction mixture was heated under reflux for a further 5 h. After removal of the solvent in vacuum the residue was extracted with diethyl ether (3 × 50 mL), the solution was filtered and washed to neutral with 2 N hydrochloric acid and water. After the organic phase was dried with magnesium sulfate the solvent was removed in vacuum and the residue purified by chromatography on silica gel eluting with *n*-pentane. After removal of the solvent in vacuum **6** (175 mg, 28%) was obtained from the light red band as red needles which do not melt at up to 230 °C. IR (KBr): $\bar{\nu} = 2959$ (C–H), 2867 (C–H), 2196 (C≡C), 2134 cm⁻¹ (C≡C); UV/Vis (*n*-hexane): $\lambda_{\text{max}}(\lg \epsilon) = 232$ nm (5.02), 308 (4.31), 492 (3.19); ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): $\delta = 1.26$ (s, 18H, 2 × C(CH₃)₃), 1.43 (s, 18H, 2 × C(CH₃)₃), 3.97 (brs, 4H, Cp-H), 4.22 (brs, 4H, Cp-H); EI-MS (70 eV): m/z (%): 912 (100) [M^+], 456 (28) [M^{2+}]; elemental analysis calcd (%) for C₆₀H₈₀Fe₂ (913.0): C 78.93, H 8.83; found: C 78.51, H 8.93.

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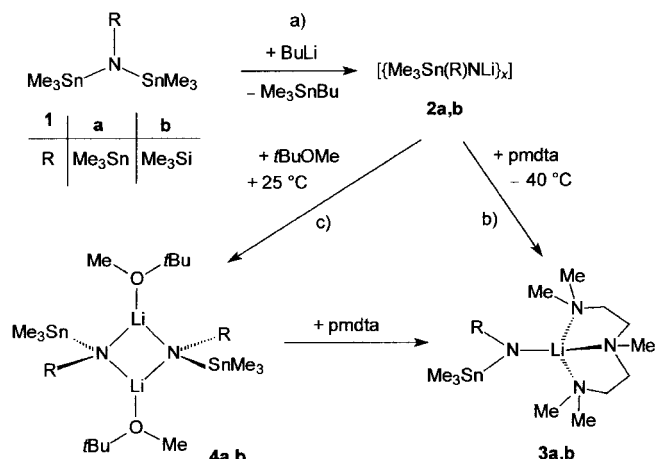
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- [10] After the addition of the chiral shift reagent europium(III)-tris[3-heptafluoropropylhydroxymethylene]-D-camphorate [Eu(hfc)₃] the ¹H NMR spectrum of **3d** shows no evidence of the presence of the racemic *anti*-isomer.
- [11] The cyclic voltammetric measurements were carried out in CH₂Cl₂ at –20 °C with Bu₄NPF₆ (0.1M) as supporting electrolyte and calibrated against cobaltocenium/cobaltocene ($E_{\text{ox}} = -1.04 \text{ V}_{\text{SCE}}$; SCE = saturated calomel electrode). The scan speed was 100 mV s⁻¹; working electrode: Pt button; reference electrode: Pt wire.
- [12] A differential scanning calorimetry (DSC) measurement carried out at up to 250 °C gave no indication of topochemical solid-state polymerization.
- [13] The oligomeric mixture is readily soluble in *n*-pentane and shows molecular masses of up to $M = 9200$ (molecular mass of the icosomer (20mer) of **3d**) in the matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum.
- [14] Broadened ¹H NMR ring-proton signals have also been observed by Watanabe et al. with ferrocene[1.1]ruthenophane. This finding was attributed to a rapid equilibrium between the *syn* conformers (*syn*-A and *syn*-B) in solution which proceeds through a *twist* form. A similar equilibrium is also possibly present in the case of the ferrocenophane **6**: a) M. Watanabe, A. Nagasawa, I. Motoyama, T. Takayama, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2127–2136; b) U. T. Mueller-Westerhoff, *Angew. Chem.* **1986**, *98*, 700–716; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 702–718.
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New Building Blocks in Amide Chemistry—*N*-Lithiobis(trimethylstannyl)amine and *N*-Lithiotrimethylstannyl(trimethylsilyl)amine**

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The enormous synthetic utility of *N*-lithiosilylamines, in particular of *N*-lithiobis(trimethylsilyl)amine, [LiN(SiMe₃)₂],^[1] has been well documented.^[2] In contrast, related tin derivatives have remained unknown so far, and *N*-lithiostannylamines in general have received scant attention,^[3] probably because of the greatly enhanced reactivity of the Sn–N bond^[4] when compared with Si–N bonds. However, this enhanced reactivity is desirable in metal amides for further transformations, and therefore, selective smooth syntheses of such amides bearing one or two trimethylstannyl groups at the nitrogen atom are an attractive goal. We have now succeeded in obtaining pure *N*-lithiobis(trimethylstannyl)amine, [LiN(SnMe₃)₂] (**2a**), and *N*-lithiotrimethylsilyl(trimethylstannyl)amine, [LiN(SiMe₃)SnMe₃] (**2b**), for the first time from the 1:1 reaction of tris(trimethylstannyl)amine, (Me₃Sn)₃N (**1a**),^[5] and trimethylsilylbis(trimethylstannyl)amine, (Me₃Sn)₂NSiMe₃ (**1b**),^[6] respectively, with butyllithium (Scheme 1). The low solubility of **2a,b** points to a mixture of oligomers ($x \approx \infty$ in Scheme 1).



Scheme 1. Synthesis of **2a,b**, **3a,b**, and **4a,b**. $x = 1, 2$.

The reaction of **1a** or **1b**, dissolved in hexane, with BuLi in hexane (Scheme 1a) afforded colorless, extremely air- and moisture-sensitive powders that could be isolated and stored

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