MS m/z 283 (M$^+$, 100), 255 (64); UV-vis (MeOH) λ_{max} (ϵ) 234 (34800), 255 sh (24200), 281 (21000), 300 sh (13200), 313 sh (9400), 375 (7500); high-resolution mass spectrum calcd for $C_{18}H_9N_3O$ m/z 283.0746, found m/z 283.0735.

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Registry No. 2, 133400-90-5; **4**, 25368-52-9; **5**, 133400-91-6; **6**, 133400-92-7; **7**, 114552-32-8; **8**, 97545-51-2; **9**, 133400-93-8; **10**, 133400-94-9; **11**, 133400-95-0; **12**, 133419-80-4; **13**, 133400-96-1; **14**, 133400-97-2; **15**, 133400-98-3; **16**, 133400-99-4; **18**, 133401-00-0; PhNHBOC, 3422-01-3; ClSnMe$_3$, 1066-45-1; CH$_2$=CHCHO, 107-02-8.

Supplementary Material Available: ^{1}H and ^{13}C NMR, COSY, and NOESY spectra for isoascididemin (**2**) (4 pages). Ordering information is given on any current masthead page.

Synthesis and Characterization of Substituted (1,2-Naphthalocyaninato)iron Compounds and Bisaxially Coordinated Isocyanide Complexes

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Tetrasubstituted (1,2-naphthalocyaninato)iron(II) compounds t-Bu$_4$-1,2-NcFe (**13**), Me$_4$-1,2-NcFe (**14**), and Ph$_4$-1,2-NcFe (**15**) are obtained from 7-substituted 1,2-dicyanonaphthalenes **12a–c** either by reaction with pentacarbonyliron in 1-chloronaphthalene (method a) or with iron(II) acetate in 1-hexanol (method b), respectively. Compounds **13–15** were characterized by UV/vis, IR, and Mössbauer spectroscopy, and the oxidation potentials, measured by cyclic voltammetry in pyridine, are compared with the oxidation potentials of 1,2-NcFe and PcFe. The substituted (1,2-naphthalocyaninato)iron compounds **13**, **14**, and **15** react with alkyl and aryl isocyanides R′NC (R′ = t-Bu, c-Hx, Bz, Me$_2$Ph), yielding the bisaxially coordinated isocyanide complexes of **13**, **14**, and **15**, R$_4$-1,2-NcFe (R′NC)$_2$. Due to their comparatively high solubility in organic solvents, it is possible to characterize the isocyanide complexes with ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectra of, for example, t-Bu$_4$-1,2-NcFe(t-BuNC)$_2$ reveal that only one of the structural isomers of the unsymmetrical 1,2-naphthalocyanine macrocycle, namely, the 1,2-naphthalocyanine with C_{4h} symmetry (see Figure 1) is formed, if the synthesis starting with 7-*tert*-butyl-1,2-dicyanonaphthalene (**12a**) is carried out according to method a. The crystal structure of the isomer obtained, t-Bu$_4$-1,2-Nc(t-BuNC)$_2$, is determined (Figure 4) and confirms these findings. All isocyanide complexes R$_4$-1,2-NcFe(R′NC)$_2$ are characterized by spectral data and thermoanalyses. The reaction of R$_4$-1,2-NcFe **13**, **14**, and **15** with diisocyanobenzene (dib) leads to the bridged compounds [R$_4$-1,2-NcFe(dib)]$_n$, R = t-Bu, Me, Ph. After being doped with iodine, the bridged complexes exhibit good semiconducting properties.

Introduction

Square-planar transition-metal macrocycles, linked by bidentate organic ligands to form bridged stacked arrangements of the macrocycles, have been investigated by us as semiconducting materials.[1] Thus phthalocyaninato (PcM), tetrabenzoporphyrinato (TBPM), or 2,3-naphthalocyaninato (2,3-NcM) transition-metal complexes can be linked bisaxially by bidentate bridging ligands L [L = pyrazine (pyz), tetrazine (tz), 1,4-diisocyanobenzene (dib), cyanide (CN$^-$), thiocyanate (SCN$^-$)] to form linear -PcM-L-PcM-L-, -TBPM-L-TBPM-L-, and -(2,3-Nc)-L-(2,3-Nc)-L- chains (M = Fe, Ru, Co, Rh).[1,2] This type of bridged metal complexes can be chemically and electrochemically doped, resulting in systems with good semiconducting properties.[3] The successful synthesis of, for example, [PcM(tz)]$_n$ (M = Fe, Ru),[2c] [2,3-NcFe(tz)]$_n$[2d] and [MacML]$_n$ (Mac = Pc, TBP; M = Fe, Co; L = CN$^-$, SCN$^-$)[1b,2g,o,4] indicates that even without additional oxidative doping, stable bridged stacked systems with relatively high powder conductivities (σ_{RT} = ~10^{-1} S/cm) can be obtained.

Bridged 2,3-NcM systems [2,3-NcML]$_n$ too exhibit, without doping, comparatively high semiconductive properties. For example, [2,3-NcFe(dib)]$_n$ shows a powder conductivity of σ_{RT} = 3.3 × 10^{-3} S/cm (E_a = 0.13 eV).[2d,4c] On the contrary the comparable [PcFe(dib)]$_n$ with σ_{RT} =

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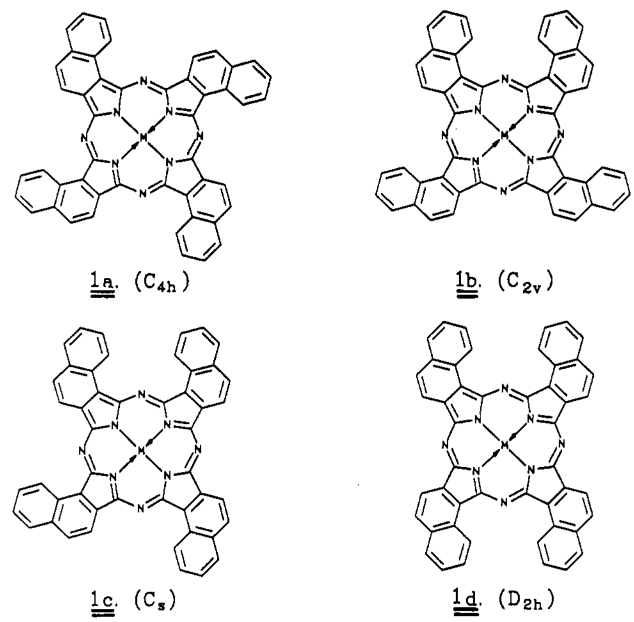

1a (C_{4h}) **1b** (C_{2v}) **1c** (C_s) **1d** (D_{2h})

Figure 1. Constitutional isomers of 1,2-NcM.

5×10^{-6} S/cm is a weak semiconducting material.[1] The higher conductivity of $[2,3\text{-NcFe(dib)}]_n$ is due to the low oxidation potential of the macrocycle, which renders oxidative doping with air oxygen possible.[2d,o,4c] The electrical properties of bridged (naphthalocyaninato)iron(II) complexes are changed drastically, however, if (1,2-naphthalocyaninato)iron(II) (1,2-NcFe) instead of 2,3-NcFe is used as metal macrocycle (see below).

Recent theoretical calculations show[5] that the extension of the aromatic structure of phthalocyanine to give rise to naphthalocyanines affects the electronic properties of the macrocycle differently depending on the way the additional benzene rings are fused to the phthalocyanine ring. Symmetric or linear annulation leading to 2,3-naphthalocyanine produces a destabilization of the HOMO level and a decrease of the first ionization potential. A narrowing of the HOMO–LUMO energy gap is calculated for 2,3-naphthalocyanine with respect to phthalocyanine. Therefore, a lower oxidation potential of the macrocycle and a bathochromic shift of the lowest energy electronic transition (Q-band) are predicted for 2,3-naphthalocyanine compared with phthalocyanine. In contrast, unsymmetric or angular annulation leading to 1,2-naphthalocyanine slightly stabilizes the HOMO level and similar oxidation potentials and transition energies in the visible are expected for 1,2-naphthalocyanine and phthalocyanine.[5]

An unsymmetrical naphthalocyanine, 1,2-naphthalocyanine ($1,2\text{-NcH}_2$), is capable of forming constitutional isomers. An isomeric mixture of 1,2-naphthalocyanines ($1,2\text{-NcH}_2$) was first mentioned and proven by Linstead et al.;[6] four isomers of $1,2\text{-NcH}_2$ or 1,2-NcM, respectively, are possible (Figure 1).

The synthesis of unsymmetrically substituted phthalocyanines is difficult, up to now only a few reports for the synthesis of only one pure isomer are known. Either a mixture of isomers is obtained (starting with unsymmetrically substituted phthalonitrile derivatives) or mixtures of differently substituted phthalocyanines are obtained (using the statistical approach with differently substituted phthalonitrile precursors).[7–19]

We have already reported on 1,2-NcFe and its derivatives, bisaxially substituted by isocyanides ($1,2\text{-NcFeL}_2$ (L = *t*-BuNC, c-HxNC, BzNC), as well as on the 1,4-diisocyanobenzene-bridged system $[1,2\text{-NcFe(dib)}]_n$.[2h] The existence of at least three isomers of the synthesized 1,2-NcFe was demonstrated, and we were able to isolate one of them as the cyclohexyl isocyanide complex $1,2\text{-NcFe(c-HxNC)}_2$ by column chromatography. That compound **1a** (see Figure 1) was the isomer in question was proven by the X-ray structure of $1,2\text{-NcFe(c-HxNC)}_2$.[2h] Contrary to $[2,3\text{-NcFe(dib)}]_n$, $[1,2\text{-NcFe(dib)}]_n$ exhibits almost insulating properties ($\sigma_{RT} = 6 \times 10^{-10}$ S/cm, powder conductivity, pressed pellet); it can, however, be doped oxidatively with iodine to give $[1,2\text{-NcFe(dib)I}_{1.8}]_n$ showing a powder conductivity of $\sigma_{RT} = 4 \times 10^{-3}$ S/cm.[2h]

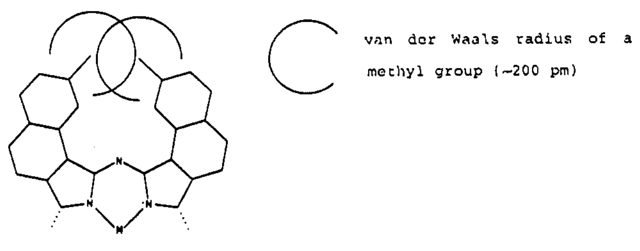

Figure 2. Section of substituted 1,2-naphthalocyanine.

In the present study we attempted to develop a specific synthesis for a tetrasubstituted 1,2-NcFe, resulting in merely a single isomer of R_4-1,2-NcFe by using suitable substituents in the periphery of the 1,2-NcFe macrocycle. Steric instead of electronic effects were to be taken advantage for the specific synthesis of one isomer of 1,2-NcFe. Considering the possible isomers of 1,2-NcFe (Figure 1), always at least two of the exterior benzene rings—except in isomer **1a**—point toward each other. With substitution with sterically demanding substituents in the 7-position of 1,2-naphthalocyanine during the formation process (Figure 2), it was expected that the formation of the isomers **1b–d** (Figure 1) would be repressed or even suppressed completely.

For carrying out the reaction, it was necessary to synthesize the appropriate starting compounds, namely, 7-substituted 1,2-dicyanonaphthalenes **12**. As substituents R in **12** the especially sterically demanding *tert*-butyl group (**12a**) and for comparison the methyl (**12b**) and phenyl (**12c**) group, respectively, were chosen.

Synthesis of 7-Substituted 1,2-Dicyanonaphthalenes 12a–c. For the synthesis of 7-substituted 1,2-dicyanonaphthalenes **12a–c**, the route shown in Scheme I was elaborated. The synthesis of substituted naphthalene-1,2-dicarboxylic acids is known,[20] and the dinitriles **12** can be obtained via the dicarboxylic acids.

The reaction sequence given in Scheme I begins with an acylation of the substituted benzenes **2a–c** with succinic anhydride (**3**). The γ-keto acids **4a–c** formed are reduced

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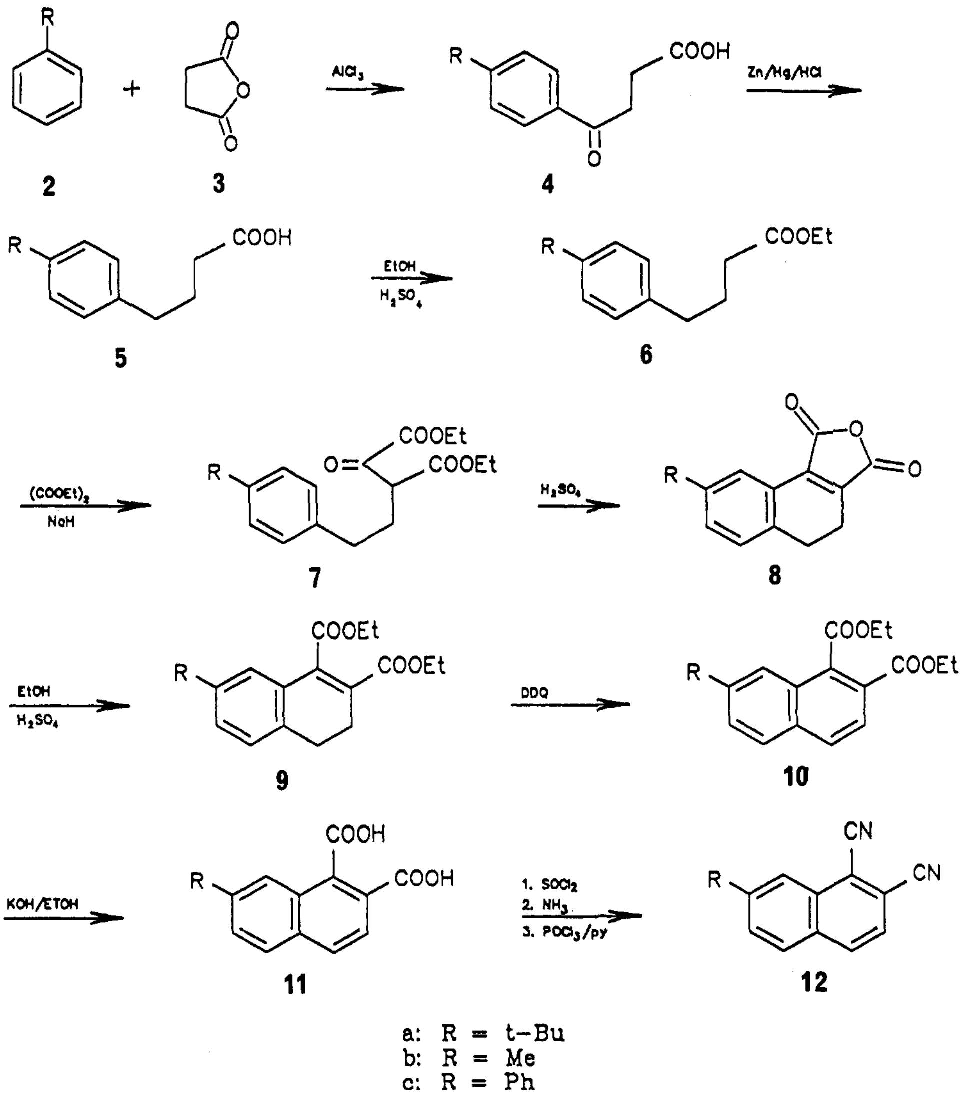
Scheme I



(Clemmensen reduction) to form the substituted phenylbutyric acids **5a–c** and subsequently esterified to give ethyl phenylbutyrates **6a–c**.

The esters **6a–c** are reacted with diethyl oxalate to form the keto esters **7a–c**. By cyclization of **7a–c** in 80% sulfuric acid, the dihydronaphthalene-1,2-dicarboxylic acid anhydrides **8a–c** are formed directly. Transformation into diesters **9a–c** allows dehydrogenation with DDQ to give the 7-substituted ethyl naphthalene-1,2-dicarboxylates **10a–c**. Saponification to form the dicarboxylic acids **11a–c**, transforming them into acid chlorides and acid amides, and subsequent dehydration with $POCl_3$ gives the desired dicyanonaphthalenes **12a–c**. The overall yield is not very high, especially due to the last step, leading to the dinitriles **12a–c**. This is due to the fact that cyclization of ortho carboxylic acids to form acid anhydrides or imides is thermodynamically more favored.[2m] However, by the route shown in Scheme I, 7-*tert*-butyl-, 7-methyl-, and 7-phenyl-1,2-dicyanonaphthalenes **12a–c** were prepared in quantities of 2–5 g, sufficient for further reactions.

Synthesis and Characterization of t-Bu_4-1,2-NcFe (13), Me_4-1,2-NcFe (14), and Ph_4-1,2-NcFe (15). For the conversion of dicyanonaphthalenes **12a–c** to tetrasubstituted (1,2-naphthalocyaninato)iron compounds **13**, **14**, and **15**, two methods were applied (Scheme II). The nitriles **12a–c** (method a) were reacted with iron pentacarbonyl in 1-chloronaphthalene,[21] or with iron(II) acetate in 1-hexanol[22] (method b). The precise reaction conditions for forming the (1,2-naphthalocyaninato)iron derivatives **13**, **14**, and **15** are given in Table I.

Table I. Reaction Conditions for the Synthesis of Tetrasubstituted (Naphthalocyaninato)iron(II) Compounds 13, 14, and 15

	method a[21]	method b[22]
substr	dicyanonaphthalene **12a–c**	dicyanonaphthalene **12a–c**
solvent	chlornaphthalene	*n*-hexanol
catalyst	DBU	DBU
iron compound	$Fe(CO)_5$	$Fe(ac)_2$
temp, °C	190	170
reactn time, h	1–2	4–5

The tetrasubstituted iron naphthalocyanines **14** and **15** are nearly insoluble in organic solvents; however, t-Bu_4-1,2-NcFe (**13**) is soluble in $CHCl_3$, CH_2Cl_2, and similar polar solvents.[23] Compounds **13–15** synthesized by methods a and b are practically identical with respect to their UV and IR spectra.

Since, with the exception of t-Bu_4-1,2-NcFe (**13**), all compounds synthesized are nearly insoluble in organic solvents (e.g., also in 1-chloronaphthalene), pyridine was used as solvent to obtain UV spectra, which means that instead of the free metal macrocycle, the bisaxially coordinated derivatives $MacFepy_2$ were investigated (see Experimental Section). The shape of all the UV/vis spectra

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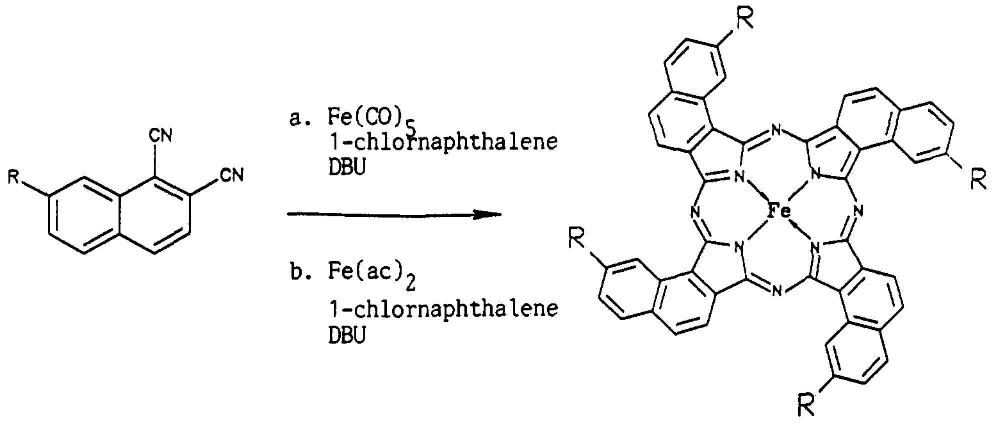
Scheme II



$R_4$1,2-NcFe

	R	
12a	t-Bu	**13**
12b	Me	**14**
12c	Ph	**15**

Table II. CV Data of R_4-1,2-NcFe 13, 14, and 15 in Comparison with 1,2-NcFe and PcFe in Pyridine/Bu_4NClO_4 vs SCE [V][a]

	oxidation		reduction			
compound	$E_{1/2}{}^1$	$E_{1/2}{}^2$	$E_{1/2}{}^3$	$E_{1/2}{}^4$	$E_{1/2}{}^5$	ref
t-Bu_4-1,2-NcFe (13)		0.67^r	-0.97^r	-1.21^q	-1.83^r	
Me_4-1,2-NcFe (14)		0.65^r	-0.97^r	-1.25^q	-1.85^r	
Ph_4-1,2-NcFe (15)		0.69^r	-0.94^r	-1.17^q	-1.75^r	
1,2-NcFe	1.01^q	0.68^r	-0.95^r	-1.21^q	-1.80^r	2o
PcFe	1.10^q	0.69^r	-1.09^r	-1.39^q	-1.93^r	24
assignmt	Mc(−2) Mc(−1)	Fe(II) Fe(III)	Fe(I) Fe(II)	Mc(−3) Mc(−2)	Mc(−4) Mc(−3)	

[a] q = quasi-reversible electron transfer. r = reversible electron transfer.

corresponds to that of 1,2-NcFepy_2.[2h] The bands of high intensity (Soret and Q) are mainly due to the π–π^* transition of the heteroaromatic π-electron systems of macrocycles (see Experimental Section).

The IR spectra of *t*-Bu_4-1,2-NcFe (**13**), Me_4-1,2-NcFe (**14**), and Ph_4-1,2-NcFe (**15**) exhibit characteristic bands at 1625, 1590 (C=C stretching vibration), 1393, and 837 cm^{-1} (see Experimental Section). These partly shifted bands are also found in the spectrum of 1,2-NcFe and are assigned to vibrations of the macrocycle.[2h]

The thermal stability of compounds **13**, **14**, and **15** is determined by thermal analyses. *t*-Bu_4-1,2-NcFe (**13**) does not change up to about 400 °C before cleavage in one step occurs. The DTA curve has its maximum at 492 °C. Me_4-1,2-NcFe (**14**) behaves similarly. Scission of the substituents, however, does not set in below 520 °C, it then directly goes over into decomposition of the macrocycle. Unlike **13**, Ph_4-1,2-NcFe (**15**) does not start to cleave or decompose until 600 °C.

Cyclic voltammograms of **13**, **14**, and **15** exhibit very similar traces, and the measured redox potentials are also very similar (Table II). The cyclic voltammograms are in good accordance with that of 1,2-NcFe,[2h] i.e., the peripheral substituents have no important influence on the redox potential of the macrocycle. Compared to the reduction potential of PcFe, the values of the substituted complexes are higher by 100 mV on average, allowing a more facile reduction of **13**, **14**, and **15**. The values of the first oxidation potential of PcFe and all of the 1,2-NcFe compounds are comparable (within the oxidative region). Thus generally it can be assumed that 1,2-NcFe[2h] and its derivatives have a redox behavior that largely corresponds to that of PcFe.[24]

Also Mössbauer data of *t*-Bu_4-1,2-NcFe (**13**), Me_4-1,2-NcFe (**14**), and Ph_4-1,2-NcFe (**15**) differ only slightly from those of PcFe[25] and 1,2-NcFe (see Experimental Section).[2h] According to the experimental data, iron in **13**, **14**, and **15** has the same oxidation state (+II) as in PcFe. As the complexes are always found to be square planar, the investigated compounds show the same distribution of electrons, and similar data of ΔE_Q were found.

In summary, according to the methods of investigation, *t*-Bu_4-1,2-NcFe (**13**), Me_4-1,2-NcFe (**14**), and Ph_4-1,2-NcFe (**15**) exhibit the same properties as 1,2-NcFe and similar properties to those of PcFe.

Whether the tetrasubstituted iron naphthalocyanines are free of isomers as desired could not yet be determined by the applied methods of characterization. NMR spectroscopy, however, renders it possible to elucidate the structure of soluble complexes. For this purpose, isocyanide complexes were chosen.

Synthesis of Bisaxially Coordinated Isocyanide Complexes R_4-1,2-NcFe(R′NC)$_2$. For synthesis of the complexes R_4-1,2-NcFe(R′NC)$_2$, the iron naphthalocyanines **13**, **14**, and **15** were reacted with the ligands L (R′NC) [*tert*-butyl- (R = *t*-Bu), cyclohexyl- (R′ = c-Hx), benzyl- (R′ = Bz), and 2,6-dimethylphenyl isocyanide (R′ = Me_2Ph)]. The corresponding iron macrocycle is stirred in excess ligand L for several hours, or in the case of 2,6-dimethylphenyl isocyanide dissolved in chloroform.

Characterization of Isocyanide Complexes of *t*-Bu_4-1,2-NcFe (13), Me_4-1,2-NcFe (14), and Ph_4-1,2-NcFe (15). ^{1}H NMR Spectra. Because of the distinct

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ring current of the heteroaromatic 18π-electron system of phthalocyanines and related systems, the macrocyclic protons as well as the protons of bisaxially substituted ligands are characteristically shifted to low or high field, respectively.[2c,h]

The same effects are expected to be found for naphthalocyanines.[2c,h,26,27] However 1,2-NcFe has six different kinds of protons, thus rendering the assignment more difficult than in the case of symmetrical compounds 2,3-NcFe and PcFe. The existence of isomers leading to a variety of peaks increases the difficulty of assignment.

The same problem also exists for the isocyanide complexes of **13**, **14**, and **15**, although the results of the corresponding 1,2-NcFe complexes[2h] can be used as reference. Isocyanide complexes of PcFe have been investigated in great detail by NMR spectroscopy.[2c,i,m] Therefore, the assignment of protons of the ligands can be carried out analogous to PcFe compounds. All ^{1}H NMR data are given in the Experimental Section.

^{13}C NMR Spectra. ^{13}C NMR data of PcFe[2c,m,28] and NcFe[2h] complexes with isocyanide as bisaxial ligands are known. Due to their enhanced solubility we could obtain the ^{13}C NMR spectra of *t*-Bu$_4$-1,2-NcFe(*t*-BuNC)$_2$ and *t*-Bu$_4$-1,2-NcFe(Me$_2$PhNC)$_2$. Spin-echo experiments were carried out to discriminate between tertiary and quaternary C atoms. However, even by using this method a complete assignment of the signals is not possible. Because of the existing isomers, many more signals are found than a symmetrical isomer is expected to have. Moreover, due to the asymmetry of the substituted macrocycle, there are five tertiary and seven quaternary C atoms of each benzene–isoindole unit at least. Hence a simple assignment is not possible without reference data at hand. Nevertheless, by means of ^{13}C NMR spectra of *t*-Bu$_4$-1,2-NcFe(*t*-BuNC)$_2$ with proton decoupling at single ^{1}H frequences, we have succeeded in assigning them. As far as C atoms of the isocyanide ligands are concerned, especially Me$_2$PhNC, known reference data of PcFeL$_2$ compounds can be employed.[2c] All ^{13}C NMR data are given in the Experimental Section.

Dependency of Isomer Ratio of R$_4$-1,2-NcFe on the Method of Preparation. As we have demonstrated recently,[2h] it is possible to detect the presence of an isomer mixture of 1,2-NcFe by NMR spectroscopy. Several results of the ^{1}H and ^{13}C NMR spectra of the complexes R$_4$-1,2-NcFeL$_2$ (L = R′NC) are summarized as follows:

Besides the expected peak around δ = 11 for the H$_1$ proton, the ^{1}H NMR spectra of all the isocyanide complexes MacFe(L)$_2$ (Mac = *t*-Bu$_4$-1,2-NcFe (**13**), Me$_4$-1,2-NcFe (**14**), Ph$_4$-1,2-NcFe (**15**), L = R′NC) often exhibit for the H$_1$ proton another peak shifted to higher field (Figure 3). As will be pointed out later, this peak can be assigned to isomers equivalent to **1b–d** (Figure 1). In the ^{1}H NMR spectra of the isocyanide complexes of Me$_4$-1,2-NcFe (**14**), this second peak is always present, whereas it is either small or has vanished completely in the spectra of Ph$_4$-1,2-NcFe(R′CN)$_2$ and especially in *t*-Bu$_4$-1,2-NcFe(R′CN)$_2$, depending on the method of synthesis. This implies that depending on the method of preparation a mixture of isomers is obtained or one isomer is formed preferentially (probably the isomer equivalent to **1a**).

Figure 3 shows the ^{1}H NMR spectra of *t*-Bu$_4$-1,2-NcFe(*t*-BuNC)$_2$, synthesized according to method a[21] and method b[22] (Table I). For both compounds the reaction yielding the complexes *t*-Bu$_4$-1,2-NcFe(*t*-BuNC)$_2$ was performed under analogous conditions. Spectrum b (Figure 3) shows a larger number of peaks in comparison with spectrum a, allowing the conclusion that several isomers exist.

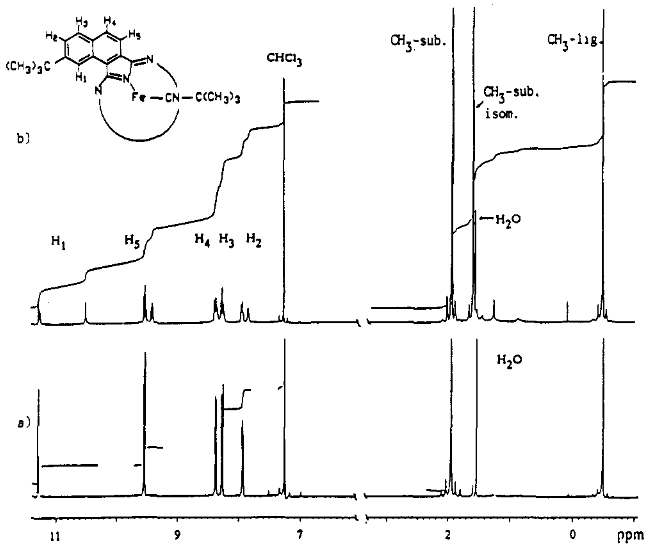

Figure 3. ^{1}H NMR spectra of *t*-Bu$_4$-1,2-NcFe(*t*-BuNC)$_2$ (400 MHz): (a) synthesis according to method a[21] (Scheme II); (b) synthesis according to method b[22] (Scheme II).

Contrary to the original assumption, method b leads to a mixture of isomers, in spite of the *tert*-butyl group introduced as the bulky substituent. Hence, isomers with peripheral substituents pointing toward each other must exist. The substituents were selected in such a way that this is impossible without torsion of the ring system. The system is forced to release the steric pressure by twisting the exterior benzene rings out of the plane ring, leading to following consequences: Both the proton H$_1$ (Figure 3), which is directed to the macrocycle, and the substituent itself are expelled from one aromatic ring current. For the isomers in which two substituents point toward each other, the protons of the *tert*-butyl group and the proton H$_1$ are shifted thereby to high field, as observed in the spectrum. Further evidence to confirm this assumption is the fact that the high-field shift of H$_1$ increases with the size of the substituent (i.e., methyl < phenyl < *tert*-butyl).[14]

Within the isomer **1a** (Figure 1 or R$_4$-1,2-NcFe **13–15** in Scheme II) each substituent is situated in the ring plane, and signals shifted to high field as compared to the butyl group and H$_1$ are not expected. In spectrum a of *t*-Bu$_4$-1,2-NcFe(*t*-BuNC)$_2$ (Figure 3), no additional peak is found for H$_1$ and only a very small signal shifted to high field shows up for the protons of the *tert*-butyl group. This implies, that method a almost exclusively gives the desired isomer **1a** in 99% enrichment compared to other isomers, as estimated by the signal intensity of the *tert*-butyl groups (Figure 3).

The ^{13}C NMR spectra of *t*-Bu$_4$-1,2-NcFe(*t*-BuNC)$_2$, obtained by methods a and b, have a similar pattern. In the spectrum of *t*-Bu$_4$-1,2-NcFe(*t*-BuNC)$_2$, synthesized by method a, the expected number of peaks belonging to one benzene–isoindole unit of the naphthalocyanine are evident. This points out again that the sample is free from other isomers with the exterior benzene rings situated in equilateral positions. In contrast, *t*-Bu$_4$-1,2-NcFe(*t*-BuNC)$_2$ prepared by method b exhibits several peaks (up to six) for each C atom. The existence of several isomers and additional stereoisomers formed by twisting of the

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[26] Schechtmann, L. A. Ph.D. Thesis, Case Western University, Evanston, 1983.

[27] Wechler, B. L.; Nagasubramanian, G.; Bard, A. J.; Schechtmann, L. A.; Dininny, D. R.; Kenney, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 7404.

[28] Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209.

exterior benzene rings is again responsible for this behavior (see above). Interestingly even the C atoms of the isocyanide ligand exhibit two peaks. This is an additional proof confirming the assumption that the exterior benzene rings are expelled from the ring plane and several isomers must exist simultaneously.

The formation of either a mixture of isomers or a single isomer, depending on the method of synthesis, could be confirmed by HPLC. For t-Bu$_4$-1,2-NcFe(Me$_2$PhNC)$_2$ synthesized according to method b, three peaks were recorded, while in the other case (method a) only a single peak was found.[14,15]

IR Spectra. Like those of the free ligand, all spectra of the isocyanide complexes are dominated by the intensive N≡C stretching vibrations of the isocyanides between 2122 and 2162 cm^{-1} (see Experimental Section). The intensity and sign of the shifted absorption strongly depends on the respective contribution of the σ-donor and π-acceptor bands of the metal–ligand bonding.[14] The NC stretching frequencies of the bisaxially coordinated tetrasubstituted iron naphthalocyanines generally show increased values in comparison with those of the free ligand. Thus the contribution of the σ-donor bond must prevail in the investigated complexes here.

The electronic influence of the different substituted macrocycles R$_4$-1,2-Nc on the iron atom and therefore on the π-acceptor bond to the ligand is approximately constant. As to the same isocyanide ligand of different macrocycles, the NC frequencies exhibit only slight variations. Hence, it is concluded that all macrocycles show the same amount of π-back donation. Compared to PcFe,[2c] 2,3-NcFe,[2d,4c] and 1,2-NcFe[2h,14] prominent variations of the NC stretching frequencies of the respective isocyanide ligand cannot be observed. By changing Pc into tetrabenzoporphyrin (TBP) or tetraphenylporphyrin (TPP) or if the central iron atom is substituted by Ru, considerable shifts of the NC absorption bands caused by varying contributions of the π-back donation are found.[30,31]

UV/vis Spectra. The shape of UV/vis spectra of 1,2-NcFe compounds is dominated by $\pi \rightarrow \pi^*$ transitions of the heteroaromatic electron system of the macrocycle. In general there is no change if the axial ligand is substituted, only the band sequences are partly shifted (see Experimental Section).

On the whole the band sequences remain unchanged, even if the macrocycle is further substituted, provided that the isocyanide ligand remains the same. Even if the ligand of the same macrocycle is substituted, variations cannot be observed. With the exception of the twin band of BzNC compounds, each complex gives the same UV/vis spectra more or less.

Thermal Analysis. The thermal stability of the coordination compounds MacFeL$_n$ (Mac = Pc, TBP, Nc) can be determined by thermal analysis.[2] Due to the high thermal stability of the macrocycles, cleavage of the coordination compounds generally takes place by the rupture of the ligand(L)–metal bond (Table III).[2c,h,m]

Splitting off of the ligands (L) in R$_4$-1,2-NcFeL$_2$ precedes to the cleavage of peripheral substituents. This can be precisely observed in complexes of t-Bu$_4$-1,2-NcFeL$_2$ exhibiting an elimination reaction of peripheral *tert*-butyl groups at about 470 °C. The cleavage of the methyl or phenyl group in complexes R$_4$-1,2-NcFeL$_2$ occurs only at higher temperature and is not found in thermograms. In general, elimination of ligands occurs between 200 and 270 °C in one step. Sometimes two maxima can be detected by DTG. Thus, cleavage of ligands takes place at different times, probably by pentacoordinated compounds as intermediates. As to the ligands, *tert*-butyl isocyanide shows the lowest elimination temperature in each macrocycle, whereas a general tendency of other isocyanides cannot be observed.

Table III. Thermal Analysis of Complexes R$_4$-1,2-NcFeL$_2$

	temp range (°C)	mass defect calcd/found	DTA signal T_{max} (°C)
	t-Bu$_4$-1,2-NcFeL$_2$		
L = t-BuNC	165–270	14.3/14.2	219[a] 251[a] 495[a] (t-Bu)
c-HxNC	150–310	18.0/17.1	275[a] 460[a] (t-Bu)
BzNC	160–290	19.1/18.9	286[a]
Me$_2$PhNC	170–270	21.0/21.2	252[a] 486[a] (t-Bu)
	Me$_4$-1,2-NcFeL$_2$		
L = t-BuNC	140–220	16.8/15.6	195[a]
c-HxNC	180–260	20.9/20.2	247[a]
BzNC	130–260	22.1/21.8	249[a]
Me$_2$PhNC	180–280	24.1/23.8	278[a]
	Ph$_4$-1,2-NcFeL$_2$		
L = t-BuNC	140–260	13.4/12.0	210[a]
c-HxNC	160–260	16.9/12.2	224[a] 233[a]
BzNC	165–270	17.9/17.2	216[a] 245[a]
Me$_2$PhNC	170–270	19.6/19.0	247[a]

[a] Endothermic.

Crystal Structure Analysis of t-Bu$_4$-1,2-NcFe(t-BuNC)$_2$. A crystal structure determination of t-Bu$_4$-1,2-NcFe(t-BuNC)$_2$ was performed to prove the structure of the isomer prepared according to method a (Table I).

n-Hexane was added carefully to a solution of t-Bu$_4$-1,2-NcFe(t-BuNC)$_2$ in CHCl$_3$ to obtain suitable crystals. Violet crystals of the n-hexane solvate were formed within 1 week. For the data collection the crystals were sealed with varnish to prevent decomposition in air with loss of solvent molecules. The lattice constants and parameters of the structure determination are given in the supplementary material.

The position of the Fe atom was derived from a Patterson synthesis.[32] A tangent expansion and subsequent Fourier syntheses[33] then gave the positions of all non-hydrogen atoms of t-Bu$_4$-1,2-NcFe(t-BuNC)$_2$ and of the disordered solvent molecule. Refinement with isotropic displacement parameters led to an R value of 0.120. After an empirical absorption correction[34] and merging, the R value was 0.109.

For the positions of the methyl-C atoms of the isocyanide ligand, split positions with the multiplicity 0.5 were assigned. Then anisotropic displacement parameters for all atoms, except those of the solvent molecule, were introduced. As the position of the solvent molecule could not be refined satisfactorily, the parameters of the relevant atoms have been fixed in the final refinement. With use of calculated H atom positions in the structure factor

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(29) Keppeler, U.; Ph.D. Thesis, University of Tübingen, 1985.

(30) Fischer, K.; Hanack, M. *Angew. Chem.* **1983**, *95*, 741; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 724; *Angew. Chem. Suppl.* **1983**, 1017.

(31) Boschi, T.; Bontempelli, G.; Mazzochin, G. A. *Inorg. Chim. Acta* **1961**, *37*, 155.

(32) Sheldrick, G. M. SHELXS-86, University of Göttingen.

(33) Frenz, B. A. The ENRAF-NONIUS CAD4-SDP—a Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Determination in *Computing in Crystallography*, 1978. Schenk, H.; Olthof-Hazekamp, R.; von Koningsveld, H.; Bassi, G. C., Eds.; Delft Univ. Press: SDP-PLUS Version 1.1 (1984) and VAXSDP, Version 2.2 (1985).

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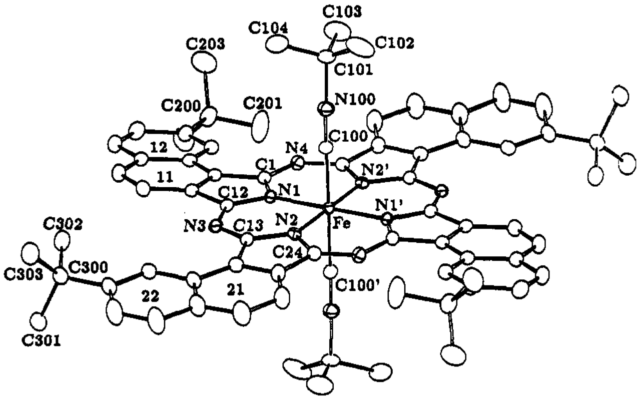

Figure 4. Structure of *t*-Bu$_4$-1,2-NcFe(*t*-BuNC)$_2$. Only one position is shown for the isocyanide ligands.

calculation and refinement of the extinction coefficient, a final *R* value of 0.062 was obtained.

Atomic coordinates and equivalent isotropic displacement parameters U_{eq} are given in the supplementary material.[35]

Figure 4 shows the complex to be a centrosymmetric molecule with the *tert*-butyl isocyanide ligands in axial positions. As expected the ring system is equivalent to isomer **1a** (Figure 1) with the *tert*-butyl substituents in the favored position 7. The arrangement of the inner 16-membered N–C ring and the iron atom is planar; the maximal deviation from the mean plane is 4 pm. The rings 11/12 and 21/22 form dihedral angles of 7° and 6°, respectively, with this plane. This slight deviation from planarity is due to packing effects, as in the structure of 1,2-NcFe(c-HxNC)$_2$.[2h] Steric reasons for the deviation are not visible (Figure 4).

Formal reflection of one of the outer benzene rings with a *tert*-butyl substituent along the Fe–N axis leads to one of the possible isomers with *tert*-butyl groups facing each other. The resulting steric hindrance proves the hypothesis, which was used for the interpretation of the NMR spectra, that the outer benzene rings must twist to form these isomers. The almost linear arrangement of the Fe–N–C–N chain indicates the sp hybridization of the atoms of the isocyano group. The observed bond angle C_{100}–N_{100}–C_{101} = 175.9° and the bond lengths in the isocyano group exclude strong back-bonding from the metal atom to the isocyano ligand. The Fe–C distance of 191.3 pm represents a single bond, while the value of the C–N distance (114.1 pm) represents a triple bond, whereas a strong π-back-bonding would increase the Fe–C bond order and decrease the C–N bond length.

By using methods a and b, the isocyanide complexes of Me$_4$-1,2-NcFe (**14**) yield a mixture of isomers. As pointed out *t*-Bu$_4$-1,2-NcFe (**13**) gives a different mixture of isomers depending on the method of synthesis. This is also the case for Ph$_4$-1,2-NcFe (**15**).

It is difficult to explain the phenomenon that the ratio of isomers depends on the route of synthesis. For this purpose it would be necessary to carry out further mechanistic studies. The following explanations based on known mechanistic theories are therefore only speculative. Theoretically a selection by the isocyanide ligand could occur when R$_4$-1,2-NcFe reacts to form bisaxially coordinated complexes. Because of steric and electronic influences, the ligand might react only with a specific isomer. However, such a selection by the isocyanide ligand can be largely excluded. By the same experimental workup of isocyanide complexes, isomers can be found in one case and not in the other. Furthermore, the mixture of isomers is not changed if different isocyanide ligands are used, e.g., *t*-Bu$_4$-1,2-NcFe(*t*-BuNC)$_2$ and *t*-Bu$_4$-1,2-NcFe(Me$_2$PhNC)$_2$ yield the same ratio of integration for H_1 in the ^1H NMR spectra (Figure 3), in spite of Me$_2$PhNC being more voluminous and having other electronic properties than *t*-BuNC. Hence the selection of isomers must occur during the synthesis of the macrocycle.

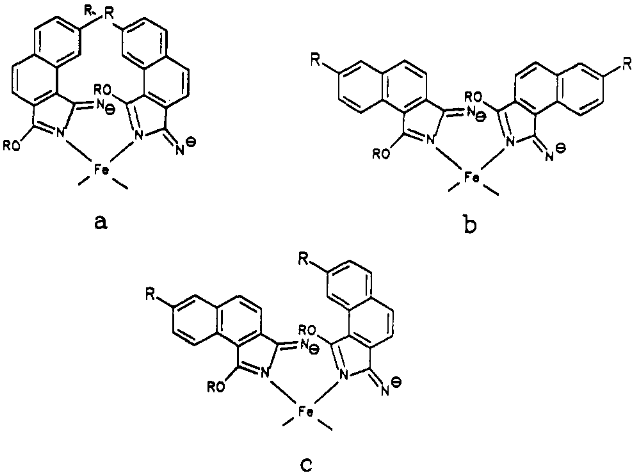

Figure 5. Template effect in method of synthesis a.

Taking a look at the differences in reaction conditions for R$_4$-1,2-NcFe (Table I and Scheme II), it is noticed that temperature and time of reaction are less important than the starting iron compounds and choices of solvent. Hence, thermodynamic or kinetic reaction control is rather improbable, particularly since the last reaction step in the phthalocyanine or naphthalocyanine synthesis is the irreversible reduction to the heteroaromatic 18π electron system.

Therefore we explain the observed differences in the isomer ratio with the lack of occurrence of a template effect. If no template effect exists, i.e., when there is no metal atom involved at the beginning of the formation of the naphthalocyanine system, the dicyanonaphthalene units are able to undergo addition without steric hindrance. The synthesized oligomers cyclize by insertion of the metal atom under reduction in a way that substituents are not directed toward each other, whereby a mixture of isomers is formed.

When applying method b with Fe(ac)$_2$ in hexanol, iron(II) is already coordinated by the acetate ligand and moreover solvated by hexanol, which can act as ligand itself. Therefore the probability of a template effect is small.

Procedure a, however, uses pentacarbonyliron as a metal donating agent, which is immediately decomposed to Fe(0) and CO because of the comparatively high temperature. As solvent 1-chloronaphthalene is used, which is only a weak ligand itself. The possibility that dicyanonaphthalenes or their derivatives are coordinated to iron is very likely and therefore a template effect probable. However, if oligomerization and cyclization occur at the iron atom, the steric hindrance caused by the substituents becomes important. A dimerization of two dicyanonaphthalene units is possible only in the case of b or c, respectively, as shown in Figure 5. A complete cyclization is successful only in case c, because nowhere in case b are two substituents directed toward each other. As the oligomerization of the starting materials is reversible, the oligomers b can still rearrange. Therefore, as a result, only the isomer equivalent to **1a** or **13–15** in Scheme II is

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(35) Fieser, L. F.; Price, C. C. *J. Am. Chem. Soc.* **1936**, *58*, 1839.

Table VII. Conductivity Data σ_{RT} (S/cm) [Pressed Pellet, 10^8 Pa]

compound	σ_{RT} (S/cm)	ref
Me_4-1,2-NcFe (**14**)	3.5×10^{-11}	
t-Bu_4-1,2-NcFe (**13**)	3.0×10^{-12}	
Ph_4-1,2-NcFe (**15**)	$<10^{-12}$	
1,2-NcFe	4.0×10^{-9}	2o
2,3-NcFe	4.0×10^{-5}	4c
PcFe	4.0×10^{-11}	
$[Me_4\text{-1,2-NcFe(dib)}]_n$	1.2×10^{-9}	
$[t\text{-}Bu_4\text{-1,2-NcFe(dib)}]_n$	1.0×10^{-11}	
$[Ph_4\text{-1,2-NcFe(dib)}]_n$	2.0×10^{-11}	
$[\text{1,2-NcFe(dib)}]_n$	6.0×10^{-10}	2v
$[\text{2,3-NcFe(dib)}]_n$	2.0×10^{-3}	4c
$[\text{PcFe(dib)}]_n$	2.0×10^{-5}	2v
$[t\text{-}Bu_4\text{-1,2-NcFe(dib)}I_{1.8}]_n$	1.0×10^{-4}	
$[Ph_4\text{-1,2-NcFe(dib)}I_{1.1}]_n$	3.0×10^{-4}	
$[\text{1,2-NcFe(dib)}I_{1.8}]_n$	4.0×10^{-3}	
$[\text{2,3-NcFe(dib)}I_{0.6}]_n$	1.0×10^{-2}	
$[\text{PcFe(dib)}I_{3.0}]_n$	3.0×10^{-2}	

formed, which has been confirmed experimentally.

The necessary reduction of the tetrameric ring system to give phthalocyanine or naphthalocyanine systems, respectively, can also be explained by the last-mentioned model. Iron(0) present in the template complex can easily transfer two electrons to the surrounding ring system and consequently causes reduction by forming the (naphthalocyaninato)iron(II) system.

Reaction of R_4-1,2-NcFe (R = *t*-Bu, Me, Ph) 13, 14, and 15 with Diisocyanobenzene. As we have pointed out in many examples, bridged compounds $[MacFeL]_n$ can be obtained, if bidentate ligands (e.g., pyz or dib) react with iron macrocycles.[1,2] The reaction of the macrocycles R_4-1,2-NcFe with diisocyanobenzene (dib) is performed in acetone or chloroform as solvent at slightly increased temperature. Thus compounds $[t\text{-}Bu_4\text{-1,2-NcFe(dib)}]_n$, $[Me_4\text{-1,2-NcFe(dib)}]_n$, and $[Ph_4\text{-1,2-NcFe(dib)}]_n$ are obtained. Besides thermogravimetry and elemental analyses (see Experimental Section) they are characterized by IR and UV spectroscopy. $[t\text{-}Bu_4\text{-1,2-NcFe(dib)}]_n$ is obtained from *t*-Bu_4-1,2-NcFe prepared by method a.

Conductivity Measurements. Both tetrasubstituted macrocycles *t*-Bu_4-1,2-NcFe (**13**), Me_4-1,2-NcFe (**14**), and Ph_4-1,2-NcFe (**15**) and compounds bridged by dib are investigated with respect to their conductivity. The conductivity data measured on compressed microcrystalline powders are shown in Table VII. For comparison the data for 1,2-NcFe, 2,3-NcFe, and PcFe are also given in Table VII.

Powder conductivities are strongly influenced by extrinsic parameters such as particle size, intergranular resistance, and purity, etc. The measured values therefore can only be interpreted semiquantitatively. The iron macrocycles **13**, **14**, and **15** all show conductivities in the lower semiconducting region. The decrease of conductivity correlates with the size of substituents in the sequence 1,2-NcFe, Me_4-1,2-NcFe (**14**), Ph_4-1,2-NcFe (**15**), *t*-Bu_4-1,2-NcFe (**13**). In comparison with **13**, **14**, and **15**, the dib-bridged complexes $[t\text{-}Bu_4\text{-1,2-NcFe(dib)}]_n$, $[Me_4\text{-1,2-NcFe(dib)}]_n$, and $[Ph_4\text{-1,2-NcFe(dib)}]_n$ exhibit a smaller increase in conductivity than is normally observed, if one compares the nonbridged macrocycles, e.g., PcFe, with the corresponding bridged systems, e.g., $[\text{PcFe(dib)}]_n$ (see Table VII). The reason for this behavior can be related to the size of the substituents in **13**, **14**, and **15**, which prevents a stacked arrangement of the corresponding bridged compounds. The conductivity of the dib-bridged systems of **13**, **14**, and **15**, however, is still much lower than the conductivity of $[\text{2,3-NcFe(dib)}]_n$. This is explained with the low oxidation potential of 2,3-NcFe leading to doping with air oxygen.[2o,4c]

As we have shown elsewhere,[3] dib-bridged systems $[MacM(dib)]_n$, in general, can be doped with iodine, leading to stoichiometric compounds $[MacM(dib)I_y]_n$. An increase in conductivity of these compounds by several orders of magnitude up to $\sigma_{RT} = 10^{-3}$ to 10^{-2} S/cm is observed.

Doping of $[t\text{-}Bu_4\text{-1,2-NcFe(dib)}]_n$ and $[Ph_4\text{-1,2-NcFe(dib)}]_n$ with iodine also leads to an increase in conductivity (see Table VII), however, the effect is somewhat smaller than that in the other reported cases. This again can be explained by the disorder of the stacked arrangement caused by the larger sized substituents. Thereby a possible band structure is interrupted, leading to a higher gap.

Experimental Section

For the synthesis of 7-substituted 1,2-dicyanonaphthalenes **12a–c**, the method of synthesis elaborated by Fieser and Price[35] has been applied up to 7-*tert*-butyl-3,4-dihydronaphthalene-1,2-dicarboxylic acid anhydride (**8**). Further reaction steps are described for compounds with *tert*-butyl substituents. Synthesis of 7-methyl- (**12b**) or 7-phenyl-1,2-dicyanonaphthalene (**12c**), respectively, was performed by analogous reaction sequences.

The template reactions leading to macrocycles were conducted under inert gas with the exclusion of moisture. If modifications are not mentioned, the commercially available compounds were used as received. The purity of all title compounds was judged to be >95% by spectral data (see supplementary material).

Diethyl 7-*tert*-Butyl-3,4-dihydronaphthalene-1,2-dicarboxylate (9a). To a solution of 7-*tert*-butyl-3,4-dihydronaphthalene-1,2-dicarboxylic acid anhydride (**8a**) (33 g, 0.13 mol) in 300 mL of $CHCl_3$ was added 40 mL of EtOH containing 9 mL of H_2SO_4 (concd). Then the mixture was refluxed on a Dean–Stark apparatus for 3 days. After cooling 150 mL of H_2O was added, the phases were separated, and the organic phase was washed to neutral with water. After drying over Na_2SO_4, $CHCl_3$ was evaporated and the residue was purified by bulb-to-bulb distillation at 160 °C/0.04 mbar, yield, 38 g (89%), as a yellow oil: IR (film) 2963 cm^{-1}, 2905 (CH), 1736, 1713 (CO), 1620, 1367, 1293, 1263, 1225, 1196, 1098, 1043, 1030, 776; ^1H NMR (90 MHz, $CDCl_3$) δ 1.2–1.5 (m), 1.27 (s, 15 H, CH_3, $C(CH_3)_3$), 2.5–3 (m, 4 H, CH_2CH_2), 4.1–4.6 (m, 4 H, OCH_2), 7.1–7.3 (m, 3 H, arom); MS (EI, 70 eV) *m/e* (rel intensity) 330 (M^+, 40), 315 ($M^+ - CH_3$, 100), 284 ($M^+ - C_2H_6O$, 50), 256 (68), 241 (43), 228 (24), 201 (33), 155 (32), 129 (28), 115 (20), 102 (14), 91 (11), 69 (10), 57 (85).

Diethyl 7-*tert*-Butylnaphthalene-1,2-dicarboxylate (10a). Compound **9a** (38 g, 0.115 mol) was added to a solution of 26.1 g (0.115 mol) of dichlorodicyano-*p*-benzoquinone (DDQ) in 300 mL of toluene (absolute) under an N_2 atmosphere. Then the dark-red solution was boiled for 18 h at 80 °C. After cooling, the precipitated hydroquinone was filtered and the solvent was removed. The residue was dissolved in ether and chromatographed on an aluminum oxide column. After removal of ether under reduced pressure, a viscous oil was obtained, which crystallized out in the refrigerator or was distilled in a Kugelrohr apparatus at 150–160 °C/4 × 10^{-2} mbar; yield 32 g (85%) as white crystals, mp 71 °C: IR (KBr) 2963 cm^{-1}, 2871 (CH), 1713 (CO), 1627, 1599, 1576, 1465, 1427, 1366, 1290, 1260, 1202, 1151, 1102, 1035, 852, 813, 774, 745; ^1H NMR (90 MHz, $CDCl_3$) δ 1.1–1.6 (m), 1.38 (s, 15 H, CH_3, $C(CH_3)_3$), 4.2–4.7 (m, 4 H, CH_2CH_2), 7.6–8.0 (m, 5 H, arom); MS (EI, 70 eV), *m/e* (rel intensity) 328 (M^+, 40), 313 (M^+ − 15, 100), 306 (8), 299 (7), 283 (9), 279 (9), 239 (32), 228 (27), 199 (52), 165 (6), 127 (5), 115 (6), 105 (4), 91 (5), 77 (4), 57 (38).

7-*tert*-Butylnaphthalene-1,2-dicarboxylic Acid (11a). Compound **10a** (4 g, 13.3 mmol) was added to a mixture of 50 mL of KOH (10%) and 100 mL of EtOH. Then the mixture was refluxed for 20 h. After cooling, water was added and the ethanol was almost completely eliminated by vacuum. The aqueous solution was slowly acidified with concd HCl, and the precipitated acid was filtered, washed to neutral, and dried in vacuo; yield, 3.3 g (91%); white solid [mp 140 °C dec]: IR (KBr) 3300–2400 cm^{-1} (OH), 2963, 2908 (CH), 1706 (CO), 1558, 1429, 1394, 1364, 1263, 1203, 1158, 1105, 961, 849, 825, 774, 748; ^1H NMR (90 MHz,

$CDCl_3$) δ 7.2–8.0 (m, 5 H, arom); MS (EI, 70 eV) *m/e* (rel intensity) 254 ($M^+ - H_2O$, 20), 239 ($M^+ - CH_3$, 100), 211 (20), 199 (8), 165 (6), 152 (6), 139 (6), 84 (6), 70 (7), 41 (8).

7-*tert*-Butyl-1,2-dicyanonaphthalene (12a). 7-*tert*-Butylnaphthalene-1,2-dicarbonyl Dichloride. Compound **11a** (10 g, 37 mmol) was added in portions to a solution of 12 g (0.1 mol) of $SOCl_2$, 4 drops of DMF, and 80 mL of toluene. Then the mixture was boiled for 3 h at 60–70 °C. After cooling, excess $SOCl_2$ was eliminated by vacuum.

7-*tert*-Butylnaphthalene-1,2-dicarboxamide. The residual toluene solution from the above reaction was slowly added to 150 mL of ether (absolute), saturated with NH_3. Gaseous NH_3 was passed through the stirred mixture during the dropwise addition and then for another hour. The excess NH_3 was allowed to evaporate (hood!), the solvent mixture was removed, and the residue was dried in vacuo.

7-*tert*-Butyl-1,2-dicyanonaphthalene (12a). $POCl_3$ (20 g, 12.16 mL; 0.13 mol) was slowly added to 80 mL of pyridine (absolute) at 0 °C. After the addition, the yellow solid diamide obtained above was added in portions at the same temperature. The mixture was allowed to come to room temperature and was stirred for another 3 h. It was then poured onto ice water, and the precipitated product was filtered, washed, and dried under vacuum.

The filtrate was extracted several times with chloroform. The $CHCl_3$ phases were washed with dilute HCl and then with H_2O to neutral. After drying with Na_2SO_4, the solvent was removed by vacuum and the residue together with the separated solid was dissolved in toluene and purified by column chromatography on silica gel using toluene as eluent. The product was sublimed at 100 °C/0.04 mbar and then recrystallized from *n*-hexane; yield 2.1 g (9 mmol); white crystals (24%, based on 7-*tert*-butylnaphthalene-1,2-dicarboxylic acid), mp 167 °C; IR (KBr) 3073 cm^{-1}, 2965, 2872, 2232, 1622, 1589, 1505, 1479, 1466, 1456, 1398, 1386, 1362, 1321, 1258, 1160, 1106, 857, 851, 614; ^1H NMR (400 MHz, $CDCl_3$) δ 1.44 (s, 1 H, CH_3), 7.65 (d, H (5), J = 8.5 Hz), 7.86 (dd, H (2), J = 8.7 Hz, J = 1.7 Hz), 7.93 (d, H (3), J = 8.7 Hz), 8.12 (d, H (4), J = 8.5 Hz), 8.17 (d, H (1), J = 0.9 Hz); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 120.8 (C-8), 125.8 (C-3), 128.4 (C-5), 129.5 (C-6), 132.1 (C-9), 132.4 (C-10), 133.1 (C-4), 154.1 (C-7); MS (EI, 70 eV) *m/e* (rel intensity) 234 (M^+, 20), 219 (100), 192 (8), 191 (36), 179 (15), 152 (5), 108 (3).

(Tetra-*tert*-butyl-1,2-naphthalocyaninato)iron(II) (*t*-Bu_4-1,2-NcFe) (13). Method a. To a solution of **12a** (600 mg, 2.56 mmol) in 1-chloronaphthalene under an N_2 atmosphere were added 3 drops of DBU. The mixture was heated up to 170 °C, and 0.45 g (0.3 mL; 2.3 mmol) of $Fe(CO)_5$ dissolved in 1-chloronaphthalene was added dropwise and stirred for another 2 h at 190 °C. After cooling, *n*-hexane was added and the precipitate formed was centrifuged. It was washed with MeOH and boiled with 1 N HCl and 1 N NaOH. It was then washed with MeOH and *n*-hexane again and finally dried under vacuum at 100 °C: yield 548 mg (0.54 mmol, 84%), dark-green powder.

Method b. Hexanol (10 mL) and 3 drops of DBU were added to 450 mg (1.92 mmol) of **12a** and 300 mg (1.72 mmol) of iron(II) acetate under an N_2 atmosphere. The mixture was heated to 170 °C and stirred for 4–5 h at this temperature. After cooling, *n*-hexane was added and the precipitate formed was centrifuged. After washing with MeOH and boiling in 1 N HCl and 1 N NaOH, it was washed again with MeOH and *n*-hexane and dried under vacuum at 100 °C: yield 380 mg (79%); IR (KBr) 3057, 2957, 2907, 1624, 1589, 1477, 1462, 1393, 1369, 1261, 1211, 1196, 1128, 1111, 1092, 841, 731; MS (FD, pyridine) *m/e* 992 (M^+); UV (pyridine) 353 nm, 604, 666; CV (pyridine, 0.1 N Bu_4NClO_4) 0.67, −0.97, −1.21, −1.83 [V] vs SCE; ^{57}Fe Mössbauer $\delta = 0.35$ mm/s (rel to Fe); $\Delta E_Q = 2.51$ mm/s.

(Tetramethyl-1,2-naphthalocyaninato)iron(II) (Me_4-1,2-NcFe) (14) was prepared from **12b** according to methods a and b as reported for **13**. **Method a**: yield 77%, dark-green powder. **Method b**: yield 60%. 14: IR (KBr) 1231 cm^{-1}, 1204, 1180, 1127, 1102; MS (70 eV) *m/e* 824 (M^+); UV (pyridine) 354 nm, 606, 668; CV (pyridine, 0.1 N Bu_4NClO_4) 0.65, −0.97, −1.25, −1.85 [V] vs SCE; ^{57}Fe Mössbauer $\delta = 0.36$ mm/s (rel to Fe); $\Delta E_Q = 2.61$ mm/s.

Anal. Calcd for $C_{52}H_{32}FeN_8$: C, 75.7; H, 3.9; N, 13.6. Found: C, 76.0; H, 4.0; N, 13.6.

(Tetraphenylnaphthalocyaninato)iron(II) (Ph_4-1,2-NcFe) (15) was prepared from **12c** according to methods a and b as reported for **13**. **Method a**: yield 83%, dark-green powder. **Method b**: yield 75%. **15**: IR (KBr) 1203, 1129, 1104; MS (FD, pyridine) *m/e* 1072 (M^+); UV (pyridine) 364 nm, 607, 670; CV (pyridine, 0.1 N Bu_4NClO_4) 0.69, −0.94, −1.17, −1.75 [V] vs SCE; ^{57}Fe Mössbauer $\delta = 0.36$ mm/s (rel to Fe); $\Delta E_Q = 2.69$.

Anal. Calcd for $C_{72}H_{40}FeN_8$: C, 80.6; H, 3.8; N, 10.4. Found: C, 80.2; H, 3.9; N, 10.2.

Reaction of R_4-1,2-NcFe 13, 14, and 15 with *t*-BuNC, c-HxNC, BzNC, and Me_2PhNC. **13**, **14**, or **15** (1 mmol) was stirred with a 20-fold excess of the liquid ligand in a vial capped with a septum at 60 °C (solid ligand in smelt or dissolved in $CHCl_3$ as solvent). After 24–48 h the mixture was dissolved in 30 mL of MeOH, and the precipitate was filtered or centrifuged and then washed with MeOH and *n*-hexane. For further purification it was chromatographed on a short silica gel column with $CHCl_3$ as eluent. After evaporating the solvent, the compound was dried under vacuum at 50 °C. Yield of the blue-green powder was 70–85%. R_4-1,2-NcFe$(Me_2PhNC)_2$ was worked up as follows. After evaporation of the solvent and elimination of the excess ligand by sublimation, the crude product was washed with MeOH. After chromatography on silica gel (eluent $CHCl_3$), the pure product was dried in vacuo (60 °C); yield of the blue-green powder 60–80%.

***t*-Bu_4-1,2-NcFe(*t*-BuNC)$_2$:** IR (KBr) 3061 cm^{-1}, 2963, 2960, 2868, 2148, 1624, 1500, 1462, 1369, 1209, 1196, 1128, 1116, 977, 840, 730; ^1H NMR ($CDCl_3$) δ −0.50 (s, 18 H, CH_3), 1.58, 1.94, (2 s, 36 H, CH_3), 7.79–7.93 (H-2), 8.2–8.26 (H-3), 8.30–8.38 (H-4), 9.39–9.55 (H-5), 10.50, 11.28 (H-1); ^{13}C NMR ($CDCl_3$) δ 28.8 (CH_3), 31.7 (CH_3), 35.7 ($C(CH_3)_3$), 55.0 ($C(CH_3)_3$), 118.7 (C-3), 122.0 (C-8), 125.2 (C-6), 128.8 (C-4), 128.6 (C-5), 129.5 (C-9), 132.5 (C-10), 136.4 (C-1), 141.1 (C-2), 147.8 (C-12), 148.9 (C-11), 150.4 (C-7); UV ($CHCl_3$) 354 nm, 602, 662.

General Procedure for the Reaction of R_4-1,2-NcFe 13, 14, and 15 with Diisocyanobenzene. A mixture of 0.1 mmol of **13**, **14**, and **15**, respectively, and 0.6–0.8 mmol of dib was refluxed in 15 mL of $CHCl_3$ for 48 h. The precipitate formed was filtered (in case of [*t*-Bu_4-1,2-NcFe(dib)]$_n$ after addition of *n*-hexane), washed with MeOH, acetone, ether, and *n*-hexane, and dried under vacuum at 50 °C.

[*t*-Bu_4-1,2-NcFe(dib)]$_n$: dark-green powder; 75–90%; IR (KBr), 2097 (NC); UV (Nujol) 252 nm, 357, 383, 620, 682; TG (dissociation range 210–310 °C; T_{max} = 292 °C).

[Me_4-1,2-NcFe(dib)$_n$]: dark-green powder; 75–90%; IR (KBr), 2090 (NC); UV (Nujol) 329 nm, 390, 637, 720; TG (dissociation range 210–330 °C; T_{max} = 287 °C).

[Ph_4-1,2-NcFe(dib)$_n$]: dark-green powder; 75–90%; IR (KBr), 2116 (NC); UV (Nujol) 274 nm, 363, 377, 629, 695; TG (dissociation range 200–380 °C; T_{max} = 251 °C).

General Procedure for Doping with Iodine. A weighed out quantity of the corresponding compound and the appropriate quantity of iodine were triturated in a mortar by adding a few drops of benzene until the benzene was evaporated (caution! hood). This procedure was repeated twice. Then the excess iodine was sublimed out under vacuum for 2 h.

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Supplementary Material Available: IR and ^1H NMR spectra of key substances including the ligand complexes of *t*-Bu_4-1,2-NcFe and tables for the X-ray structure for a pure isomer of *t*-Bu_4-1,2-NcFe(*t*-BuNC)$_2$ (74 pages). Ordering information is given on any current masthead page.