Formation and Fate of Iron–Carbene Complexes in Reactions between a Diazoalkane and Iron–Porphyrins: Relevance to the Mechanism of Formation of N-Substituted Hemes in Cytochrome P-450 Dependent Oxidation of Sydnones

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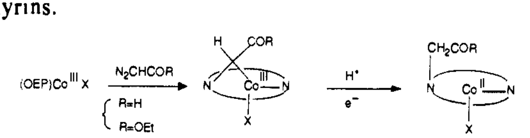
Abstract: Reaction of the diazocompound $PhCH_2CHN_2$ with Fe(TpClPP = tetra-*p*-chlorophenylporphyrin)(Cl) at −30 °C and under argon led to a bridged carbene complex $\overline{Fe^{III}–CH(CH_2Ph)–N}(TpClPP)(Cl)$ (**1**) with a $PhCH_2CH$ moiety inserted between the iron and a pyrrole nitrogen atom. The visible and ^1H NMR spectra of complex **1** were very similar to those of the previously described Fe(III)–porphyrin complex with a vinylidene moiety ($C = CAr_2$) inserted into an Fe–N porphyrin bond, suggesting that **1** was also an intermediate spin ($S = 3/2$) Fe(III) complex. Upon electrochemical and chemical (Zn–Hg) reduction of complex **1**, a diamagnetic $(TpClPP)Fe^{II}(CHCH_2Ph)$ carbene complex was obtained and characterized by visible and ^1H NMR spectroscopy and mass spectrometry. The electrochemical and chemical oxidation of complex **1** led to the $Fe^{II}(NCH{=}CHPhTpClPP)(Cl)$ complex **3** with an E configuration of the double bond in high yields. Treatment of **1** by HCl under anaerobic conditions also led to this *N*-vinylporphyrin complex and to the $Fe^{II}(NCH_2CH_2PhTpClPP)(Cl)$ complex. The formation of complex **1** and its transformation into complex **3** provide a first model for the previously described formation of N-CH=CHPh– heme during the cytochrome P-450 dependent oxidative metabolism of a sydnone derivative which involves $PhCH_2CHN_2$ as a reactive metabolite. Possible mechanisms for the reactions leading from **1** to **3** are discussed and compared to those proposed for the corresponding cytochrome P-450 reactions.

Introduction

It has been shown recently that sydnones acted as suicide substrates of cytochromes P-450 by irreversible alkylation of a pyrrole nitrogen of the heme of this cytochrome.[1] Intermediate formation of diazoalkanes has been shown during cytochrome P-450-dependent oxidation of 3-alkyl-4-methylsydnones, and it has been proposed that the *N*-alkylhemes isolated from the livers of rats treated by these sydnones were derived from reactions between diazoalkanes and the cytochrome P-450 heme.[1] In fact, very little is known about the possible reactions of diazoalkanes with iron- or cobalt–porphyrins. Much more is known about reactions between iron- or cobalt–porphyrins and diazoketones or diazoesters, and the eventual formation of *N*-alkylporphyrins in those reactions. For instance, reaction between Co^{III}(OEP = octaethyl porphyrin) and ethyl diazoacetate[2] or diazoacetaldehyde[3] was found to give (N, Co)-bridged carbene complexes (eq 1). Upon acidic treatment under reducing conditions, protonation of their Co–C bond occurred with the formation of N-substituted porphyrins.



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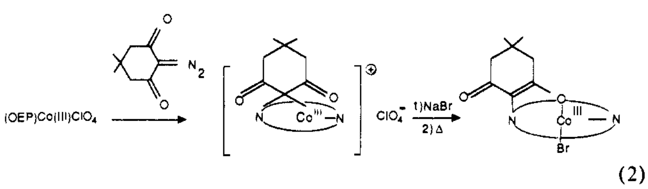
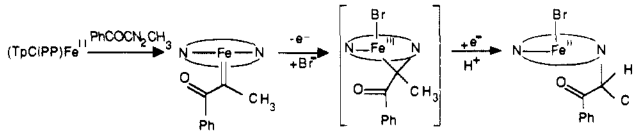
Such a (N,Co)-bridged carbene complex derived from diazodimedone[4] was decomposed by heating with concomitant formation of a $\overline{NC{=}COCo}$ metallacyclic complex (eq 2).



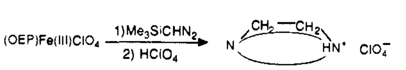
(2)

Recently, reactions between diazoketones and iron–porphyrins were found to eventually lead to N-substituted porphyrins. Diazoacetophenone reacted with iron(II)–tetraphenylporphyrin in CH_3OH to yield the iron(II)–NCH_2COPh–tetraphenylporphyrin complex.[5] No intermediate was detected. On the contrary, reaction between $PhCOCN_2CH_3$ and iron(II)–tetra-*p*-chlorophenylporphyrin led to an α-ketocarbene–iron(II) complex which exhibited a great propensity to undergo a migration of its carbene moiety to a pyrrole nitrogen atom either upon acidic treatment or by oxidation.[6] No (Fe,N)-bridged carbene complexes analogous to the Co complexes of eqs 1 or 2 could be detected, but their intermediate formation was postulated to explain the final formation of *N*-alkylporphyrins (eq 3).



(3)

As far as interactions of iron–porphyrins with diazoalkanes are concerned, only one example was reported showing that an N,-N′-ethanobridged porphyrin was formed via a possible bridged carbene complex, as suggested by UV–visible spectroscopy, upon reaction of $Fe^{III}(OEP)(ClO_4)$ with trimethylsilyldiazomethane (eq 4).[7]



(4)

In order to obtain information on the formation of NCH_2CH_2Ph– and NCH=CHPh–protoporphyrin IX by reaction of cytochrome P-450 with $PhCH_2CHN_2$, an intermediate in 3-[2-phenylethyl]-4-methylsydnone oxidation (eq 5),[1b] we studied the reaction of this diazoalkane with iron–porphyrins and showed that two carbene complexes were formed and could act as pre-

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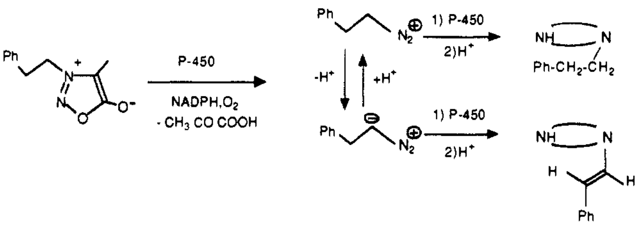
Table I. ^{1}H NMR Characteristics of Complexes **1**, **1′**, **2**, **5**, and **6**

	porphyrin ring		ligand			
			phenyl H			
complex[a]	pyrrole H	phenyl H	ortho	meta	para	non-phenyl H
1	−41.1 (1 H), −39.3 (1 H), −33.1 (1 H), −24.9, −7.7 (1 H), −3.9 (1 H), +28.9 (1 H), +32.2 (1 H)	10.05, 10.54, 11.05, 11.8 (8 H), 7.94, 8.15, 8.38, 8.58 (8 H)	4.35 (1 H), 6.1 (1 H)	7.07 (2 H)	8.75 (1 H)	−1.64 (3 H)
1′ (ref 11)	−40.5 (2 H), −23.9 (2 H), −19.7 (2 H), +25.7 (2 H)	8.0, 9.5, 10.3[b] (6 H), 7.9, 8.1, 8.2, 10.2 (8 H), 8.1 (4 H)	0 (2 H)[b]	2.6 (2 H), 4.9 (2 H)		
2	8.35 (8 H, s)	7.5, 7.81 (AB system, 8 H, 5), 7.46, 7.62 (AB system, 8 H, 5)	4.5 (2 H, d, 7)	6.32 (2 H, t, 7)	6.37 (1 H, t, 7)	−1.4 (2 H, d, 7) +16 (1 H, t, 7)
5	8.82, 8.89 (AB system, 4 H, 4.5), 8.33 (2 H, s), 8.8 (2 H, s)	8.64 (2 H), 7.65 → 8.3 (14 H, m)	4.45 (2 H, d, 7.5)	6.15 (2 H, t, 7.5)	6.35 (1 H, t, 7.5)	−1.13 (1 H, d, 15) +2.05 (1 H, d, 15)
6	8.84, 8.93 (AB system, 4 H, 4.5), 8.18 (2 H, s), 8.81 (2 H, s)	7.6 → 8.4 (16 H, m)	5.49 (2 H, d, 7.5)	6.63 (2 H, t, 7.5)	6.76 (1 H, t, 7.5)	−4.40 (2 H, t, 7.5) +0.35 (2 H, t, 7.5)

[a] ^{1}H NMR of complexes **1** and **2** in CD_2Cl_2, respectively, at −30 °C and −10 °C; ^{1}H NMR of complexes **1′**, **5**, and **6** at 20 °C in $CDCl_3$; δ (ppm/Me_4Si); *J* in Hz; d, t, m abbreviations used for doublet, triplet, and multiplet. [b] 2 H ortho of the phenyl groups of the porphyrin and 2 H ortho of the phenyl groups of the ligand were not assigned.[11]

cursors of the NCH_2CH_2Ph– and NCH═CHPh–porphyrins isolated as end products.



(5)

Results

Reaction of an Excess of the diazoalkane $PhCH_2CHN_2$ with Fe^{III} (TpClPP)(Cl). Reaction of an excess of the diazoalkane $PhCH_2CHN_2$[8] with Fe(TpClPP)(Cl) ($PhCH_2CHN_2$:Fe = 45), in CH_2Cl_2 at room temperature under aerobic conditions, led to a mixture characterized by a UV-visible spectrum exhibiting a Soret peak at 434 nm with two shoulders at 453 and 470 nm and one broad band at 646 nm. After addition of a few drops of 1% HCl in CH_2Cl_2, this mixture gave a green product with a UV-visible spectrum (453, 470 sh, 570, 628, 684 nm) characteristic of an iron(II)-*N*-alkylporphyrin.[9] After acidic demetalation and treatment by $Zn(OAc)_2$, the corresponding Zn(II) complex was purified by column chromatography. The visible and ^{1}H NMR spectra of this complex were characteristic of a Zn–N-substituted porphyrin, the signals of the protons of the *N*-alkyl chain indicating a NCH═CHPh structure with an *E* configuration of the double bond as shown by the large coupling constant (*J* = 15 Hz) between the vinylic protons (Table I). The deduced Zn(NCH═CHPhTpClPP)(Cl) structure **5** was also found in complete agreement with the elemental analysis and mass spectrum of the complex.

Formation of Complex 1 by Reaction of $PhCH_2CHN_2$ and Fe(III)(TpClPP)(Cl). In order to get data on possible intermediate complexes in the formation of the *N*-vinylporphyrin complex **5**, reaction between $PhCH_2CHN_2$ and Fe^{III}(TpClPP)(Cl) was performed under milder conditions (−30 °C under argon, diazo:Fe = 5). Upon addition of a deaerated pentane solution of $PhCH_2CHN_2$ to a deaerated CH_2Cl_2 solution of Fe(TpClPP)(Cl) at −30 °C, the solution turned instantaneously green because of the appearance of a complex characterized by a Soret peak at 433 nm and a broad band around 650 nm. After partial evaporation of the solvents, this complex, **1** (Figure 1), was precipitated by pentane addition at −30 °C. The peculiar visible spectrum of complex **1** was very similar to that of a bridged carbene complex

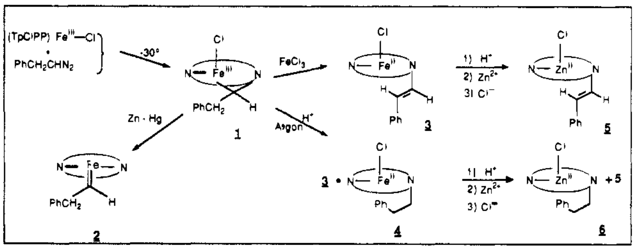


Figure 1. Formation and various observed reactions of complex **1** (−30 °C, CH_2Cl_2, anaerobic conditions).

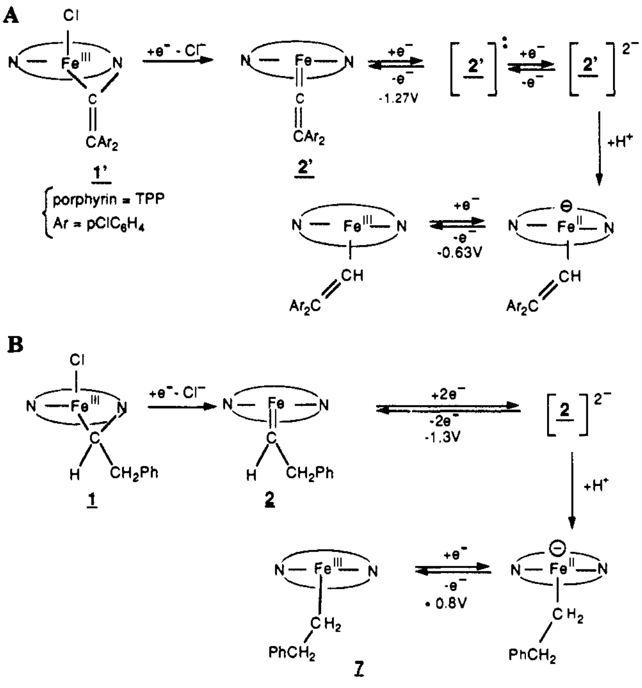


Figure 2. Mechanisms of reduction of complexes **1′** (A) and **1** (B). For **1′** from previously reported electrochemical results (in DMF).[15] For **1** from chemical and electrochemical results (in CH_2Cl_2).

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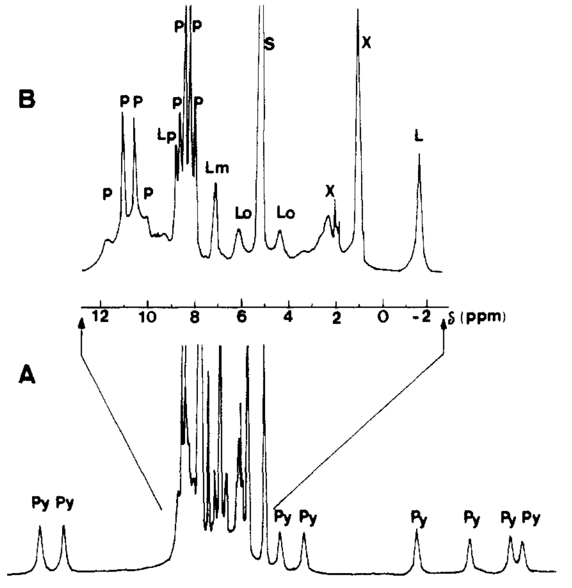

Figure 3. 250-MHz ^{1}H NMR spectrum of the bridged carbene complex **1** in CD_2Cl_2 at -30 °C (δ in ppm from Me_4Si): (A) -35 to +45 ppm region and (B) expanded region from -2 to +12 ppm. Peaks are labeled as followed: S residual undeuterated solvent; X impurities between 0 and 2 ppm; Lo, Lm, and Lp, respectively, for the ortho, meta, and para phenyl protons of the ligand; L for $CHCH_2$ of the carbene ligand; P and Py, respectively, for the phenyl and pyrrole protons of the porphyrin ring.

1′ (Figure 2A) with a vinylidene group inserted into a Fe–N bond of Fe(TPP = tetraphenylporphyrin)(Cl), which was previously reported and completely characterized.[10,11] In fact the structure of complex **1**[12] deriving formally from the insertion of the $PhCH_2CH$ carbene moiety into a Fe–N bond was also deduced from a comparison of its ^{1}H NMR spectrum (Figure 3) with that of complex **1′**.[10,11] Both complexes were paramagnetic with resonances from -40 to +30 ppm. The pyrrole protons of **1** were assigned by comparison with the spectrum of complex **1**-d_8 prepared from tetra-*p*-chlorophenylporphyrin selectively deuterated on the pyrrole rings. The pyrrole protons of complex **1′** were found at -40.5, -23.9, -19.7, and +25.7 ppm.[11] Those of complex **1** were similarly located, but, because of the lower symmetry of **1** compared to **1′**, appeared as eight signals at -41.1, -39.3, -33.1, -24.9, -7.7, -3.9, 28.9, and 32.2 ppm (Table I).

The phenyl protons of the porphyrin ring appeared as two systems of four peaks (8 H each) centered around 8 and 10 ppm.

The proton resonances of the $PhCH_2CH$ moiety were assigned through both their chemical shifts and their intensity ratios. The phenyl group being at three bonds from the iron in both complexes **1** and **1′**, the phenyl protons of **1** were assigned by comparison with the chemical shifts of the same protons in complex **1′** at 8.75 and 7.07 ppm for the para and meta protons and at 6.1 and 4.35 ppm for the ortho protons. Finally, the last signal, at -1.64 ppm corresponding to 3 H was attributed to the $-CHCH_2$ protons (Table I).

Reactivity of the Bridged Carbene Complex 1. Acidic Treatment. Under anaerobic conditions, addition at -30 °C of a few drops of an acidic CH_2Cl_2 solution (1% HCl) to a CH_2Cl_2 solution of the previously purified complex **1** led to its complete transformation into iron(II)-*N*-alkylporphyrins. After acidic demetalation and Zn(II) insertion as described previously, the ^{1}H NMR study of the corresponding complexes showed that they were a 70/30 mixture of the two zinc-*N*-alkylporphyrins Zn(NRTpClPP)(Cl) with R = *trans*-CH=CHPh, **5**, and R = CH_2CH_2Ph, **6** (Figure 1). The structure of complex **6** was established by ^{1}H NMR spectroscopy (Table I) and mass spectrometry.

Table II. Characteristic Electrochemical Potentials (in V vs SCE) of the Iron–Carbene Complexes **1** and **2** and of the Iron(III) σ Complexes **7** and **8**

complex[a]	reduction potential[b]	oxidation potential[b]
1	$E_{pc} = -0.6$	$E_{pa} = +0.53$
2	$E° = -1.32$	$E_{pa} = +0.55$
7	$E° = -0.8$	$E° = +0.51$
8	$E° = -0.6$	$E_{pa} = +0.7$ $E_{pc} = +0.53$

[a] Values determined at -15 °C for the two iron–carbene complexes **1** and **2** and at 20 °C for the iron σ-complexes **7** and **8**. [b] $E°$ was referred to the half wave potential of reversible processes, while for irreversible processes E_{pa} and E_{pc} were referred, respectively, to potentials of the anodic and cathodic peaks at a sweep rate of 200 mV/s.

Oxidation. Oxidation of complex **1** at -30 °C under argon by a few equivalents of $FeCl_3$ in CH_3CN gave a quantitative yield of an iron(II)-*N*-alkylporphyrin which after acidic demetalation and Zn(II) insertion led quantitatively to the Zn(NCH=CHPhTpClPP)(Cl) complex **5** (Figure 1). The formation of complex **3** in the above described reaction of excess $PhCH_2CHN_2$ with Fe(TpClPP)(Cl) followed by HCl treatment should correspond to an oxidation of complex **1**, formed in this reaction, by O_2 in the presence of H^+.

Reduction: Formation of the Carbene Complex 2. Complex **1** was reduced under argon in CH_2Cl_2 at -30 °C by Zn/Hg amalgam. The green solution turned rapidly red exhibiting a new UV-visible spectrum (413, 519, 547 (sh) nm). The corresponding complex, which was only stable in the absence of O_2, was purified by precipitation into pentane. Its visible spectrum and the porphyrin signals of its ^{1}H NMR spectrum were almost identical with those of other previously described diamagnetic porphyrin-iron(II)-carbene complexes[13] with a sharp singlet at 8.35 ppm for the pyrrole protons (Table I). The ^{1}H NMR signals of the iron axial ligand showed the presence of the $PhCH_2CH$ carbene with two triplets and one doublet between 4 and 7 ppm as expected for the phenyl protons and one doublet at -1.4 ppm for the CH_2 benzylic protons. The triplet observed at 16 ppm was assigned to the carbene CH proton, this chemical shift being in the range of those previously reported for such porphyrin-metal=CHR complexes.[14] For instance the carbene proton of (TPP)Fe=CHSPh[14a] and (TPP)Ru=CHR (R = CH_3 or COOEt)[14b] was found around 13 ppm, while in the case of (TPP)Ru=$CHSi(CH_3)_3$[14c] it was around 19 ppm. The (TpClPP)Fe=$CHCH_2Ph$ structure clearly demonstrated by the visible and ^{1}H NMR spectra of complex **2** (Figure 1) was completely supported by its mass spectrum.

Electrochemical Studies on Complexes 1 and 2 (Table II). The reduction of the bridged carbene complex **1** into the iron(II)-carbene complex **2** has only one precedent in the iron-porphyrin chemistry: the reduction of the bridged vinylidene carbene complex **1′** into the iron(II)-vinylidenecarbene complex **2′**. The redox behavior of complexes **1′** and **2′** was previously studied,[15] and the

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(11) (a) Latos-Grazynski, L.; Cheng, R. J.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1981**, *103*, 4270-4272. (b) Balch, A. L.; Cheng, R. J.; La Mar, G. N.; Latos-Grazynski, L. *Inorg. Chem.* **1985**, *24*, 2651-2656.

(12) Complex **1** was relatively unstable, leading slowly to an iron(II)-*N*-alkylporphyrin by increasing the temperature. At low temperature under argon, in the presence of an excess of $PhCH_2CHN_2$, the green solution of complex **1** turned red exhibiting a new UV-visible spectrum (λ_{max} 411, 517, 544 (sh) nm). Oxidation of the red solution by a few equivalents of $FeCl_3$ in CH_3CN led to an iron(II)-*N*-alkylporphyrin. ^{1}H NMR analysis of the corresponding zinc N-alkylated derivative showed that the *N*-alkyl chain had the NCH=CHPh structure of **5**. Complete purification of complex **1** was very difficult because of its instability and also because of the difficulties in purifying the starting diazo compound which had to be used directly as a pentane solution obtained after KOH treatment of the nitrosoamine precursor.[8b]

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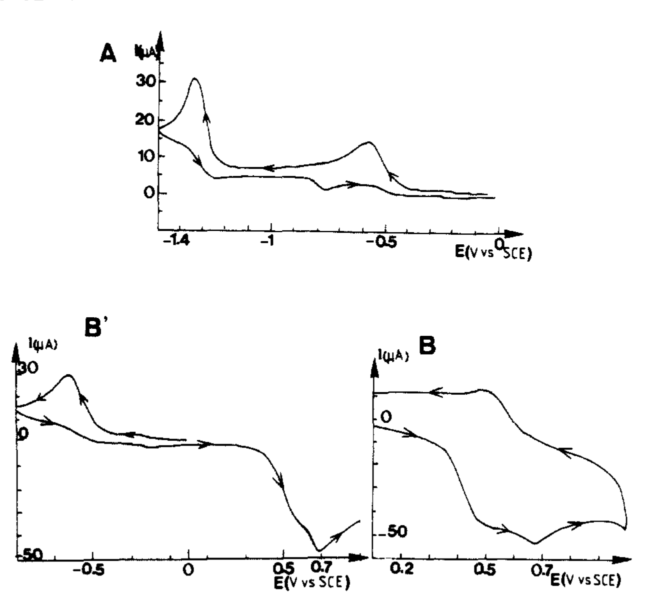

Figure 4. Cyclic voltammograms of the bridged carbene complex **1** (1 mM in CH_2Cl_2 at −15 °C, 0.2 M NBu_4BF_4, sweep rate 200 mV/s): (A) in reduction, potential scanning, 0 → −1.5 → 0 V; (B) in oxidation 0 → 1 → 0 V; and (B′) first in reduction then in oxidation 0 → −0.9 → +0.9 V.

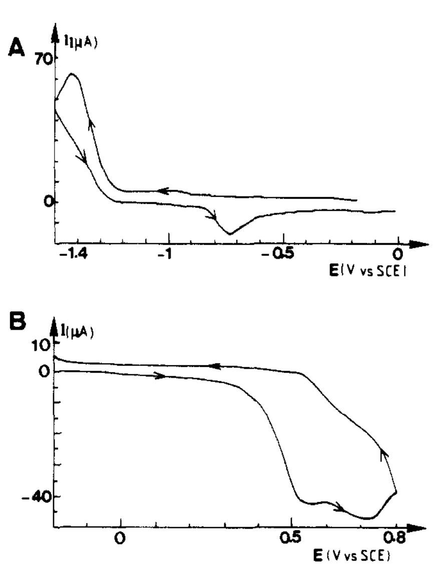

Figure 5. Cyclic voltammograms of the carbene complex **2** (1 mM in CH_2Cl_2 at −15 °C, 0.2 M NBu_4BF_4, 200 mV/s): (A) in reduction, potential scanning, 0 → −1.5 → 0 V and (B) in oxidation, −0.2 → +0.8 → −0.2 V.

results are schematically shown in Figure 2A. An electrochemical study of complexes **1** and **2** was performed to compare their redox properties to those of **1′** and **2′**.

All electrochemical studies were performed in CH_2Cl_2 with NBu_4BF_4 or NBu_4ClO_4 as supporting electrolytes and at −15 °C because of the relative instability of complex **1** versus temperature.[12]

Electrochemical Reduction of Complexes 1 and 2. As shown by cyclic voltammetry, complex **1** was reduced in two successive steps: first a one-electron irreversible reduction at −0.6 V and second a two-electron reduction at −1.35 V (Figure 4A). Electrolysis at −0.8 V provided a red complex exhibiting a UV–visible spectrum and an electrochemical behavior identical with those of complex **2**. In the same solvent (CH_2Cl_2) complex **1′** exhibited an almost identical type of reductive cyclic voltammetry with first a one-electron reduction at −0.65 V and second a two-electron reduction at −1.4 V with two small reoxidation peaks at −1.22 and −0.7 V.

Reductive cyclic voltammetry of complex **2** gave the reduction peak, already observed in the case of **1**, at −1.4 V, giving back in oxidation two small peaks at −1.25 and −0.75 V (Figure 5A). An oxidative cyclic voltammetry run after microelectrolysis at −1.4 V showed that the reoxidation at −0.75 V was reversible ($E°$ = −0.8 V). This suggests that complex **2** was reduced at −1.4 V with formation of the corresponding two-electron reduction product $[2]^{2-}$ (dianion of **2**) which could either be oxidized back to complex **2** at −1.25 V or, after protonation of the carbenic carbon, could lead to the σ-alkyl $Fe^{II}CH_2CH_2Ph$ complex (Figure 2B) which was reversibly reoxidized to the Fe^{III}–σ-alkyl complex **7** at −0.75 V.

The only difference between the results obtained for reduction of **2′** (or **2**) in CH_2Cl_2 and those previously described for the reduction of **2′** in DMF[15] was the formation of $[2']^{2-}$ occurring in a single two-electron step (as in Figure 2B) instead of two successive one-electron steps (Figure 2A).

Preparation and Electrochemistry of the σ-Complexes (TpClPP)$Fe^{III}CH_2CH_2Ph$ (7) and (TpClPP)$Fe^{III}CH{=}CHPh$ (8). We have prepared the σ-alkyl complex **7**, which appeared to be formed upon electrochemical reduction of complex **2** and the σ-vinyl complex **8**, which could be a possible intermediate in the formation of the *N*-vinylporphyrin obtained upon reaction of Fe^{III}(TpClPP)(Cl) with $PhCH_2CHN_2$, in order to compare their electrochemical behavior to those of complexes **1** and **2**.

These two complexes were prepared by reaction of the corresponding Grignard reagents $PhCH_2CH_2MgBr$ and $PhCH{=}CHMgBr$ with the cationic porphyrin [Fe(TpClPP)][CF_3SO_3] in THF, according to previously published procedures.[16] These complexes identified by their typical visible spectra were precipitated in pentane and used without further purification for the electrochemical studies. In reductive cyclic voltammetry, complex **7** exhibited a reversible reaction leading to the corresponding iron(II)–σ-alkyl complex at −0.8 V, a potential identical with that found for the complex obtained after reduction of **2** at −1.4 V (see above). Reversible reduction of complex **8** occurred at −0.6 V (Table II). These results were in agreement with those previously reported for tetraarylporphyrin–iron(III)–σ-alkyl[17] or -σ-vinyl[18] complexes. Complex **7** led to a quasi-reversible oxidation at +0.51 V and complex **8** to an irreversible oxidation at E_{pa} = +0.7 V (sweep rate 200 mV/s) (Table II). The same kind of oxidation, at similar potentials, was previously reported for tetraaryl–iron(III)–σ-alkyl[17] or -σ-vinyl[18] complexes. It corresponded to an irreversible oxidation of the metal to the iron(IV) state followed by migration of the σ-ligand to a pyrrole nitrogen. Accordingly, the quasi-reversible oxidation of **7** at +0.51 V became completely reversible by decreasing the temperature at −40 °C, as previously found for the oxidation of the (TPP)Fe^{III}Ph complex.[19] Moreover, electrolysis of complex **7** at +0.6 V and −40 °C allowed us to prepare in a 20% yield the *N*-alkyl derivative **4** which was characterized as its zinc derivative by mass spectrometry and UV-visible and ^1H NMR spectroscopy (Table I).

Electrochemical Oxidation of Complexes 1 and 2. Complexes **1** and **2** were oxidized by a two- and three-electron process involving two waves respectively at 0.53 and 0.68 V for **1** (Figure 4B) and at 0.55 and 0.75 V for **2** (Figure 5B), the last two waves at 0.68 and 0.75 V giving back a small reduction peak around 0.5 V. Electrolysis of complex **2** at 1 V and 0 °C provided an iron(II)-*N*-alkylporphyrin in a 50% yield as estimated by visible spectroscopy. Structure **3** was demonstrated for this iron(II)–*N*-alkylporphyrin after acidic demetalation, Zn(II) insertion, and ^1H NMR study of the final Zn(II) complex.

Although the reduction of complexes **1** and **2** was found very similar to that previously reported for complexes **1′**[10a] and **2′**,[15]

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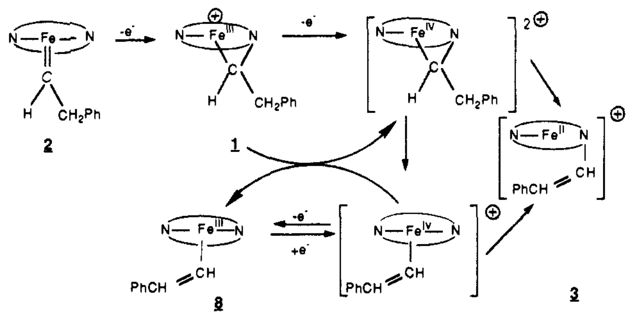

Figure 6. Mechanisms proposed for the oxidation of complexes **1** and **2** into the unsaturated iron(II)-*N*-alkylporphyrin **3** (from the electrochemical results).

with the passage from **1** (or **1′**) to **2** (or **2′**), and the final formation of a σ-alkyl-Fe(II) complex by two-electron reduction and protonation of **2** (Figure 2A,B), their oxidation appeared more complex. In fact, in the case of **1′** and **2′**, the only reported data concerned the one-electron chemical oxidation of **2′** into **1′**[10a] and the chemical oxidation of **1′** into a bridged *N,N′*-vinylidene porphyrin.[20] The oxidative cyclic voltammograms of **1** and **2** were very similar with two peaks around 0.5 and 0.7 V, suggesting that, at 0.5 V, the oxidation of complex **2** into **1** was followed by the same oxidation reactions that occurred on complex **1**. The system of the anodic peak at +0.7 V giving back to the small cathodic peak at 0.5 V was nearly identical with that observed during the irreversible oxidation of the σ-vinyl-iron(III) complex **8**. This suggests that a σ iron-CH=CHPh complex is involved in the electrochemical oxidation of complex **1** and **2**.[21]

A likely mechanism for the formation of such a σ-vinyl complex would be a one-electron oxidation of complex **1** followed by the loss of a β-proton and formation of a σ Fe^{IV}-CH=CHPh complex (Figure 6). This complex cannot exist at 0.5 V in the iron(IV) state (see Table II) and should be instantaneously reduced to the iron(III) σ-complex **8** and further reoxidized at 0.68 V. In fact, it is likely that complex **1** was oxidized not only at the electrode surface but also by the intermediate iron(IV)-σ-vinyl complex in a reproportionation reaction (Figure 6). It was probably why the peak at 0.53 V appeared in some experiments as a more or less well-defined shoulder of the peak at 0.68 V. Then, the σ Fe^{IV}CH=CHPh complex should lead to the iron(II)-*N*-vinylporphyrin **3** by migration of the σ-vinyl group from iron to a pyrrole nitrogen, a well-known reaction of iron(IV)-σ-vinyl complexes.[19,22] Another way of formation of the iron(II)-*N*-vinylporphyrin **3** could be a direct conversion of the Fe(IV)-bridged carbene complex into **3**, by elimination of a β-hydrogen and cleavage of the Fe-C bond (Figure 7). Whatever its way of formation, complex **3** was rapidly oxidized to the corresponding Fe(III) complex since oxidation of iron(II)-*N*-alkylporphyrins associated to ClO_4^- or BF_4^- counteranions occurred at 0.06 V.[19]

The very different behavior of the bridged carbene complexes **1** and **1′** after one-electron oxidation is due to the presence of hydrogens in the β-position relative to the iron only in complex **1**. Similarly, the (Co,N)-bridged carbene complex isolated at -50 °C from reaction of Co^{III}(TPP)(Cl) with ethyl diazopropionate was quantitatively transformed at 20 °C into the σ-vinyl complex $\text{Co}^{III}\text{C(COOEt)=CH}_2$.[2b] Elimination of one of the two β-hydrogens as a proton in complex **1** should lead either directly to the Fe(II)-*N*-vinylporphyrin **3** (mechanism a of Figure 7) or to the σ-vinyl-Fe(IV) complex which is expected to give **3** upon migration of its σ-vinyl ligand to a pyrrole nitrogen atom (mechanism b of Figure 7). The *E* configuration of the double bond of the isolated *N*-vinylporphyrin **5** is in complete agreement with these two mechanisms. Thus, if one admits that the two bonds (C-H and either C-Fe or C-N) broken during the reaction are antiperiplanar, the preferred conformations leading to the *E* isomer are much more stable than that leading to the *Z* isomer which forces the phenyl group of the PhCH_2CH ligand to strongly interact with the porphyrin ring. Therefore, the *N*-vinylporphyrin formed by mechanism a of Figure 7 as well as the Fe(IV)-σ-vinyl complex formed by mechanism b of Figure 7 must have an *E* configuration of their double bond. As it has been shown that the migration of the σ-vinyl ligand of a Fe(IV)-porphyrin from the iron to a pyrrole nitrogen atom occurs with retention of configuration of the double bond,[23] formation of **3** by mechanism b of Figure 7 must also give an *E* configuration of the double bond.

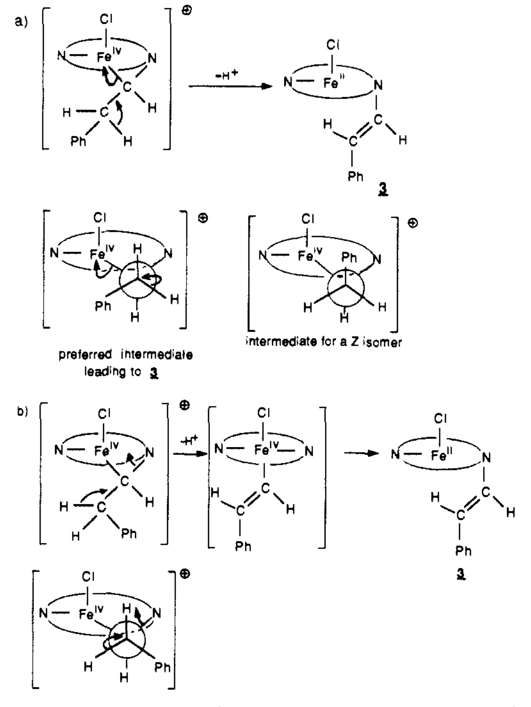

Figure 7. Possible mechanisms for the stereoselective formation of **3** upon one-electron oxidation of **1**.

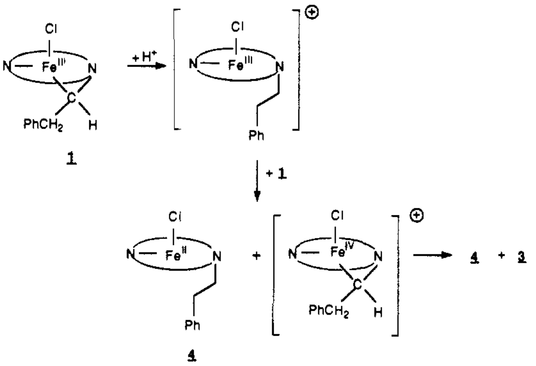

Figure 8. Possible mechanism for the formation of the two N-substituted porphyrins **3** and **4** upon anaerobic acidic treatment of **1**.

Conclusion

The aforementioned results show that the reaction of $\text{PhCH}_2\text{CHN}_2$ with Fe^{III}(TpClPP)(Cl) under controlled conditions (-30 °C under argon) leads to complex **1** which is the first isolated bridged porphyrin-Fe(III)-carbene complex with a $\overline{\text{Fe}^{III}\text{CRR}'\text{N}}$ structure. Complex **1** exhibits visible and ^{1}H NMR characteristics very similar to those of the previously reported bridged vinylidene carbene complex **1′**, suggesting that **1**, as **1′**,[24] is an intermediate

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[21] It is noteworthy that the σ-vinyl complex **8** was not already present in the samples of complex **1** used in this study, since, in the voltammogram of complex **1**, reduction at -0.6 V was found irreversible with no appearance of the reoxidation peak observed in the reversible reduction of the σ-vinyl complex **8** (Figure 4B′).

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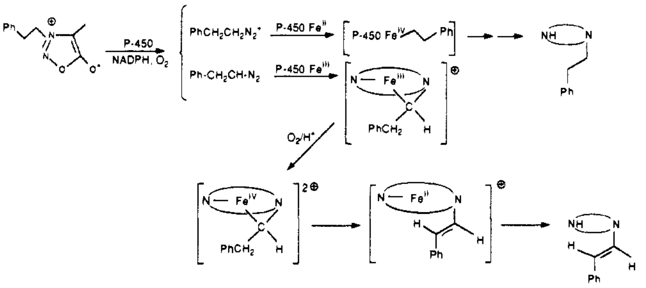

Figure 9. Tentative mechanisms for the formation of N-substituted hemes upon metabolism of a sydnone (after ref 1b and this work).

spin ($S = 3/2$) Fe(III) complex. It is a reactive complex which leads to the carbene complex **2** by reduction, to the Fe(II)–*N*-vinylporphyrin complex **3** by electrochemical or chemical ($FeCl_3$ or $H^+ + O_2$) oxidation, and to a mixture of **3** and of the Fe(II)–NCH_2CH_2Ph–porphyrin complex **4** upon HCl treatment. Possible mechanisms for the formation of **3** upon oxidation of **1** have been discussed (Figure 7). The formation of **3** in addition to **4** upon treatment of **1** by HCl under anaerobic conditions is more surprising. It is possible that the $Fe^{III}NCH_2CH_2Ph$–porphyrin complex formed upon acidic cleavage of the Fe–C bond of complex **1** is able to oxidize complex **1** to the corresponding Fe(IV)-bridged carbene complex which leads to the Fe(II)–*N*-vinylporphyrin **3** by previously discussed mechanisms (Figure 8).

Coming back to the formation of N-substituted hemes upon oxidative metabolism of 3-phenethyl-4-methylsydnone, it has been clearly shown that the NCH_2CH_2Ph–protoporphyrin IX was derived from reaction between cytochrome P-450 and the diazonium salt $PhCH_2CH_2N_2^+$, whereas the $NCH{=}CHPh$–protoporphyrin IX was derived from reaction between cytochrome P-450 and the diazo $PhCH_2CHN_2$.[1b] Our data provide the first model system clearly confirming the intermediate formation of a bridged carbene complex analogous to **1**, upon reaction of $PhCH_2CHN_2$ with P-450–Fe(III), which was proposed previously.[1b] They indicate a mechanism for its transformation into a $Fe^{II}NCH{=}CHPh$–porphyrin complex by oxidation (presumably by O_2 and H^+) and an explanation for the *E* stereochemistry of the double bond of the isolated *N*-vinylheme (Figure 9). Finally, they suggest a general mechanism for the formation of N-substituted porphyrins upon reaction of iron(III)–porphyrins and diazo compounds $RR'CN_2$. These reactions could involve as a first common step the formation of a bridged Fe(III)–carbene complex resulting from the insertion of the RR′C carbene moiety into a Fe–N bond of the starting iron(III) complex. As a function of R and R′, this complex could lead either to a NCHRR′–porphyrin by simple protonation, as in the case of $PhCOCHN_2$[5] or $PhCOCN_2CH_3$[6] where the eventual formation of a NCHR-COPh–porphyrin was observed, or to a *N*-vinylporphyrin after oxidation in the medium, when a β-hydrogen is present in the diazo compounds, as observed in this study.

Experimental Section

UV–visible spectra were recorded by using an Aminco DW2 or a Varian CARY 210 spectrophotometer. Mass spectra were obtained on a VG 70-250 double focussing instrument equipped with a fast atom bombardment gun operating with Xenon. The matrix used was thioglycerol. ^1H NMR spectra were recorded on a Brucker WM 250 spectrometer operating at 250 MHz (sweep width 6000 or 25 000 Hz, 128 or 1024 scans).

Materials. $TpClPPH_2$ was synthesized according to the Adler's method,[25] made chlorin free by Smith's procedure,[26] and metalated by $FeCl_2{\cdot}4H_2O$ in dimethylformamide.[27] The diazo compound $PhCH_2CHN_2$ was prepared by heating at pentane-refluxing temperature a stirred mixture of pentane and a diethyleneglycol solution of potassium hydroxide and *N*-[[[(*N*-nitrosophenyl)ethyl]amino]methyl]benzamide, $PhCONHCH_2N(NO)CH_2CH_2Ph$ (KOH:nitrosoamine = 20),[8b] obtained from the corresponding *N*-[[(phenylethyl)amino]methyl]benzamide.[8a] The pentane solution of the diazo compound was titrated by reaction of an aliquot of this solution with an excess of acetic acid in diethyl ether.[28] The bromide derivatives $PhCH_2CH_2Br$ and $PhCH{=}CHBr$ (*E*:*Z* 85/15) were commercially available from Aldrich.

Preparation of the Bridged Iron–Carbene Complex 1. Five equivalents of $PhCH_2CHN_2$ in pentane was added to a deaerated CH_2Cl_2 solution of Fe(TpClPP)(Cl) (50 mg/30 mL) maintained under stirring at −30 °C. The solution turned rapidly green-brown exhibiting a UV–visible spectrum with three bands at 430, 484 (sh), and 650 nm. After concentration of the solution by evaporation of the solvent at −30 °C under vacuum (0.2 mmHg), complex **1** was precipitated by addition of a pentane solution at −30 °C. The green powder thus obtained was analyzed by ^1H NMR after dissolution in deaerated CD_2Cl_2 at −30 °C (Table I).

Preparation of the Iron–Carbene Complex 2. A CH_2Cl_2 solution of the previously prepared complex **1** (50 mg/30 mL) was reduced under argon at −30 °C, by using 1 mL of zinc–amalgam as reducing agent. Under stirring, the solution turned red instantaneously exhibiting the characteristic visible spectrum of a porphyrin–iron–carbene complex (411, 517, 544 (sh) nm). The red solution was then filtered into a schlenk tube maintained under argon and concentrated under vacuum. After precipitation by addition of pentane under argon, complex **2** was directly analyzed by ^1H NMR in deaerated CD_2Cl_2 (Table I) and by mass spectrometry: mass spectrum 910 (10) M^+, 806 (100) Fe(TpClPP).

Oxidation of Complex 1 by $FeCl_3$. Three to four equivalents of $FeCl_3$ dissolved in deaerated CH_3CN (0.05 M; 80 mg/10 mL) was added dropwise to a deaerated CH_2Cl_2 solution of complex **1** (10^{-3} M; 50 mg/50 mL), at −30 °C. The green-brown solution of complex **1** turned green in a few minutes exhibiting the visible spectrum of an iron(II)–*N*-alkylporphyrin (453, 470, 570, 630, 686 nm). The iron(II) derivative was demetalated by addition of a few drops of concentrated HCl, leading to the corresponding cationic *N*-alkylporphyrin (λ_{max} 459, 694 nm). The CH_2Cl_2 layer was then washed with water, dried over Na_2SO_4, and filtered. The free base (λ_{max} 436, 532, 574, 618, 682 nm) was metalated by addition of 20 mg of $Zn(OCOCH_3)_2$ dissolved in 5 mL of MeOH (2.5 equiv relative to **1**). The CH_2Cl_2 solution of the Zn(II)–*N*-alkylporphyrin was then washed with water and with a saturated NaCl aqueous solution, dried over Na_2SO_4, and filtered. After evaporation of the solvent, the zinc complex **5** was precipitated from CH_2Cl_2 into pentane, purified by column chromatography (silica gel, 35–70 μm, 60A, Amincon, elution with CH_2Cl_2/CH_3COOEt, 90/10), and then lyophilized in benzene under high vacuum. UV–visible spectrum of **5**: λ_{max} (log ε) 452 (5.15), 562 (4.54), 614 (4.7), 662 (4.47); mass spectrum 955 (60) (M + 1), 919 (100) (M − Cl), 814 (30) [Zn(TpClPP) − 1]. Elemental analysis of complex **5** $Zn(NCHCHPhTpClPP)(Cl){\cdot}2H_2O{\cdot}2C_6H_6$ calcd (found) for $C_{58}N_4H_{47}Cl_5ZnO_2$: C, 67.04 (67.56); H, 4.10 (4.36); N, 4.89 (5.00); Cl, 15.49 (15.35).

Acidic Treatment of Complex 1 under Anaerobic Conditions. To a solution of complex **1** (50 mg) in CH_2Cl_2 (50 mL) at −30 °C under argon were added a few drops of an acidic CH_2Cl_2 solution (1% vv mixture of HCl 11 N in CH_2Cl_2). The green solution obtained exhibited the typical visible spectrum of iron(II)–*N*-alkylporphyrins. After demetalation by concentrated HCl and neutralization, Zn(II) was inserted into the free bases by $Zn(CH_3COO)_2$ as previously described in the previous paragraph. The zinc(II)–*N*-alkylporphyrins were purified by thin-layer chromatography (silica gel, Merck F-254, 2 mm, elution with CH_2Cl_2). ^1H NMR analysis showed it was a 70/30 mixture of the two zinc–*N*-alkylporphyrins **5** and **6**.

Reaction of an Excess of $PhCH_2CHN_2$ with Fe(TpClPP)(Cl). To 50 mg of Fe(TpClPP)(Cl) dissolved in CH_2Cl_2 (50 mL) was added 45 equiv of $PhCH_2CHN_2$ in pentane. The solution turned green-brown exhibiting in UV–visible spectroscopy a peak at 434 nm shouldered at 453 and 470 nm, with one broad band at 646 nm. Addition of a few drops of 1% HCl in CH_2Cl_2 led to the quantitative formation of complex **3**. After treatment by the above described procedure, the obtained Zn(II) complex **5** was identified by ^1H NMR analysis and UV–visible spectroscopy (453, 564, 614, 663).

Electrochemistry. Experiments were carried out with the F-GG-PAR Model 173 potentiostat monitored with an Apple IIe microcomputer through the EGG-PAR Model 276 interface. Cyclic voltammetry was performed through a classical three-electrode system: a glassy carbon disk as working electrode, a platinum wire as counter electrode, and a saturated calomel electrode as reference electrode. Macroelectrolysis was carried out with a platinum grid and an auxiliary compartment separated from the bulk solution by a Nafion R membrane. The solvent was methylene chloride of analytical grade purchased from SDS. Supporting electrolyte was 0.2 M NBu_4BF_4 purchased from FLUKA. In a typical

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experiment 20 mL of a 10^{-3} M substrate solution was deoxygenated and cooled at −15 °C. Controlled potential electrolysis was performed within a few hours, with an average current of about 5 mA. Products were analyzed both by cyclic voltammetry and UV-visible spectroscopy.

Electrochemical Oxidation of the Iron σ-Complex 7. The macroelectrolysis was run at −40 °C and OV. Analysis of the UV-visible spectrum of the solution at room temperature allowed us to estimate a 20% yield in iron(II)-*N*-alkylporphyrin (λ_{max} 418, 446, 460 sh, and 570, 615, 660 nm). The solution was evaporated to dryness, and then the supporting electrolyte was eliminated by flash chromatography (Florisil, Sigma, elution CH_2Cl_2, 1% HCl). After neutralizing the cationic *N*-alkylporphyrin CH_2Cl_2 solution by washing with water and Zn(II) insertion into the free base, the zinc complex **6** was analyzed by UV-visible spectroscopy (λ_{max} 444, 450 sh, 565, 615, 660 nm), mass spectrometry, and ^1H NMR spectroscopy (Table I): mass spectrum 956 (30) (M + 1), 815 (100) Zn(TpClPP).

Conformations of $(\eta^5\text{-}C_5H_5)_2Nb(S\text{-}p\text{-}C_6H_4X)_2^n$ (n = 0, 1): Responsiveness to Para Substituents on Aryl Groups and to d-Electron Count

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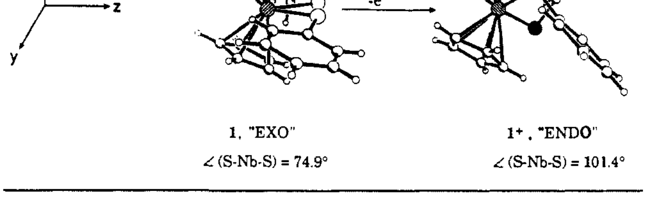
Abstract: The balance of factors that determine the S–M–S angle and M–S–R conformational preference have been examined in a systematic study of aryl thiolate derivatives of the bent metallocenes $(\eta^5\text{-}C_5H_5)_2Nb(S\text{-}p\text{-}C_6H_4X)_2^n$, where for n = 0, X = OMe (**2**), Me (**3**), H (**1**), and Cl (**4**), and for n = +1, X = H (**1**$^+$) and Cl (**4**$^+$). Cyclic voltammographs showed two reversible waves for the Nb(III) → Nb(IV) and Nb(IV) → Nb(V) redox processes whose positions varied uniformly with the Hammett σ parameter of the X substituent. X-ray crystal structure determinations are presented for **2**, **3**, **4**, and [**4**$^+$][PF_6^-] and compared with **1** and **1**$^+$ (*Organometallics*, **1989**, *8*, 1315). The S-aryls of Nb(V) complexes (the d^0 derivatives, **1**$^+$ and **4**$^+$) as well as the d^1 complex **4**, $(\eta^5\text{-}C_5H_5)_2Nb(S\text{-}p\text{-}C_6H_4Cl)_2$, adopt an endo arrangement relative to the cyclopentadienyl rings and have wide S–Nb–S angles of 101.4°, 102.3°, and 98.7°, respectively. Complexes **1**, **2**, and **3** have an exo configuration with aryl groups bent back into the cleft between the Cp rings. The exo isomers have small S–Nb–S angles of 75.4°, 79.1°, and 77.1°, respectively. Complex **2** crystallized in the monoclinic space group *C*2/*c*, with a = 22.869 (9) Å, b = 6.962 (3) Å, c = 13.951 (4) Å, β = 98.38 (3)°, V = 2197.6 Å^3, and Z = 4. Complex **3** crystallized in the orthorhombic space group *Aba*2, with a = 13.536 (4) Å, b = 22.659 (2) Å, c = 7.017 (3) Å, V = 2152 Å^3, and Z = 4. Complex **4** crystallized in the monoclinic space group *C*2/*c*, with a = 20.252 (6) Å, b = 9.847 (2) Å, c = 12.403 (4) Å, β = 124.00 (2)°, V = 2050.5 Å^3, and Z = 4. Complex **4**+ crystallized in the triclinic space group $P\bar{1}$, with a = 10.488 (6) Å, b = 10.672 (6) Å, c = 11.226 (8) Å, α = 96.29 (5)°, β = 94.28 (5)°, γ = 112.57 (4)°, V = 1143.8 Å^3, and Z = 2. Details of the structures will be presented and placed in context with other bent metallocene analogues.

Introduction

Recently the molecular structures of the bent metallocenes d^1 $(\eta^5\text{-}C_5H_5)_2Nb(SC_6H_5)_2$ (**1**) and d^0 $(\eta^5\text{-}C_5H_5)_2Nb(SC_6H_5)_2^+$ (**1**$^+$)[1] and, later, $(\eta^5\text{-}C_5H_5)_2NbCl_2^+$,[2] for comparison with $(\eta^5\text{-}C_5H_5)_2NbCl_2$,[3] were reported as the first examples of the structural changes resulting from different d-electron counts for identical metal centers. For the latter, oxidation resulted in a large increase in the Cl–Nb–Cl angle of the pseudotetrahedral complex of 12.5° (from 85.6° for the neutral d^1 complex to 98.1° for the d^0 cation). Even more dramatic, as demonstrated below, were the differences observed for the thiolate derivatives. Not only did the S–Nb–S angle change by a remarkable 25°, the largest (by over 12°) known value for a $d^1 \rightarrow d^0$ interchange, but, additionally, there was a $M(SPh)_2$ conformational change from the so-called "exo" to the "endo" form.



1, "EXO" ∠(S-Nb-S) = 74.9°

1$^+$, "ENDO" ∠(S-Nb-S) = 101.4°

The configuration change just described was unprecedented in that the analogous light metal neutral derivatives, d^1, $Cp_2V(SPh)_2$ and d^0, $Cp_2Ti(SPh)_2$ whose ∠(S–M–S) are 94.1° and 99.1°, respectively,[4] are isomorphous with the SPh groups of both adopting the "endo" conformation. The titanocene and vanadocene SMe analogues were also structurally characterized with largely the same results.[5] The change in ∠(S–M–S) angle (from 88.7° for d^1, $Cp_2V(SMe)_2$, to 93.7° for d^0, $Cp_2Ti(SMe)_2$) was in the order predicted by established theory,[6,7] and, once again, the endo $M(SR)_2$ conformation was obtained for both of the light metal complexes. In fact, prior to the report of the niobium structures, the only report of an exo orientation of SR groups was that of d^2, $Cp_2Mo(S\text{-}t\text{-}Bu)_2$, whose extremely small ∠(S–Mo–S) of 71° is explained both by electronic (metal based $1a_1$/sulfur lone pair orbital repulsions) and steric (t-Bu/Cp ring repulsions) effects.[8]

Although the configurational change described above (**1**, "EXO" → **1**$^+$, "ENDO") is the first example of such with d electron count for the same metal, the possible influence of π-donor ligands on configuration in Cp_2ML_2 complexes was broached by Hoffmann

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