

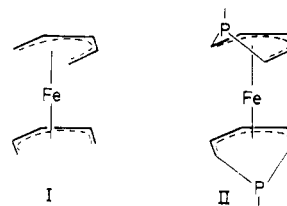
Preliminary results of an X-ray structure analysis⁸ of bis(1,1-dimethyl-2,4,6-triphenyl-phosphini-um)iron bis-(tetrafluoroborate) solvate (2) indicate a very similar coordination geometry of iron in the dicationic complex which has the gauche-eclipsed conformation as well and nearly the same Fe-C distances. However, a significant difference between the neutral (1) and the cationic (2) complexes was found for the Fe-P distances, which are shorter in 1 (mean 2.91 Å, Table III) than in 2 (mean 2.96 Å). In consequence, the dihedral angles in the phosphinine rings ("chair angles") between the C₅ planes and the C1-P-C5 planes are much smaller for 1 (mean 35°, Table IV) than for 2 (mean 47°). The severe differences between the two ligands within each complex which are documented, e.g., in the variation of dihedral angles between the phosphinine C₅ planes and the phenyl planes (Table IV), will be due to packing effects.

The C-C distances are equal within the esd's (mean 1.41 Å) in the phosphinine ring of 1, indicating a high degree of π -electron delocalization. Therefore, an allyl-ene-like η^3, η^2 -bonding scheme is not correct (for discussion of the bonding properties see ref 1 and 9). The same distances

(8) Crystal data: space group $P2_1/c$, $a = 19.711$ (8) Å, $b = 14.766$ (10) Å, $c = 17.153$ (10) Å, $\beta = 92.46$ (4)°. Due to disorder of the BF_4^- anions and solvent molecules only poor quality of the structural parameters could be obtained ($R = 0.125$ for 2637 reflections). Following the suggestion of a reviewer we intend to treat the disorder by the back Fourier transform method: Rae, A. D.; Baker, A. T. *Acta Crystallogr. Sect. A: Found. Crystallogr.* 1984, A40, C-428. The results will be published separately. A different monoclinic form of 2 has been found in another single crystal claimed by a different method showing also strong disorder effects at the BF_4^- sites (Allmann, R. unpublished work, Marburg, 1984).

(9) See ref 6 in the preceding paper.

of 1.41 Å have been found for bis(2,4-dimethyl-pentadienyl)iron² which also has the gauche-eclipsed conformation. Thus, the relationship of the phosphinine sandwich complexes (II) to the "open ferrocenes" (I) is obvious.¹



In the neutral phosphinine ligand of 1 the methyl group at the three-coordinate P atom is in the axial position (Figure 1). Thus, the lone electron pair at the P atom points toward the C₅ plane, and an interaction with the central Fe atom leading to the observed smaller "chair angle" may be discussed. Nevertheless, repulsion interaction of the positive charges at the four-coordinate P atoms of the cationic complex would explain the different chair angles as well.

Acknowledgment. We thank Professor K. Dimroth and Dr. T. Dave for providing the crystals.

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Supplementary Material Available: Tables of anisotropic temperature factors for non-hydrogen atoms, complete bond lengths and angles, and observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

Integrated Molecular Systems. Fixation of Carbon Monoxide on Iron(I) in Simple and Superstructured Porphyrins

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Investigation of a series of superstructured iron porphyrins showed that the fixation of carbon monoxide on iron(I) is significantly enhanced by the presence of amide groups in the protecting chain. Axial ligation of iron also increases the CO affinity. It was thus possible to obtain and characterize by their UV-vis, IR, and ESR spectra iron(I)-carbon monoxide complexes from amide-linked superstructured porphyrins in the presence of a complexing agent in the solution. The IR and ESR data as well as the remarkable electron push (axial ligation)-pull (NHCO) stabilizing effect indicate a significant electron transfer from the iron atom to the CO ligand. The complex bearing two amide-linked chains with a pending imidazole ligand in one of them is an example of an integrated molecular system, protected from solvent interaction, ensuring a good CO affinity for iron(I) independent of the reaction medium.

Introduction

Direct electrochemical reduction of carbon monoxide requires very high voltages, close to the discharge of the supporting electrolyte, yielding acetylene diolate and other condensed products.² It is therefore of interest to attempt to chemically catalyze³ the reaction through fixation of CO

on a transition metal and reduction of the ensuing complex. The aim of such a mediated reduction is to decrease the overpotential and, possibly, vary the products. Synthetic and naturally occurring iron(II) porphyrins are known to strongly bind CO.⁴ We thus set out to use this property for transferring electrons from the electrode to

(1) (a) Université de Paris 7. (b) Institut Curie.
(2) (a) Silvestri, G.; Gambino, S.; Filardo, G.; Guainazzi, M.; Ercoli, R. *Gazz. Chim. Ital.* 1972, 102, 818. (b) Silvestri, G.; Gambino, G.; Filardo, G.; Sparado, G.; Palmisano, L. *Electrochim. Acta* 1978, 23, 413. (c) Bockmair, G.; Fritz, H. P. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* 1975, 30, 330. (d) Uribe, F. A.; Sharp, P. R.; Bard, A. J. *J. Electroanal. Chem.* 1983, 152, 173.

(3) (a) Andrieux, C. P.; Dumas-Bouchiat, J. M.; Savéant, J. M. *J. Electroanal. Chem.* 1978, 87, 39. (b) Lexa, D.; Savéant, J. M.; Soufflet, J. P. *J. Electroanal. Chem.* 1979, 100, 159.

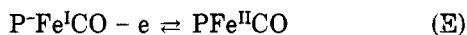
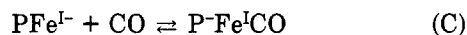
(4) (a) Perutz, M. F. *Annu. Rev. Biochem.* 1979, 48. (b) Collman, J. P. *Acc. Chem. Res.* 1977, 10, 265. (c) Traylor, T. G. *Acc. Chem. Res.* 1981, 14, 102. (d) Jameson, G. B.; Ibers, J. A. *Comments Inorg. Chem.* 1983, 2, 97.

Table II. Cyclic Voltammetric and UV-vis Spectrometric Criteria for a Qualitative Estimate of the Fe^I-CO Affinity

CO affinity	reversibility of the Fe ^{II} CO/Fe ^I CO ⁻ wave II	rel heights of waves III and IV	UV-vis spectra upon reductn of Fe ^{II} in the presence of CO
very poor	not reversible down to 0.1 V·s ⁻¹		
poor	reversible at 0.1 V·s ⁻¹ ; not reversible at 10 V·s ⁻¹	wave III practically unaffected by the presence of CO	Fe ^I spectrum practically unaffected by the presence of CO
fair	reversible up to 10 V·s ⁻¹		
good	reversible up to and above 10 V·s ⁻¹	both waves III and IV present	mixture of Fe ^I CO ⁻ and Fe ^I spectra
excellent	reversible up to and above 10 V·s ⁻¹	complete disappearance of wave III at the expense of wave IV	pure Fe ^I CO ⁻ spectrum

It is located in the 1960 cm⁻¹ region as expected for a single CO ligand,^{6b,c} whereas bonding of two CO molecules should give rise to a band in the 2040 cm⁻¹ region.^{6b} The starting complex in the electrochemical experiments described below is thus predominantly the Fe^{II}CO monoadduct.⁷

Parts a and b of Figure 1 shows the effect of CO on the cyclic voltammetry of Fe^{II}TPP in DMF. In the absence of CO (dashed line in Figure 1a) two reversible waves are observed corresponding to the Fe^{II}/Fe^I- and Fe^I/Fe^I.²⁻ couples, respectively. The complex obtained upon transfer of one electron appears to be best rationalized as an iron(I) complex while the second electron transfer gives rise to a species best represented by an iron(I) having an extra electron in the porphyrin ring.⁹ Upon addition of CO, the first wave, while remaining reversible, is shifted negatively (by 290 mV). The second wave remains almost the same while a small cathodic wave (wave IV) appears at more negative potentials. The fact that the first wave remains reversible could, at first sight, be taken as an indication that the complex formed upon one-electron transfer to Fe^{II}CO, formally the ⁻Fe^ICO complex, is stable. However with reference to Scheme I, the anodic current in wave II may involve a "CE mechanism":¹⁰



which implies that even if the Fe^I- complex prevails, at equilibrium, over the ⁻Fe^ICO complex, the oxidation process may go entirely through the latter complex since this is easier to oxidize than the former. The fact that wave II is reversible then indicates that the conversion of Fe^I-

(7) It is noted that this is not a critical requirement for the electrochemical investigation of the Fe^{II}CO monoadduct. Even in the case where the CO diadduct would predominate at equilibrium over the monoadduct, the reduction would nevertheless proceed through the monoadduct since it is easier to reduce than the diadduct, provided that the conversion of the latter into the former is rapid in the time scale of the CV experiments (0.1–0.5 s). The diadduct/monoadduct equilibrium would then simply influence the location of the reduction potential.

(8) (a) The same complex gives a band at 1965 cm⁻¹ in benzene + 1-methylimidazole.^{6b,c} (b) Collman, J. P.; Gagne, R. R.; Reed, C. A.; Halbert, T. R.; Lang, G.; Robinson, W. T. *J. Am. Chem. Soc.* 1975, 97, 1427. (c) Collman, J. P.; Brauman, J. I.; Doxsee, K. M. *Proc. Natl. Acad. Sci. U.S.A.* 1979, 76, 6035.

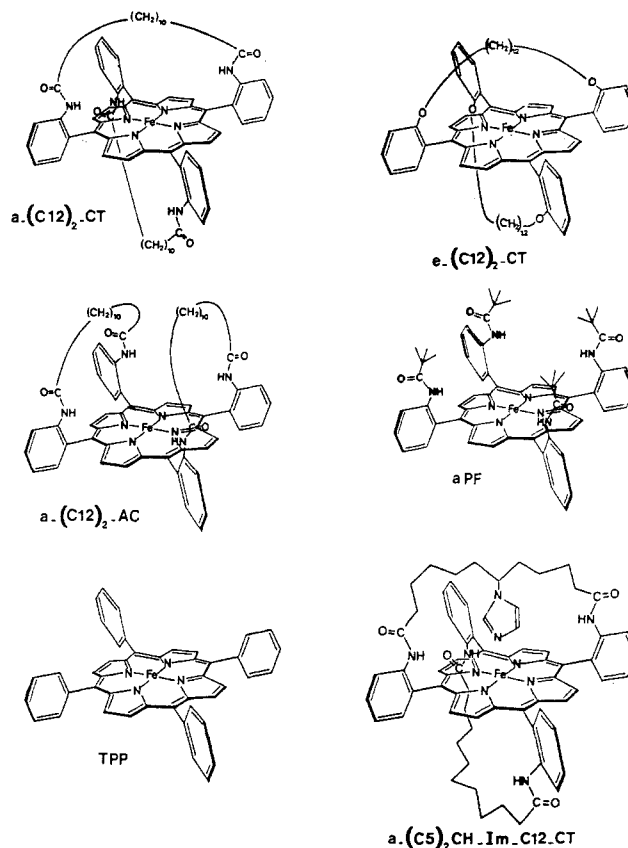
(9) (a) Reed, C. A. "Iron(I) and Iron(IV) Porphyrins" in "Biological Redox Components"; Kadish, K. M., Ed.; American Chemical Society: Washington, D.C., 1982; *Adv. Chem. Ser. No. 201*, Chapter 15, pp 333–356 and references cited therein. (b) Lexa, D.; Mispelter, J.; Savéant, J. M. *J. Am. Chem. Soc.* 1981, 103, 6806. (c) Mashiko, T.; Reed, C. A.; Haller, K. J.; Scheidt, W. R. *Inorg. Chem.* 1984, 23, 3192.

(10) (a) "C" for the chemical step (here removal of CO from the iron(I) complex, reaction 2 in Scheme I) preceding the electron-transfer step "E" (here the oxidation of ⁻Fe^ICO into Fe^{II}CO). (b) Savéant, J. M.; Vianello, E. *Electrochim. Acta* 1963, 8, 905.

(11) Note however that, under such circumstances, the apparent standard potential should become more negative according to $E^{\circ}_{\text{Fe}^{\text{II}}/\text{Fe}^{\text{I}-}} = E^{\circ}_{\text{Fe}^{\text{II}}/\text{Fe}^{\text{I}-}} - RT/F \ln K/(1 + K)$, where K is the $[\text{Fe}^{\text{I}-}]/[\text{Fe}^{\text{I}}\text{CO}]$ at equilibrium.

(12) a and e stand for amide and ether linking of the chains to the ortho position of the phenyl ring, respectively; CT for the cross-trans arrangement of the chains and PF for the "picket-fence" structure.^{4a}

Scheme II



into ⁻Fe^ICO is fast within the time scale of the cyclic voltammetric experiment (i.e., approximately (1/40 v) s at room temperature, v being the sweep rate expressed in V·s⁻¹^{10b}). The shift in reduction potential then reflects the ratio of the CO affinities for iron(II) and iron(I), respectively:

$$E^{\circ}_{\text{Fe}^{\text{II}}\text{CO}/\text{Fe}^{\text{I}}\text{CO}^-} = E^{\circ}_{\text{Fe}^{\text{II}}/\text{Fe}^{\text{I}-}} - RT/F \ln (K^{\text{II}}_{\text{CO}}/K^{\text{I}}_{\text{CO}})$$

If the ⁻Fe^ICO complex is not stable, i.e., if the equilibrium ratio of its concentration over that of the Fe^I- complex, is significantly smaller than 1, it is therefore expected that reversibility will be altered upon raising the sweep rate, i.e., decreasing the time scale of the experiment. That this does occur with TPP is seen in Figure 1b: at 10 V·s⁻¹ the anodic trace splits into two waves, the most negative featuring the oxidation of the ⁻Fe^ICO complex (kinetically controlled by reaction 2) and the less negative, the oxidation of the remaining portion of Fe^I- that has not been reoxidized through the ⁻Fe^ICO complex. We thus have a first qualitative criterion for a rough estimation of the iron(I)-carbon monoxide affinity: the higher the sweep rate at which reversibility breaks down, the larger the affinity.

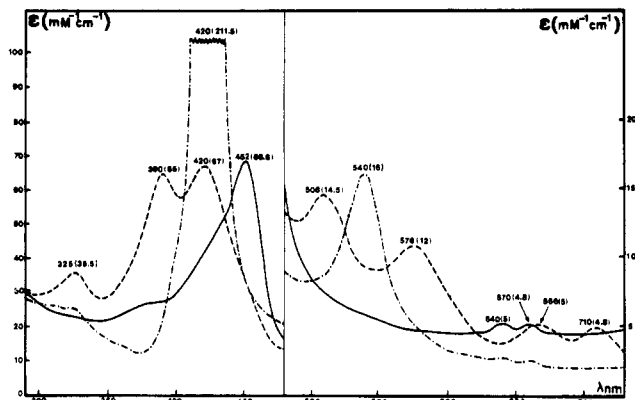
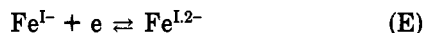
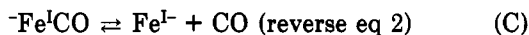


Figure 2. Thin-layer electrochemistry UV-vis spectra obtained upon reduction of Fe^{III} -aPF in DMF + 0.1 M NBu_4BF_4 at room temperature in the absence and presence of CO: (---), $\text{Fe}^{\text{II}}\text{CO}$ ($E = -0.7$ V vs. SCE); (-.-), $\text{Fe}^{\text{I}-}$ ($E = -1.20$ V vs. SCE); (—), $\text{Fe}^{\text{I}}\text{CO}^-$ ($E = -1.35$ V vs. SCE).

A second source of information is provided by the behavior of the second electron transfer wave (the "ring" wave noted wave III in Figure 1a). Upon addition of CO a decrease of the wave at the expense of a more negative wave (wave IV) was observed. If the $\text{Fe}^{\text{I}}\text{CO}$ complex was very stable, wave III should disappear upon addition of CO. However, for moderate stabilities it must be taken into account the possibility that the reduction of the $\text{Fe}^{\text{I}-}$ complex in the presence of CO also follows a CE mechanism:¹⁰



Thus, even if $\text{Fe}^{\text{I}}\text{CO}$ prevails, at equilibrium, over $\text{Fe}^{\text{I}-}$, its reduction may well take place through the $\text{Fe}^{\text{I}-}$ complex provided its rate of decomposition is sufficiently fast within the time scale of the experiment. In such case, the height of the "ring wave" III would remain unaffected and wave IV would not be detected.

Cyclic voltammetry thus provides criteria for a qualitative estimate of the magnitude of the $\text{Fe}^{\text{I}-}/\text{CO}$ affinity as summarized in Table II. Starting from the various superstructured porphyrins listed in Scheme II, variations of the wave system upon addition of CO were observed which allowed us to relate the $\text{Fe}^{\text{I}-}/\text{CO}$ affinity to the structure of the porphyrin. Parts c and d of Figure 1 show a typical example of a strong CO affinity as revealed by the cyclic voltammetric behavior. In this case, i.e., with the a-(C5)₂CH-Im-C12-CT porphyrin, the stability of the $\text{Fe}^{\text{I}}\text{CO}$ complex is so high that the ring wave III has totally disappeared at the expense of wave IV which features the further reduction of the $\text{Fe}^{\text{I}}\text{CO}$ complex. As expected the $\text{Fe}^{\text{II}}\text{CO}/\text{Fe}^{\text{I}}\text{CO}$ wave II remains fully reversible at 10 V s⁻¹ (Figure 1d).

A way of checking the stabilities of the $\text{Fe}^{\text{I}}\text{CO}$ complexes suggested by cyclic voltammetry is UV-vis thin-layer spectroelectrochemistry at the potential of the $\text{Fe}^{\text{II}}\text{CO}/\text{Fe}^{\text{I}}\text{CO}$ wave II. The correspondence between the results expected from this technique and those suggested by the cyclic voltammetric behavior is shown in Table II.

On these bases we found the following order of $\text{Fe}^{\text{I}-}/\text{CO}$ affinity for the various porphyrins in DMF: e-(C12)₂-CT < TPP < a-(C12)₂-CT < a-(C12)₂-AC \approx a-PF < a-(C5)₂CH-Im-C12-CT. With the three last porphyrins a pure $\text{Fe}^{\text{I}}\text{CO}^-$ spectrum was found. With the first two, no modification of the $\text{Fe}^{\text{I}-}$ spectrum was found upon addition of CO. With the remaining porphyrin, a mixture of the two spectra was obtained. Figure 2 shows a typical ex-

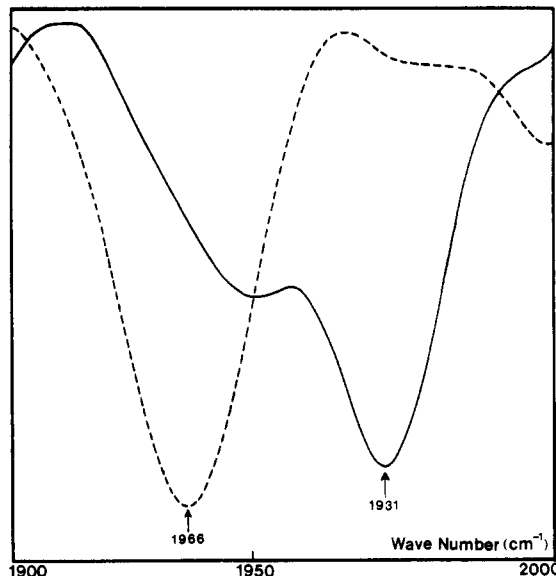


Figure 3. IR spectrum of a solution of Fe^{III} -aPF (1 mM) in PhCN + 0.24 M 1-methylimidazole + 0.1 M NBu_4NBF_4 under a 1 atm CO pressure after electrolysis at -0.6 V (---) ($\text{Fe}^{\text{II}}\text{CO}$) and -1.3 V vs. SCE (—) ($\text{Fe}^{\text{I}}\text{CO}^-$).

ample (the a-PF porphyrin) of a pure $\text{Fe}^{\text{I}}\text{CO}^-$ spectrum obtained upon electrolysis of the Fe^{II} complex in the presence of CO. The same behavior was observed for the last three porphyrins. For the first two, the $\text{Fe}^{\text{I}-}$ spectrum remained practically unaffected by the presence of CO whereas for a-(C12)₂-CT a mixture of the two spectra was obtained.

Besides the effect of the superstructures and of the nature of the linking functions described above, we also discovered that axial ligation of the iron atom plays quite important role in the control of the $\text{Fe}^{\text{I}-}/\text{CO}$ affinity. The first observation of this connection was that the affinity, for a given porphyrin, is significantly less in PhCN than in DMF paralleling their complexing power.¹³ Thus it was no longer possible to obtain a $\text{Fe}^{\text{I}}\text{CO}$ UV-vis spectrum with the a-(C12)₂-AC and a-PF porphyrins. They both gave rise to a $\text{Fe}^{\text{I}-}$ spectrum practically unaffected by the presence of CO. The same was observed for the a-(C12)₂-CT porphyrins. On the contrary, the a-(C5)₂CH-Im-C12-CT porphyrin still exhibited an excellent $\text{Fe}^{\text{I}-}/\text{CO}$ affinity (pure spectrum) in PhCN, in accordance with the fact that the pending imidazole is available for complexing the iron atom. Likewise, addition of 1-methylimidazole, in decimolar concentrations, to the PhCN solution was observed to restore the $\text{Fe}^{\text{I}-}/\text{CO}$ affinity found in DMF. It was actually observed that the affinity is even better in PhCN + 1-methylimidazole than in DMF solutions: the a-(C12)₂-CT porphyrin exhibits a pure $\text{Fe}^{\text{I}}\text{CO}^-$ spectrum in the former case while only a mixed spectrum was obtained in DMF.

In order to further characterize the $\text{Fe}^{\text{I}}\text{CO}^-$ complex, we investigated their IR and ESR spectra with the porphyrins and medium conditions that were shown, from the cyclic voltammetric and UV-vis spectroscopic data, to give rise to a good $\text{Fe}^{\text{I}-}/\text{CO}$ affinity. Figure 3 shows a typical example of an IR spectrum obtained under these conditions, obtained with the a-PF porphyrin in PhCN + 0.24 M 1-methylimidazole. The starting $\text{Fe}^{\text{II}}\text{CO}$ complex exhibited a CO stretching band at 1966 cm^{-1} while the complex obtained upon electrolysis at -1.3 V vs. SCE shows a band

(13) (a) Their donor numbers are 11.9 and 26.6, respectively.^{13b} (b) Gutman, V. "The Donor Acceptor Approach to Molecular Interactions", Plenum Press: New York, 1978; p 20.

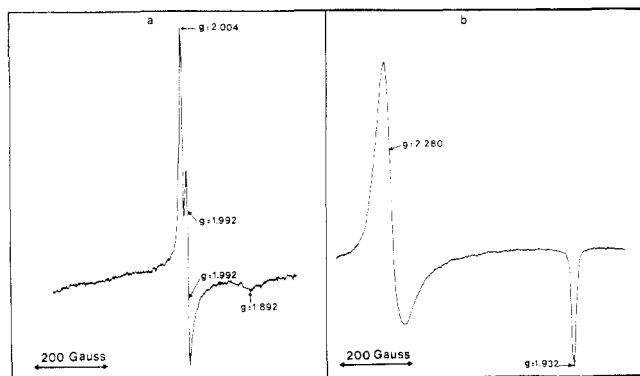


Figure 4. ESR spectra (77 K) of $\text{Fe}^{\text{I}}\text{CO}^-$ (a) and $\text{Fe}^{\text{I}-}$ (b) obtained with the a-PF porphyrin in DMF after electrolysis of a solution of the Fe^{III} complex at -1.3 V vs. SCE presence (a) and absence (b) of CO.

at 1931 cm^{-1} . The presence of some starting $\text{Fe}^{\text{II}}\text{CO}$ complex can be seen in the spectrum of the electrolyzed solution. It is indeed difficult to completely avoid reoxidation by air oxygen ($E^{\circ}_{\text{O}_2/\text{O}_2^-} = -0.94$ V vs. SCE) of the strongly reducing $\text{Fe}^{\text{I}}\text{CO}^-$ complex ($E^{\circ}_{\text{Fe}^{\text{II}}\text{CO}/\text{Fe}^{\text{I}}\text{CO}^-} = -1.21$ V vs. SCE) during the transfer from the electrolytic cell to the IR cell. Very similar results were obtained in DMF: bands at 1964 and 1935 cm^{-1} , respectively.

Figure 4a shows a typical ESR spectrum of the $\text{Fe}^{\text{I}}\text{CO}^-$ complex of the a-PF porphyrin in DMF. It is considerably different from the spectrum of the $\text{Fe}^{\text{I}-}$ complex¹⁴ (Figure 4b) and exhibits three bands: $g_1 = 2.004$, $g_2 = 1.995$, and $g_3 = 1.842$. No hyperfine structure due to the coupling with the imidazole nitrogen is seen. No hyperfine structure resulting from coupling with ^{13}C was likewise observed in a similar experiment carried out in the presence of ^{13}CO . Almost identical results were obtained with the same porphyrin in PhCN + 0.24 M 1-methylimidazole and with a-(C5)₂CH-Im-C12-CT in pure PhCN.

Discussion

Combined use of cyclic voltammetry, UV-vis, IR, and ESR spectroscopies allowed to show unambiguously that (porphyrin)iron(I)-carbon monoxide adducts can be obtained provided that an appropriate superstructure is attached to the porphyrin ring and that the reaction is carried out in a complexing medium.¹⁵

When passing from the $\text{Fe}^{\text{II}}\text{CO}$ to the $\text{Fe}^{\text{I}}\text{CO}^-$ complex, a significant shift of the CO stretching band toward small wavenumbers is observed. This is an indication of a substantial transfer of electron density from the iron atom to the CO molecule.^{16a} Transfer of electron density from the iron atom toward the porphyrin ring so as to obtain as the limiting form an $\text{Fe}^{\text{II}}\text{CO}$ anion radical is ruled out by the observation that partial hydrogenation of the tetrapyrrolic system does not significantly affect the location of the CO band of monocarbonyl adduct of iron porphyrins.^{16b}

The ESR spectrum of $\text{Fe}^{\text{I}}\text{CO}^-$ appears as that of a low spin complex. The absence of hyperfine coupling with the ^{13}C at 77 K (in ^{13}CO experiments) and with the liganding nitrogen of the 1-methylimidazole ligand indicates the

absence of a significant unpaired electron density in the d_{z^2} orbital (as discussed below, there is strong evidence that the $\text{Fe}^{\text{I}}\text{CO}^-$ complex bears a second axial ligand). The ESR spectrum exhibits some resemblance with that of a low-spin iron(III) complex which would indicate that considerable transfer of electron density from the iron atom to the CO molecule occurs.

The comparison of the various porphyrins investigated in this work, in the same reaction medium, shows that a substantial increase of the $\text{Fe}^{\text{I}}/\text{CO}$ affinity results from the presence of amide groups as links between the chains and the ortho-phenyl carbons. As discussed recently, the presence of amide groups in the same structures strongly stabilizes the negatively charged $\text{Fe}^{\text{I}-}$ and $\text{Fe}^{\text{I}2-}$ complexes through hydrogen bonding and/or dipolar interactions.^{5a} The NHCO groups then play the role of a local solvent born by the molecule itself. The observation that $\text{Fe}^{\text{I}}\text{CO}^-$ is stabilized vis-à-vis $\text{Fe}^{\text{I}-}$ by these groups in spite of the fact that the two complexes bear the same charge points to the conclusion that the charge is more concentrated in the former complex than in the latter, allowing a stronger H bonding and/or dipolar interaction. These facts fall in line with the conclusion, derived from the IR and ESR data, that iron(I) transfers a substantial portion of its electronic density to the CO moiety in what we designed formally as an iron(I)-carbon monoxide complex.

It is also remarkable, in this connection, that the presence of an ether-linked superstructure decreases the $\text{Fe}^{\text{I}}/\text{CO}$ affinity. These structures have been previously shown to destabilize the negatively charged $\text{Fe}^{\text{I}-}$ and $\text{Fe}^{\text{I}2-}$ complexes owing to the fact that they create a steric hindrance to solvent stabilization.^{5a} Protection of the complex then reduces the solvent stabilization to a larger extent with $\text{Fe}^{\text{I}}\text{CO}^-$ than with $\text{Fe}^{\text{I}-}$ which again matches the conclusion that the negative charge is more concentrated in the former complex than in the latter.¹⁷

The $\text{Fe}^{\text{I}}/\text{CO}$ affinity appears to be larger with the amide-linked superstructure porphyrins offering four NHCO groups on the same side of the macrocycle (a-PF, a-(C12)₂AC) than with those offering two NHCO groups on each side (a-(C12)₂CT). This is easily understood if addition of CO to $\text{Fe}^{\text{I}-}$ in the first series is viewed as occurring on the side where the four NHCO groups stand. Stabilization then involves four NHCO groups instead of two in the second series.

Another important effect is that of axial ligation: the presence of a complexing agent, DMF or 1-methylimidazole, strongly increases the $\text{Fe}^{\text{I}}/\text{CO}$ affinity. On the overall, there is thus a remarkable electron push (axial ligand)-pull (NHCO groups) mechanism for the stabilization of the $\text{Fe}^{\text{I}}\text{CO}^-$ adduct. In this connection it is interesting to note the parallelism with the stabilization of the porphyrin $\text{Fe}^{\text{II}}\text{O}_2$ adduct. Both axial ligation^{18a} and the presence of NHCO groups^{18b} increase the $\text{Fe}^{\text{II}}/\text{O}_2$ affinity, indicating partial electron transfer from Fe^{II} to O_2 in the adduct.

In this context, the a-(C5)₂CH-Im-C12-CT structure (Scheme II) appears as ideally suited for obtaining a good fixation of CO on iron(I). This integrated molecular system, protected from medium interactions, contains the two elements, the pending imidazole ligand and the presence of amide groups, ensuring a large CO affinity independent from the reaction medium as shown by the fact that an

(14) Lexa, D.; Momenteau, M.; Mispelter, J. *Biochim. Biophys. Acta* 1974, 338, 151.

(15) (a) It is interesting to note in this connection that addition of CO to a tetrahydrofuran solution (a complexing medium) of $\text{Na}[\text{Fe}^{\text{I}}\text{TTP}]$ give a UV-vis spectrum in which the Soret maximum occurs at 455 nm ,^{16b} i.e., very close to that found for the $\text{Fe}^{\text{I}}\text{CO}^-$ complexes in the present study. (b) Collman, J. P.; Sorrell, T. N.; Dawson, J. H.; Trudell, J. R.; Bunnenberg, E.; Djerassi, C. *Proc. Natl. Acad. Sci. U.S.A.* 1976, 73, 6.

(16) (a) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds"; Wiley: New York, 1978; pp 279-284. (b) Strauss, F. H.; Holm, R. H. *Inorg. Chem.* 1982, 21, 863.

(17) An electronic destabilizing effect of the ortho phenyl ether groups cannot be completely excluded although it does not seem very likely since an increase of the electron density at the iron atom tends to increase the CO affinity as revealed by the effect of axial ligands described in the following.

excellent fixation is obtained in a poor complexing solvent such as benzonitrile. The concept of such integrated molecular systems may prove useful in the comprehension and mimicry of the functioning of metalloenzymes and in the design of homogeneous or heterogeneous (modified surfaces) catalysts for chemical and electrochemical reactions.

Further work is now in progress in two directions: quantitative measurement of the $\text{Fe}^{\text{I}}/\text{CO}$ affinity as a function of the superstructure and axial ligation and determination of the species resulting from a further electron transfer. It is interesting to note, in this connection, that partial electron transfer to CO has already occurred in the $\text{Fe}^{\text{I}}\text{CO}$ complex as results from the above described study. On the other hand, preliminary results point to the formation of the formyl complex¹⁹ at the potential of wave IV similar to what was previously found with $\text{C}=\text{S}$ and vinylidene ligands.²⁰

Experimental Section

Chemicals. The various basket-handle porphyrins were synthesized and characterized as already described: $\text{e}-(\text{C}_{12})_2\text{CT}$,^{21a}

(18) (a) Collman, J. P.; Brauman, J. O.; Iversen, B. L.; Sessler, J. L.; Morris, R. M.; Gibson, Q. H. *J. Am. Chem. Soc.* **1983**, *105*, 3052. (b) Momenteau, M.; Lavalette, D. *J. Chem. Soc., Chem. Commun.* **1982**, 341.

(19) (a) A formyl complex of rhodium octaethylporphyrin has been recently described.^{19b} (b) Wayland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1981**, 700.

(20) (a) Battioni, J. P.; Lexa, D.; Mansuy, D.; Savéant, J. M. *Angew. Chem.* **1981**, *20*, 578. (b) Lange, M.; Battioni, J. P.; Mansuy, D.; Lexa, D.; Savéant, J. M. *J. Chem. Soc., Chem. Commun.* **1981**, 888. (c) Battioni, J. P.; Lexa, D.; Mansuy, D.; Savéant, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 207.

(21) (a) Momenteau, M.; Mispelter, J.; Loock, B.; Bisagni, E. *J. Chem. Soc., Perkin Trans. 1* **1983**, 189. (b) Momenteau, M.; Mispelter, J.; Loock, R.; Lhoste, J. M. *J. Chem. Soc., Perkin Trans. 1* **1985**, 0000. (c) Momenteau, M.; Loock, B.; Lavalette, D.; Tetreau, C.; Mispelter, J. *J. Chem. Soc., Chem. Commun.* **1983**, 962.

the three $\text{a}-(\text{C}_{12})_2$ isomers,^{21b} a-PF ,^{8b} $\text{a}-(\text{C}_5)_2\text{CH-Im-C}_{12}\text{-CT}$.^{21b,c} The solvents and supporting electrolytes were the same as in previous related studies.^{5a,c}

Cyclic Voltammetry and Thin-Layer UV-Visible Spectroelectrochemistry. The cell and instrumentation was the same as previously described.^{5a,c} The working electrode was either a 1.5-mm diameter, platinum disk or a 3-mm diameter glassy carbon disk. The temperature was 20 °C. All potentials are referred to the aqueous saturated calomel electrode (SCE).

IR Spectroscopy. The IR spectra were recorded on a Fourier transform apparatus (Nicolet 5MX) using millimolar solutions. The solutions were preelectrolyzed in a 8 cm³ coulometric cell equipped with a graphite working electrode (20 cm²), a platinum wire counterelectrode, and an aqueous SCE reference electrode and transferred to the IR (KBr) 0.1-mm cell under a CO stream. The spectrum obtained with the same solvent and supporting electrolyte with the same concentration of the starting Fe^{II} porphyrin was recorded and subtracted from the spectrum of the electrolyzed solution.

ESR Spectroscopy. The spectra were recorded at 77 K on a Varian (V4502) X-band spectrometer as described in ref 14. The solutions were preelectrolyzed either directly in the cavity of the spectrometer using a previously described cell¹⁴ or in a coulometric cell and then transferred to an ESR cell as described above for IR spectroscopy.

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Registry No. $[\text{Fe}(\text{TPP})\text{CO}]$, 66746-94-9; $[\text{Fe}(\text{a-PF})\text{CO}]$, 97233-16-4; $[\text{Fe}(\text{a}-(\text{C}_{12})_2\text{CT})\text{CO}]$, 97170-78-0; $[\text{Fe}(\text{e}-(\text{C}_{12})_2\text{CT})\text{CO}]$, 97170-79-1; $[\text{Fe}(\text{TPP})]$, 16591-56-3; $[\text{Fe}(\text{a}-(\text{C}_5)_2\text{CH-Im-C}_{12}\text{-CT})]$, 97170-80-4; $[\text{Fe}(\text{aPF})]^+$, 94729-74-5; $[\text{Fe}(\text{aPF})]^-$, 90857-60-6; $[\text{Fe}(\text{aPF})\text{CO}]^-$, 97170-81-5; $[\text{Fe}(\text{e}-(\text{C}_{12})_2\text{CT})\text{CO}]^-$, 97170-82-6; $[\text{Fe}(\text{TPP})\text{CO}]^-$, 97170-83-7; $[\text{Fe}(\text{a}-(\text{C}_{12})_2\text{CT})\text{CO}]^-$, 97170-84-8; $[\text{Fe}(\text{a}-(\text{C}_5)_2\text{CH-Im-C}_{12}\text{-CT})\text{CO}]^-$, 97170-86-0; $[\text{Fe}(\text{a}-(\text{C}_{12})_2\text{-AC})\text{CO}]^-$, 97170-85-9; CO, 630-08-0; Pt, 7440-06-4; C, 7440-44-0.