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Generation and Characterization of Alkyl- and Aryl-Bridged Dinuclear Iron(III) Porphyrin Complexes

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Substrate activation by cytochrome P-450 and monosubstituted hydrazine reactions with myoglobin and hemoglobin have revealed the formation of σ-bonded alkyl- or aryliron(III) porphyrin complexes.[1] The potential biochemical relevance of organometallic complexes has led in large part to the synthesis of σ-bonded alkyl- or aryliron(III) porphyrins. Similar σ-bonded derivatives with other transition or nontransition metals have been prepared in order to demonstrate the specific roles of the porphyrin ligand and metal ion in reactions and properties of these organometallic complexes.[2] Wayland and co-workers[3] have reported preparation of a diamagnetic dinuclear alkyl-bridged rhodium porphyrin through oxidative addition of a dibromoalkane to a rhodium(I) porphyrin or by an insertion reaction of an alkene to the rhodium octaethylporphyrin dimer.[4]

Synthetic alkyl- or aryliron(III) porphyrins have been prepared and characterized by a number of groups.[2,5] There are three primary routes for synthesis of the alkyl- or aryliron(III) porphyrins: (1) reaction of iron(III) porphyrins with a source of carbanions; (2) combination of an alkyl or aryl radical with an iron(II) porphyrin; and (3) reaction of iron(I) porphyrin anions with a source of carbocations, typically alkyl or aryl halides. The alkyl- or aryliron(III) porphyrins, (P)Fe(R), generally exist as five-coordinate, low-spin iron(III) complexes in noncoordinating solvents. Herein is described the synthesis of the first paramagnetic alkyl- or aryl-bridged dinuclear iron(III) porphyrin compounds.

1,4-Dilithiobutane was prepared from the reaction of 5.5 mL of 1,4-dichlorobutane with 1.4 g of lithium (1% Na) in 25 mL of diethyl ether at 0 °C.[6] 1,4-Dilithiobenzene was synthesized by modifications of a previously reported method.[7] Typically, 0.28 g of 1,4-dibromobenzene is dissolved in 5 mL of THF solution in a dry ice–acetone slush bath. A 1.5-mL quantity of *n*-butyllithium (1.6 M in hexanes) is added slowly down the side of the cold glass over a period of 10 min under an argon gas atmosphere. The temperature is slowly increased to 0 °C, and the solution is stirred for 5 min at 0 °C. One-half equivalent of a fresh solution of 1,4-dilithiobutane or 1,4-dilithiobenzene is titrated into a chloroiron(III) tetraphenylporphyrin [(TPP)FeCl] toluene-d_8 solution under anaerobic conditions at ambient temperature. Excess lithium reagent or poor mixing gives rise to the iron(II) porphyrin.

The proton NMR spectrum of (TPP)FeCl with 0.5 equiv of 1,4-dilithiobutane shows a pyrrole proton signal at −16.5 ppm (assigned by deuterium NMR spectroscopy of the (TPP-d_8) Fe derivative) and a bridged alkyl β-CH_2 resonance at −29.9 ppm at 25 °C (shown in Figure 1).[8] The upfield pyrrole proton signal is diagnostic for a low-spin iron(III) porphyrin complex.[10] Pyrrole, β-CH_2, and γ-CH_2 proton NMR signals for the previously described (TPP)FeBu are observed at −18.2, −64.8, and 18.9 ppm at 25 °C, respectively.[5m,9] The α-CH_2 signal is not detected probably due to extreme line broadening.

Addition of 0.5 equiv of 1,4-dilithiobenzene in THF solution to (TPP)FeCl or chloroiron(III) tetrakis(pentafluorophenyl)porphyrin [(F_{20}–TPP)FeCl] results in appearance of identical pyrrole proton signals and bridged phenyl proton signals at −17.7 and −74.1 ppm at 25 °C, respectively (shown in Figure 1). The intensity ratio of the low-spin pyrrole signal vs the bridging phenyl signal is approximately 4:1. Pyrrole and ortho, meta, and para phenyl proton signals for the known mononuclear complex (TPP)Fe(C_6H_5) are located at −17.64, −81.00, 13.55, and −26.97 ppm at 21 °C, respectively[5b] (−17.3, −80.0, 13.5, and −26.5 ppm, respectively, calculated for 25 °C).

The chemical shift data for coordinated alkyl and aryl mononuclear and dinuclear iron(III) porphyrin complexes are summarized in Figure 2. The broad, hyperfine-shifted alkyl and aryl bridging proton signals can be explained by delocalization of unpaired density from both iron(III) sites. The locations of the bridged alkyl and aryl proton signals might be expected to approximate the sums of the hyperfine chemical shift values of corresponding proton signals in monomeric alkyl- or aryliron(III) porphyrin complexes. On this basis the secondary CH_2 signal of the butyl bridge at −29.9 ppm is qualitatively similar to the calculated −48 ppm (TMS reference) value. The observed signal for the bridging phenyl group at −74.1 ppm is almost identical with the −75 ppm calculated value.

The aryl-bridged dinuclear iron(III) complex is not EPR active at liquid nitrogen temperature, in contrast to the mononuclear aryl complex, which shows a three-line spectrum for low-spin iron(III). Presumably, the EPR silence is due to spin–spin relaxation of adjacent iron(III) centers. However, magnetic coupling between iron centers must be very small, as the pyrrole proton signals for dinuclear and mononuclear complexes are approximately the same.

Insertion reactions of the alkyliron porphyrins with small molecules such as O_2 and CO are of interest.[9,11] Both $[(TPP)Fe]_2C_4H_8$ and $[(TPP)Fe]_2C_6H_4$ complexes react rapidly with O_2 at room temperature to form the dinuclear (μ-oxo)iron(III) porphyrin complex. However, the fluorinated-phenyl iron(III) aryl-bridged analogue is not reactive with O_2 at room temperature and no evidence was found for CO insertion into the Fe–C bond. Hence, addition of 1 atm of molecular oxygen or carbon monoxide to the fluorinated-phenyl iron(III) aryl-bridged compound contained in toluene solution did not affect the pyrrole proton signal

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(1) (a) Augusto, O.; Kunze, K. L.; Ortiz de Montellano, P. R. *J. Biol. Chem.* **1982**, *257*, 6231. (b) Saito, S.; Hans, H. A. *Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5508. (c) Ortiz de Montellano, P. R.; Kunze, K. L. *J. Am. Chem. Soc.* **1981**, *103*, 6534.

(2) Brothers, P. J.; Collman, J. P. *Acc. Chem. Res.* **1986**, *19*, 209.

(3) Wayland, B. B.; Van Voorhees, S. L.; Wilker, C. *Inorg. Chem.* **1986**, *25*, 4039.

(4) Ogoshi, H.; Setsume, J.; Yoshida, Z. *J. Am. Chem. Soc.* **1977**, *99*, 3869.

(5) (a) Clarke, D. A.; Grigg, R.; Johnson, A. W. *J. Chem. Soc., Chem. Commun.* **1966**, 208. (b) Lancon, D.; Cocolios, P.; Guilard, R.; Kadish, K. M. *Organometallics* **1984**, *3*, 1164. (c) Clarke, D. A.; Dolphin, D.; Grigg, R.; Johnson, A. W.; Pinnock, H. A. *J. Chem. Soc. C* **1968**, 881. (d) Reed, C. A.; Mashiko, T.; Bentley, S. P.; Kastner, N. E.; Scheidt, W. R.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1979**, *101*, 2948. (e) Ortiz de Montellano, P. R.; Kunze, K. L.; Augusto, A. *J. Am. Chem. Soc.* **1982**, *104*, 3545. (f) Cocolios, P.; Laviron, E.; Guilard, R. *J. Organomet. Chem.* **1982**, *228* C39. (g) Mansuy, D.; Battioni, J.-P. *J. Chem. Soc., Chem. Commun.* **1982**, 638. (h) Cocolios, P.; Lagrange, G.; Guilard, R. *J. Organomet. Chem.* **1983**, *253*, 65. (i) Battioni, J.-P.; Lexa, D.; Mansuy, D.; Saveant, J.-M. *J. Am. Chem. Soc.* **1983**, *105*, 207. (j) Lexa, D.; Mispelter, J.; Saveant, J.-M. *J. Am. Chem. Soc.* **1981**, *103*, 6806. (k) Ogoshi, H.; Sugimoto, H.; Yoshida, Z. I.; Kobayashi, H.; Sakai, H.; Maeda, Y. *J. Organomet. Chem.* **1982**, *234*, 185. (l) Mansuy, D.; Battioni, J.-P.; Dupre, D.; Sartor, E. *J. Am. Chem. Soc.* **1982**, *104*, 6159. (m) Lagrange, G.; Cocolios, P.; Guilard, R. *J. Organomet. Chem.* **1984**, *260*, C16. (n) Cocolios, P.; Lagrange, G.; Guilard, R.; Oumous, H.; Lecomte, C. *J. Chem. Soc., Dalton Trans.* **1984**, 567.

(6) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529.

(7) Baldwin, R. A.; Cheng, M. T. *J. Org. Chem.* **1967**, *32*, 1572.

(8) An additional minor signal seen at −18.4 ppm is due to the monomeric chlorobutyl- or butyliron(III) tetraphenylporphyrin complex [(TPP)-FeBu].[9] Signals at 12.0, 11.6, and 13.5 ppm in Figure 1A,B and 49.0 ppm in Figure 1B are due to unreacted (TPP)FeCl, and iron(II) porphyrin from autoreduction by local excess quantities of the lithium reagent during mixing, and from the dinuclear oxoiron(III) porphyrin, resulting from trace water or oxygen contamination. Porphyrin phenyl proton NMR signals for the dinuclear butyl- and phenyl-bridged iron(III) porphyrin complexes are observed in the 4.0–6.0 ppm region.

(9) Arafa, I. M.; Shin, K.; Goff, H. M. *J. Am. Chem. Soc.* **1988**, *110*, 5228.

(10) (a) La Mar, G. N.; Walker, F. A. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, pp 61–157. (b) Goff, H. M. In *Iron Porphyrins—Part* I; Lever, A. B. P., Gray, H. B., Eds.; Addison Wesley: Reading, MA, 1982; pp 237–281.

(11) Arasasingham, R. D.; Balch, A. L.; Latos-Grazynski, L. *J. Am. Chem. Soc.* **1987**, *109*, 5840.

0020-1669/90/1329-0889$02.50/0

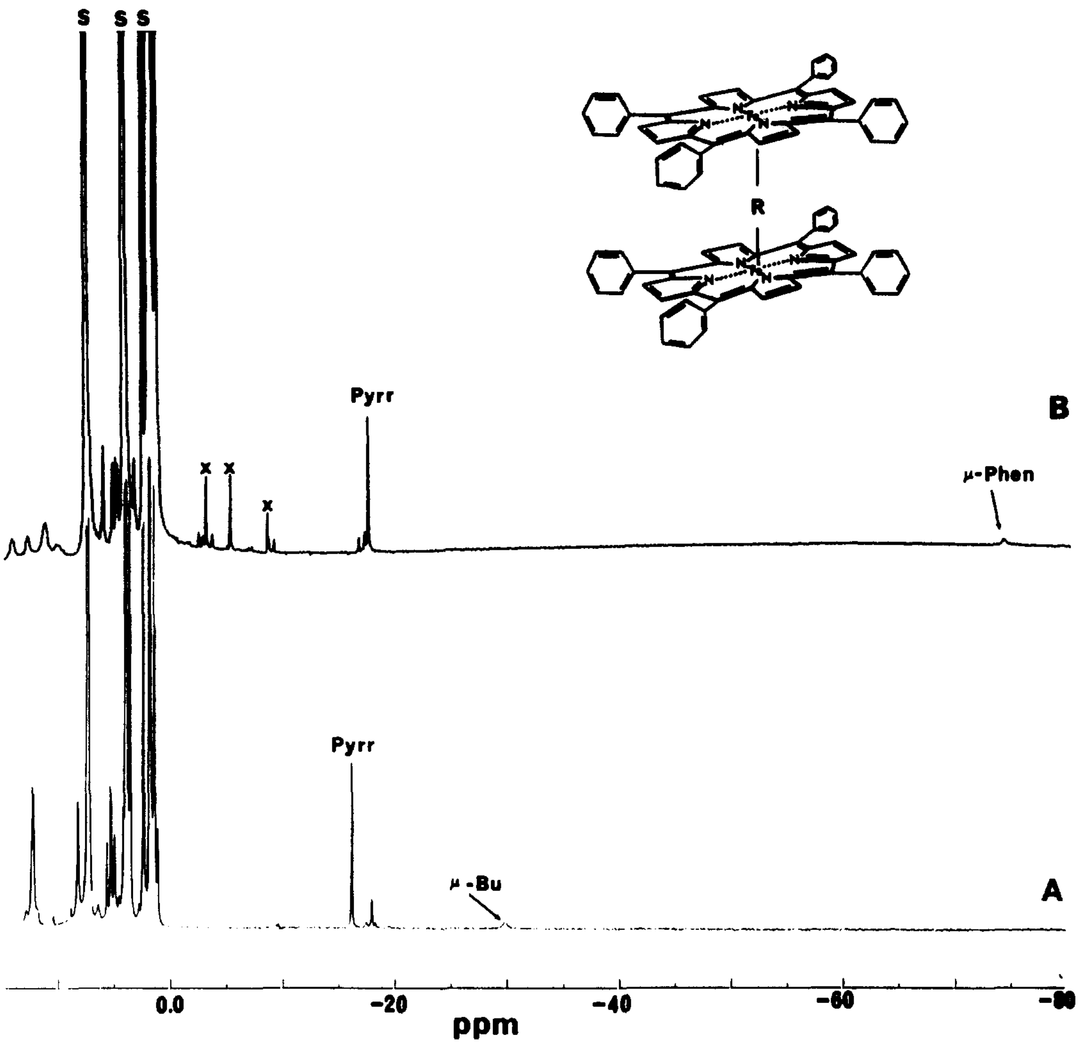

Figure 1. (A) Proton NMR spectrum (300 MHz) for $[(TPP)Fe^{III}]_2C_4H_8$ in toluene-d_8 solution, at 25 °C (chemical shifts referenced to $(CH_3)_4Si$). (B) Proton NMR spectrum (360 MHz) for $[(TPP)Fe^{III}]_2C_6H_4$ in toluene-d_8 solution, at 25 °C ("X" represents instrumental artifacts).

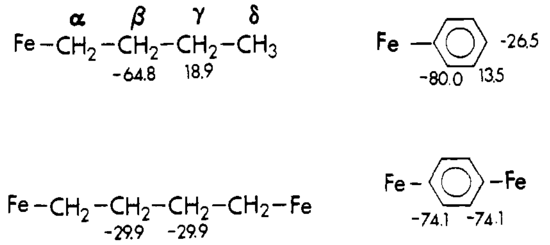

Figure 2. Chemical shift data for coordinated alkyl and aryl mononuclear and dinuclear iron(III) porphyrin complexes, at 25 °C ($(CH_3)_4Si$ reference).

position at −17.7 ppm and the bridged phenyl proton signal position at −74.1 ppm for at least 24 h at room temperature.

In summary, the dinuclear alkyl- and aryl-bridged iron(III) porphyrins were generated by reaction of chloroiron(III) porphyrins with appropriate dilithium reagents. The aryl-bridged iron(III) dimer is EPR inactive at liquid nitrogen temperature. Although the dinuclear iron(III) tetraphenylporphyrin complexes are readily decomposed by O_2, the fluorinated-phenyl iron(III) aryl-bridged complex $[(Fe_{20}\text{-}TPP)Fe\text{-}(C_6H_4)\text{-}Fe(F_{20}\text{-}TPP)]$ shows remarkable stability against CO and O_2 at room temperature.

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