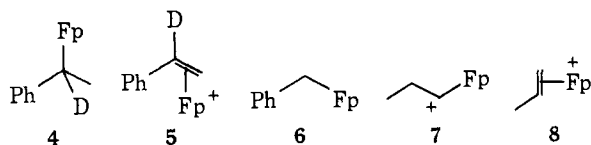yield sparingly soluble, brightly colored, uncharacterized metal-containing solids and **1a**.

α-Hydride abstraction from a hydrocarbon ligand to our knowledge is without precedent. Generally β-hydride abstraction occurs if possible. Thus **4** is

converted to the styrene complex **5** by β-hydride abstraction with complete retention of deuterium. In the absence of β-hydrogens such as in the benzyl complex **6**, trityl adds directly to the ligating carbon to form 1,1,1,2-tetraphenylethane. It is interesting that **1a** undergoes neither of these processes. The reluctance of **1a** to undergo β-hydride abstraction to form **3** suggests that the *dihapto*benzocyclobutadiene ligand in **3** may retain some of the antiaromaticity of the parent hydrocarbon and thus destabilize **3** relative to **2**. A further indication that **3** may be unusually energetic is the failure of **2** to rearrange to **3** in a manner similar to the reported rearrangement of the propylidene complex[3] (**7**) to the corresponding propene complex (**8**). The addition of trityl to the ligating carbon in **1a** seems to be precluded on steric grounds.

Acknowledgment. We gratefully acknowledge the generous support of the Graduate School of Boston University and the donors of the Petroleum Research Fund, administered by American Chemical Society.
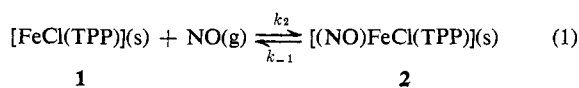
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Reversible Addition of Nitric Oxide to a Solid Ferric Porphinato Complex. Thermodynamics of Formation and Characterization of a Peculiar NO Adduct

Sir:

We wish to report an unusual interaction involving chlorotetraphenylporphinatoiron(III) ([FeCl(TPP)]) and nitric oxide (eq 1) and producing a weakly bonded NO

$$[\text{FeCl(TPP)}](s) + \text{NO}(g) \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} [(\text{NO})\text{FeCl(TPP)}](s) \qquad (1)$$

$$\mathbf{1} \qquad\qquad\qquad\qquad \mathbf{2}$$

addition compound (**2**) which rapidly reverts to the square-pyramidal starting material (**1**)[1] on removal of nitric oxide from the environment. NO gas (purified, $-78°$, KOH) uptake by crystalline **1** is slow under mild conditions: at $P_{\text{NO}} = 760$ mm and $25°$, the equilibrium is attained after *ca.* 7 days, and about 92% conversion to **2** is observed (98% at 0°). In solution (CH_2Cl_2 or CHCl_3), the formation of the same NO adduct is complete within seconds, and purple crystals of **2** are obtained when solutions of **1** (CHCl_3) and NO (EtOH) are mixed. *Anal.* Calcd for $\text{FeClON}_5\text{C}_{44}\text{H}_{28}$:

(1) J. L. Hoard, G. H. Cohen, and M. D. Click, *J. Amer. Chem. Soc.*, **89**, 1992 (1967).

Fe, 7.61; N, 9.54; C, 71.99; H, 3.85. Found: Fe, 7.96; N, 9.71; C, 71.28; H, 4.01; N:Fe = 4.9.

Complex **2** instantly loses nitric oxide when dissolved in (NO-free) organic solvents. In the solid state (in air), gradual dissociation of NO from **2** occurs, and a quantitative recovery of [FeCl(TPP)] has been observed within 3 days; on pumping ($25°$), the conversion (k_{-1}, eq 1) is complete in minutes. The thermodynamics of the solid–gas reaction (eq 1) have been determined by measuring the equilibrium NO pressure (220–685 nm) as a function of temperature (25–$70°$).[2] At $25°$, the calculated parameters are: K_p, 3.45 atm^{-1}, $\Delta G = -0.74$ (0.03) kcal/mol, $\Delta H = -5.26$ (0.14) kcal/mol, $\Delta S = -15$ (0.5) eu. These data conform with the qualitative observations on the facile reversibility of the reaction, and it is seen that the small enthalpy change (ΔH)[3,4] barely compensates for the unfavorable negative entropy (expected for simple addition reactions of this type[4]).

The spectral properties of the NO adduct are also somewhat unexpected. (a) No change in the Fe–Cl stretching frequency accompanies the reaction; in both **1** and **2**, $\nu_{\text{FeCl}} = 378$ cm^{-1}.[5] (b) There is no significant change in the electronic spectrum in the 400–1000-nm region when nitric oxide is added to a degassed CH_2Cl_2 solution of [FeCl(TPP)];[6] however, a new weak band at 380 nm and a stronger one near 250 nm are observed. (c) The ir spectrum of **2** shows a strong absorption band at 1881 cm^{-1}, assignable to coordinated ν_{NO}, but which only slightly differs from the corresponding value of gaseous nitric oxide, 1876 cm^{-1}.[7a] There is another new band at 680 cm^{-1} which may derive from $\nu_{\text{Fe--NO}}$.[7b]

Some of these spectral data, together with the facile removal of NO even from crystalline [(NO)FeCl(TPP)], and the low heat of its formation, may seem to suggest that the nitric oxide in **2** is associated with a peripheral part of the complex (ligands), rather than the central metal atom, and/or involve some kind of "physical adsorption."[3] The latter possibility, however, is excluded by the observed *stoichiometry* of the reaction (eq 1) substantiated above.

Evidence for a Fe–NO linkage in **2** (supported by the rapidity of the reaction in solution) and a possible explanation for the relative weakness of this bond derive from magnetic data. Addition of NO to the high-spin

(2) We thank Professor H. H. G. Jellinek for loan of the apparatus; H. H. G. Jellinek and J. E. Clark, *Can. J. Chem.*, **41**, 355 (1963).

(3) (a) It is generally considered that heats ($-\Delta H$) of gas–solid interactions in the range of 2–5 kcal reflect physical adsorption; (b) G. C. Bond, "Catalysis by Metals," Academic Press, New York, N. Y., 1962, p 52.

(4) (a) For simple addition reactions related to the type reported here, the negative enthalpies are usually larger than the one found here. (b) L. Vaska, *Accounts Chem. Res.*, **1**, 335 (1968); (c) L. Vaska and M. F. Werneke, *Trans. N. Y. Acad. Sci.*, **33**, 70 (1971); (d) L. Vaska, L. S. Chen, and C. V. Senoff, *Science*, **174**, 587 (1971).

(5) (a) There are, however, precedents for similar insensitivities when axial ligands are added[5b] or the oxidation state of the metal is changed.[5c] (b) M. Tsutsui, D. Ostfeld, and L. M. Hoffman, *J. Amer. Chem. Soc.*, **93**, 1820 (1971); (c) J. Takemoto, B. Hutchinson, and K. Nakamoto, *Chem. Commun.*, 1007 (1971).

(6) (a) This observation is compatible with a report that no visible spectral changes are detected when iron porphyrinato complexes are treated with NO in *neutral* aqueous solution; changes do occur, however, when the solution is alkaline or acidic.[6c] See also (b) J. C. W. Chien, *J. Amer. Chem. Soc.*, **91**, 2166 (1969); (c) J. Keilin, *Biochem. J.*, **59**, 571 (1955).

(7) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley-Interscience, New York, N. Y., 1970, (a) p 78; (b) p 201.

ferric complex **1** (μ = 5.8 BM)[8] reduces the magnetic moment to 4.5 BM (25°)[8] in **2**. This change may tentatively be interpreted as a reduction of **1** by NO to give a high-spin and formally octahedral ferrous complex (although the μ of **2** is somewhat lower than the calculated spin-only value, 4.9 BM; alternatively, the magnetic result may reflect the presence of a spin equilibrium). The relatively high ν_{NO} is consistent with the presence of formal NO⁺ in **2**. These observations and their interpretation have interesting analogies pertaining to related systems in molecular biology and surface chemistry: (a) it has been shown that the reaction of nitric oxide with methemoglobin is accompanied by the reduction of the latter,[6b] and (b) the reversible chemisorption of NO on ferric oxide gel results in ir absorption bands ranging from 1738 to 1927 cm⁻¹, the principal ν_{NO} occurring at 1806 cm⁻¹.[9]

If our NO adduct **2** is viewed as a high-spin Fe(II) complex, one is then tempted to speculate that the apparently low Fe–NO bond energy results from the inability of the ferrous atom to move into the porphinato plane, and is thus responsible for the implied relatively long Fe–NO linkage. The iron atom in **1** is known to be located out of the planar N_4 porphinato core by *ca.* 0.4 Å,[1] and there is much current evidence for and discussion of the importance of the relationship between the out-of-plane high-spin (large) and in-plane low-

spin (small) Fe(II) in biological heme[10] and model heme-like[11] systems (*cf.* also ref 5b).

The preliminary interpretation considered here involves pairing of two electrons whose energy may amount to several tens of kilocalories[12] and which would hence rationalize the low heat of NO adduct formation and "elevate" the Fe–NO bond energy to a "weak single bond" category even when other energy terms (associated with changes in crystal structure and NO bond order) are neglected.[13] According to a suggested scheme,[14] the formally octahedral **2** is a 22-electron system and should exhibit a linear Fe–N–O bonding. It should be noted that no detectable reactions of [FeCl(TPP)] (in the solid state or solution) take place with CO, SO₂, or O₂ under normal conditions. Complex **1** does, however, take up N_2O_4 and the reaction appears to include nitration of the porphinato ligand.[15]

(8) Corrected for the diamagnetism of the complex.
(9) A. N. Terenin and L. M. Roev, as quoted by L. H. Little, "Infrared Spectra of Adsorbed Species," Academic Press, New York, N. Y., 1966, pp 86, 87.

(10) R. E. Dickerson, *Annu. Rev. Biochem.*, **41**, 815 (1972).
(11) D. M. Collins, R. Countryman, and J. L. Hoard, *J. Amer. Chem. Soc.*, **94**, 2066 (1972), and references quoted; J. P. Collman and C. A. Reed, *J. Amer. Chem. Soc.*, **95**, 2048 (1973).
(12) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience-Wiley, New York, N. Y., 1972, p 565.
(13) See ref 4c for discussion of a related problem.
(14) C. G. Pierpont and R. Eisenberg, *J. Amer. Chem. Soc.*, **93**, 4905 (1971).
(15) We thank the Environmental Protection Agency and National Institutes of Health for the support of this research.

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Book Reviews

Carbon-13 Spectroscopy. By J. B. STOTHERS (University of Western Ontario). Academic Press, New York and London. 1972. xi + 599 pp. $24.00.

Carbon-13 Nuclear Magnetic Resonance for Organic Chemists. By GEORGE C. LEVY and GORDON L. NELSON (General Electric Corporate Research and Development). Wiley-Interscience, New York and London. 1972. xii + 222 pp. $9.95.

Stothers' book, which is Volume 24 of "Organic Chemistry. A Series of Monographs," will be very useful to any type of scientist who is considering the application of ¹³C nmr. The author has presented us with a well-written, superbly organized, and highly documented account of developments in ¹³C spectroscopy through mid-1970 at a time when instrumental developments have made the acquisition of ¹³C nmr spectra practical on a routine basis. The book is divided into four parts. Part I is a survey of the experimental methods which have been and are being used (including pulse-Fourier transform techniques) for the detection of ¹³C resonances. This section is particularly useful, for it discusses the errors which were inherent in the early measurements. Carbon-13 shieldings are exhaustively dealt with in Part II. The chemical shifts of hydrocarbons, their functional derivatives, organometallic compounds, carbonium ions, heterocyclic systems, and metal carbonyls are tabulated and discussed. Empirical additivity relationships and data trends are presented and analyzed. A separate chapter deals with the theory of hydrocarbon shielding The author should be applauded for presenting all the chemical shift data relative to a single standard (tetramethylsilane). In Part III the author surveys the area of carbon-13 coupling constants. The discussion includes experimental techniques, theory, and a concise tour of the ¹³C–¹H, ¹³C–¹⁹F, ¹³C–¹³C, and ¹³C–X coupling constant literature. It was not the author's intention to present an exhaustive treatment in this section since there are several other good

reviews in existence. In Part IV, the author illustrates the application of ¹³C nmr to structure elucidation, stereochemical assignments, conformational analysis, natural products, polymers, tracer techniques, and solute-solvent interaction. An especially useful feature of this book is that in addition to a subject index and an author index it possesses a compound index. The clarity of writing, the depth of organization and presentation, the frequent and lucid use of tables and structures, and the extensive cross referencing all make this a very useful and enjoyable book.

Levy and Nelson have used principally the ¹³C nmr literature of 1970-1971 as a data base to construct a concise discussion of the application of ¹³C nmr to organochemical problems. It is the authors' goal to bring the reader to a state of knowledge which will enable him to use ¹³C in his research, and it appears that this is the case as long as the book is used carefully and the references are consulted frequently. The book emphasizes the use of ¹³C nmr in structure assignment and includes problems with answers. The authors have not attempted to present theory in anything but a very qualitative manner and have also not attempted to cover the literature prior to 1970. The differences between ¹H and ¹³C nmr are continually pointed out, and the book begins by discussing pulse-Fourier transform nmr techniques and the general characteristics of ¹³C spectra. Data trends in the chemical shifts of hydrocarbons and their functional derivatives are discussed in the next several chapters. The data are clearly tabulated, and the various methods of spectral assignment are presented with emphasis on the more recent literature. Additivity relationships, steric and electronic effects, and solvent effects are appropriately mentioned where they are important but are not amplified or critically analyzed. Succeeding chapters deal with ions, organometallic species, polymers, and biomolecules. One of the strong points of this book is the discussions of relaxation studies and their applicability to struc-