3 (8%). When **2** was obtained as pure nitrilium salt (free from excess Et₃OBF₄ and volatile impurities) and hydrolyzed, the reaction products were exceptionally dependent on temperature and reaction times. For example, when **2** was hydrolyzed with boiling water for 60 min, boric acid was the only boron-containing product observed. However, when hydrolysis time was reduced to 5 min, a 12% yield of **4** was obtained apart from boric acid formation. At 40–50 °C for 30 min, there was no acid **4** formation but only imine **3** product. A systematic study using different reaction times and temperatures showed that hydrolysis of pure **2** at 60–70 °C for 15 min offers **4** in reasonably good yield (41%).

Cold alkaline hydrolysis of **2** gave **5**, whose IR and ¹H NMR data (Table I) are consistent with the anticipated structure. Characteristic absorptions of boranocarbamoyl at 1593 and 1488 cm⁻¹ (amide I and II bands) were observed.

Reaction of **2** with methanol in CH₂Cl₂ followed by alkaline treatment gave C₅H₅N·BH₂C(OCH₃)=NEt (**6**). The IR spectrum showed an absorption at 1620 cm⁻¹ for C=N, overlapping with the C=C band at 1625 cm⁻¹. The ¹H NMR spectrum was consistent with the structure. For an acyclic imidate, the typical products of hydrolysis at low pH are an ester and amine.[9] Acidic hydrolysis of **6** with 0.5 N HCl did not proceed to the ester even at 50 °C for 6–8 h but formed a stable salt of imino ether. This may be due to greater basicity of the imino ether adjacent to a boron moiety, as was observed for boranocarbamoyl derivatives.[10] Under forced reaction conditions (100 °C) boric acid formation resulted. However, hydrolysis of **6** at neutral pH (50 °C, 8 h) gave a 40% yield of the ester C₅H₅N·BH₂COOCH₃ **7**. The IR spectrum exhibited characteristic B–H and C=O absorptions, and the ¹H NMR spectrum was consistent with the structure (Table I).

The ¹¹B NMR spectrum (Table I) of each compound consisted of a distinct triplet (except **2**, which was a very broad triplet, which collapsed to a singlet upon ¹H-decoupling. Only salts **2** and **3** showed another boron signal, but this was attributable to BF₄⁻.

Since other amine·BH₂X adducts (X = CN, CONHR, COOR, CO₂H) including C₅H₅·BH₂CO₂H possess biological activity,[2–4] these compounds are being examined to determine the effect these functional groups have on the biological activity of the molecule.

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Convenient Small-Scale Method for the Insertion of Iron into Porphyrins

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The use of isotopes in the study of complex molecules is becoming increasingly important because of the rapid advance in NMR techniques. Isotope-edited 2D NMR experiments will allow assignment of complex spectra and direct observation of "odd" nuclei provide unique information about structure and bonding that is not otherwise accessible. In many cases, this strategy

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requires isotopic enrichment using expensive materials. Convenient and efficient preparative methods are therefore needed. In our ongoing studies of heme models and heme proteins using ⁵⁷Fe NMR,[1] we needed an efficient and mild small-scale insertion procedure for iron. In this note, we report a novel method for the incorporation of iron that is enriched in ⁵⁷Fe, the only NMR and Mössbauer active nucleus, into a number of heat-sensitive porphyrins, namely the "picket-fence" porphyrin[2] and some of the "basket-handle" porphyrins.[3]

Iron porphyrins are the prosthetic groups in many biological systems that are essential to the life processes. Well-known examples are the cytochromes, hemoglobin, and myoglobin. Several synthetic models have been designed and synthesized in order to study carbon monoxide and dioxygen binding[3–6] and electron transport.[7] A critical step in these syntheses is the insertion of the iron atom.[8] Only ferrous salts will react with porphyrins, but trace amounts of oxygen will oxidize the iron atom to the unreactive ferric state. A common solution to this problem is to use large excesses of ferrous salts. With isotopically enriched iron, this is however not possible. We therefore present a new route for insertion of iron into porphyrins using Fe₂O₃ as starting material that is based on in situ reduction of the ferric chloride. This method is quite convenient, mild, relatively fast, and easy to handle on a small scale. In contrast, a separate preparation of ferrous salts on a milligram scale for insertion into the reaction mixture is impractical.

A slight excess of iron (typically 1.7 times the molar amount of porphyrin) is used to make the insertion quantitative. The excess can easily be recovered after the reaction is complete. The iron oxide is dissolved in hot, concentrated hydrochloric acid, and the mixture is taken to almost dryness. Chlorobenzene is added, and the water is removed by azeotrope distillation. The ferric chloride is then reduced to ferrous chloride at 132 °C by the chlorobenzene, which acts both as a reagent and a solvent in the reaction.[9] After the reduction is complete, as judged by the change of color, the temperature is allowed to drop to a suitable level for the iron insertion, typically 70 °C, and the porphyrin is added, dissolved in chlorobenzene. It is of great importance that the reaction atmosphere is oxygen-free. The reaction mixture is therefore kept under a slight positive pressure of argon, and the porphyrin solution is degassed by three freeze–pump–thaw cycles, before entering the reaction flask.

⁵⁷Fe has been inserted into the following series of porphyrins in quantitative yield by this route: tetraphenylporphyrin, α,α,-α,α-*meso*-tetrakis(*o*-pivalamidophenyl)porphyrin,[2] α-5,15-(2,2′-(nonanediamido)diphenyl)-α,α-10,20-bis(*o*-pivalamido-phenyl)porphyrin, α-5,15-(2,2′-(decanediamido)diphenyl)-α,α-10,20-bis-(*o*-pivalamidophenyl)porphyrin, α-5,15-(2,2′-(dode-canediamido)diphenyl) α,α-10,20-bis(*o*-pivalamidophenyl)-porphyrin. Apart from tetraphenylporphyrin, these porphyrins will all isomerize at high temperature. The reaction time has been 4–16 h, and very little, if any, isomerization occurred.

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Experimental Section

^{57}Fe$_2$O$_3$ (16.2 mg, 0.100 mmol) was heated to 50 °C in concentrated hydrochloric acid (5 mL) for 1 h or until there was no trace of solid Fe$_2$O$_3$. The hydrochloric acid was evaporated in vacuo to near dryness. Chlorobenzene (100 mL, freshly distilled from CaH$_2$) was added to the aqueous ferric chloride, and the mixture was heated to reflux under argon. About 50 mL of the solvent was distilled off in order to remove the remaining water as an azeotrope. The color of the suspension shifted from pale yellow to dark brown as the anhydrous iron was reduced.[9] The temperature was then allowed to drop to 70 °C. The porphyrin (0.118 mmol) was dissolved in chlorobenzene (4 mL, freshly distilled from CaH$_2$) and 2,4,6-trimethylpyridine (0.15 mL) was added. The solution was degassed by three freeze–pump–thaw cycles and transferred to the ferrous chloride suspension via a gastight syringe. The atmosphere in the reaction flask was carefully kept free from oxygen.

The reaction was followed by measurement of the electronic absorption spectra of aliquots of the solution. After 4–16 h, the insertion was complete and the solvent was evaporated. The residue was dissolved in toluene (50 mL) and extracted with several portions of water to remove the excess of iron, which can thus be recycled. The porphyrin solution was then washed with hydrochloric acid (4 × 15 mL, 0.2 M) and water (2 × 20 mL). The organic layer was dried over Na$_2$SO$_4$, and the solvent was evaporated. The iron(III) porphyrin chloride was recrystallized from CH$_2$Cl$_2$/hexane, and a typical yield was 0.112 mmol (95%). It is easily identified by the electronic absorption spectrum in the visible region and the ^{1}H NMR spectrum, which shows large, positive paramagnetic shifts.[3]

Registry No. ^{57}Fe$_2$O$_3$, 64886-55-1; HCl, 7647-01-0; ^{57}FeCl$_3$, 120028-37-7; ^{57}FeCl$_2$, 75297-20-0; ^{57}Fe(tetraphenylporphyrin), 124419-55-2; ^{57}Fe[$\alpha,\alpha,\alpha,\alpha$-*meso*-tetrakis(*o*-pivalamidophenyl)porphyrin], 124419-56-3; ^{57}Fe[α-5,15-(2,2′-(nonanediamido)diphenyl)-α,α-10,20-bis(*o*-pivalamidophenyl)porphyrin], 124419-57-4; ^{57}Fe[α-5,15-(2,2′-(decanediamido)diphenyl)-α,α-10,20-bis(*o*-pivalamidophenyl)porphyrin], 124419-58-5; ^{57}Fe[α-5,15-(2,2′-(dodecanediamido)diphenyl)-α,α-10,20-bis(*o*-pivalamidophenyl)porphyrin], 124419-59-6.

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Electronic Energy Transfer from Zerovalent Binuclear Tungsten Carbonyl Complexes to Organic Triplet States

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There has been substantial interest in the mechanism of electron-, charge-, and energy-transfer reactions of coordination complexes.[1,2] Lately, much attention has been paid to optically induced energy and electron transfer between transition-metal chromophores that are covalently linked in a supermolecular structure.[3] Intramolecular mechanisms of mixed-valence dimer and trimer complexes have been extensively studied.[4]

The most systematic investigations to date, however, have been concerned with the quenching of organic triplet states by a series

of Cr(III) complexes.[5] Notably, even though all of the acceptors have lowest energy excited states (^2E_g) considerably below the donor energy levels (^{3}D*), the obtained quenching rate constants (k_q) are abnormally low and differ substantially over the range of complexes. A general classical treatment of vertical and nonvertical energy transfer has been applied by Balzani et al. to explain this nonadiabatic behavior, and these authors have concluded that the preexponential factor of the energy-transfer rate constant is the rate-determining parameter in the exothermic energy-transfer mechanism.[6] This classical approach to energy transfer is analogous to the treatment of outer-sphere electron-transfer reactions.[6,7] In related work, Wilkinson et al. have illustrated that these lower transmission coefficients for collisional energy transfer are, in part, due to steric effects of the ligand substituent groups in these Cr(III) complexes[5b,8] and in other metal complex acceptors.[9]

Most investigations at this time have involved organic triplet states as energy donors, and relatively few have been concerned with energy-transfer mechanisms for inorganic molecules as the energy donors.[10] In particular, detailed quenching studies of transition-metal organometallic complexes as energy donors have not previously appeared. A number of metal carbonyl complexes have now been established to luminesce in room-temperature hydrocarbon solution, and although the radiative routes are invariably thought to originate from metal-to-ligand charge-transfer excited states,[11] the precise energy positions of these emitting levels have rarely been determined. Moreover, the opportunity now exists to explore energy transfer from low-valent organometallic molecules to organic triplet states. In this paper we report the results of such a study for the ligand-bridged zerovalent (OC)$_5$W-(bpy)W(CO)$_5$ (bpy = 4,4′-bipyridine) complex.

Experimental Section

Materials and Synthesis. Starting material tungsten hexacarbonyl was obtained from Strem Chemical Co. and used without further purification. The ligand 4,4′-bipyridine (bpy) was obtained from Aldrich Chemical Co. and recrystallized prior to use. Quenchers employed were all purchased from Aldrich Chemical Co. and purified by vacuum sublimation or distillation under N$_2$, as appropriate. Benzene used as solvent in the photophysical measurements was obtained from J. T. Baker Chemical Co. as Photrex grade. All other chemicals and solvents used in the synthesis of (OC)$_5$W(bpy)W(CO)$_5$ were of reagent grade. Nitrogen used for purging samples was rigorously deoxygenated and dried according to a reported procedure.[12] The complex (OC)$_5$W(bpy)W(CO)$_5$ was prepared and purified as described previously.[13]

Equipment and Procedures. Absorption spectra were recorded on a Hewlett-Packard 8450A spectrometer, which utilizes a microprocessor-controlled diode-array detector. In the emission experiments the sample

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