The emission decays are nonexponential and can be fit with a sum of two exponentials (typically τ_1 was less than a factor of 2–5 longer than τ_s). The weighted averages of the lifetimes are reported in Table I. From the average τ values, radiative and nonradiative rate constants were calculated. Radiative lifetimes are on the order of hundreds of microseconds. The two apparent lifetimes may arise from cis–trans isomer pairs. However, the need for a double exponential fit for **2**, which has only a single isomer, suggests a different explanation. These complexes exist in a variety of different conformations, each with a potentially different lifetime. We suggest that the nonexponentiality arises from site heterogeneity. We have seen heterogeneity effects in mononuclear Pt complexes.[13]

In the presence of heterogeneity, the decomposition of the luminescence decays into their components is not meaningful. Further, since we do not know the number of or the quantum yields for the different conformers, there is no reason to use anything other than an average lifetime in our estimation of the radiative and nonradiative rate constants.

X-ray crystallographic structure determinations have been performed for complexes **1, 3, 5, 8,** and **12.**[3,12] Figure 1 diagrams the skeletal geometry of the dinuclear platinum complexes with bridging alkenylidene ligands. The principal coordination planes of the two platinum centers are nearly orthogonal to one another, but the two Pt atoms and the alkenylidene ligand are essentially coplanar.

The geometrical complexity and the low symmetry of these complexes results in a large number of possible electronic transitions. Phenylacetylene absorbs below 250 nm, and for those complexes with the phenylacetylide ligand, the absorption spectrum in this region must involve at least some contribution from ligand-localized transitions involving this species. PEt_3 absorbs at 230 and 325 nm, but these absorptions are far too weak to give rise to the bands observed in the dinuclear platinum spectra. We conclude that the bands at longer wavelengths than 250 nm must be charge-transfer or metal-centered transitions.

We now consider in detail the nature of the chromophoric group and the direction of charge movement in the lowest energy excited state. In view of the similarity of the lowest absorption and the emission of **1** and **2**, these transitions must involve the acetylide, the Pt—Pt group, and the C=C moiety. Since removing the acetylide does not affect the nature of the lowest state (compare **3–5** with **7–9**), the chromophoric group must be the Pt_2C=C portion. As we will now show, the lowest state must arise from a Pt_2 to C=C charge-transfer transition.

The spectrum of **2** is similar to the spectra of the phenyl-substituted complexes, although the <280-nm region is less intense, suggesting that this region is dominated by CT transitions. The lowest energy band is blue-shifted relative to the analogous band of **1**. We attribute this band to a Pt_2-to-alkenylidene charge-transfer transition (MLCT) and explain the dependence of the band position on the identity of the substituent in terms of the ability of a Ph group to stabilize the negative charge relative to a H atom. This band is present in complexes **1–11**, which all have bridging alkenylidene ligands, and is absent from the spectrum of **12**, which does not have this structural feature (see Figure 2C).

The position of the low-energy band is also dependent upon the substitution on the Pt_2 in a manner that supports our assignment. As more electronegative groups are substituted for the PEt_3 and phenylacetylide ligands, the low-energy band shifts to higher energy. The electronegative groups drain electron density from the platinum atoms, making transfer of charge away from the metals a more energetic process. This trend is echoed in the shortening of the Pt–Pt bond lengths as ligands of increasing electronegativity and number are substituted on the complex: **1,** 2.750 (2) Å; **3,** 2.721 (1) Å; **5,** 2.711 (1) Å; and **8,** 2.685 (1) Å. The interatomic repulsion between the two formally negative Pt atoms is alleviated as the charge is decreased by the electron-withdrawing substituents. This argument holds, whether or not

one accepts the antibonding Pt–Pt interactions of the molecular orbital calculations.[3]

The emissions of these complexes track the MLCT absorption bands, having a nearly constant energy separation of ~11 000 cm^{-1} for all the alkenylidene complexes with phenyl substituents. The radiative lifetimes, τ_r, which are all in the 10–330-μs range, indicate that the process is not a fluorescence, and we attribute the emission to the spin-forbidden Pt_2-to-alkenylidene CT transition. The large Stokes shift implies a significant distortion of the geometry of the complexes upon excitation. This effect may be a manifestation of the decreased Pt–Pt repulsion when an electron is promoted from the dinuclear fragment.

Complexes **1, 6,** and **11** do not emit. If these complexes have the same energy separation between the low-energy absorption band and the emission band as do the other complexes in the series, the emission bands would occur at 725, 1051, and 771 nm, respectively. The energy gap law predicts that the nonradiative decay rates for these complexes would be larger than those for complexes with higher energy emissions. Also, the sensitivity of our phototube is poor this far to the red, and so, we would not expect to be able to detect even the 725-nm emission easily.

Our results suggest ways to design molecules with enhanced luminescence efficiency. The low quantum efficiency of most of the complexes can be largely ascribed to the low emission energy and to efficient radiationless deactivations. Increasing the emission energies will result in increased emission efficiency. Complex **2** has a hydrogen atom substituted for the phenyl substituent of the phenylethenylidene ligand, and the emission energy is the highest of all the complexes studied. The phenyl analogue (**1**) does not emit all, presumably due to a very low energy of the emitting state. Thus, building a series of complexes analogous to **3–11** with hydrogen atoms replacing the phenyl groups should raise the MLCT state energy, reduce radiationless deactivation, and enhance the luminescence efficiencies.

Clearly, there is a spectator ligand effect on both the lifetimes and quantum yields. The SCN is singular in its impact, having a profound effect on the luminescent efficiency. The origin of this remarkable change is not obvious as neither the ligand field strength nor the π-bonding capability of this ligand is exceptional when compared to Et_3P. At this point we can only note that this and similar ligands are clearly worth additional attention.

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Small-Carborane-Stabilized Iron–Indole and Iron–Thiophene π-Complexes[1,2]

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The scope of organometallic transition-metal sandwich chemistry has been substantially broadened by the introduction of cyclic $R_2C_2B_3H_3^{4-}$ and pyramidal $R_2C_2B_4H_4^{2-}$ ligands in combination with aromatic hydrocarbons.[3] The carborane ligands not only

(1) Organotransition-Metal Metallacarboranes. 22. (a) Part 21: Chase, K. J.; Bryan, R. F.; Woode, M. K.; Grimes, R. N. *Organometallics,* in press. (b) Part 20: Benvenuto, M. A.; Grimes, R. N. *Inorg. Chem.* **1991,** *30,* 2836.
(2) Based in part on the Ph.D. thesis of K.J.C., University of Virginia, 1990.

Scheme I
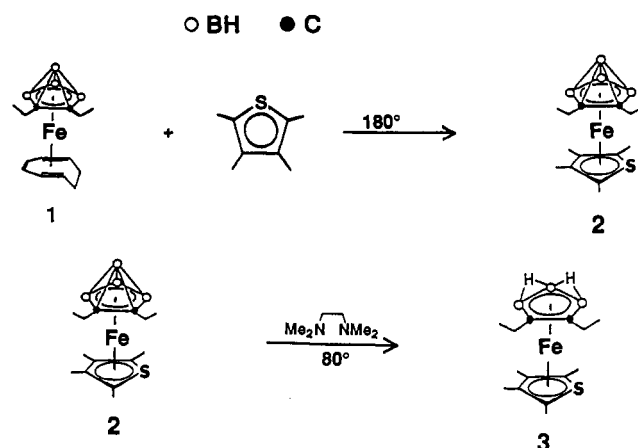
Table I. 115.8-MHz ^{11}B FT NMR Data

compd	δ (J_{BH}, Hz)$^{a-c}$	rel areas
$(Me_4C_4S)Fe(Et_2C_2B_4H_4)$ (2)	4.2 (154), 2.4 (159), 0.5 (207)	1:2:1
$(Me_4C_4S)Fe(Et_2C_2B_3H_5)$ (3)	4.7 (135), -0.5 (127)	1:2
$(HNMe_2C_8H_4)Fe(Et_2C_2B_4H_4)$ (4)	3.6 (138), 0.8,^{d} -0.7	1:1:2
$(MeNMe_2C_8H_4)Fe(Et_2C_2B_4H_4)$ (6)	3.5 (131), 0.6,^{d} -0.9	1:1:2

^{a}Shifts relative to $BF_3 \cdot OEt_2$; positive values downfield. ^{b}Dichloromethane solution. ^{c}H–B coupling constant is given in parentheses, when resolved. ^{d}Overlapping doublets.

serve as electronic stabilizing agents, allowing the generation of otherwise unstable or nonexistent compound types (e.g., Fe-(III)–arene complexes[4]), but also provide convenient loci for controlled attachment of functional groups. This, in turn, has opened possibilities for exploiting this chemistry in the designed synthesis of new materials.[3a,5] Recently, we reported a significant extension of this area with the incorporation of pyrrolyl (C_4N) and phospholyl (C_4P) ligands, including the synthesis of the first known triple-decker sandwiches containing these heterocycles.[1a,6]

The remarkable versatility, stability, and redox chemistry of this class of compounds led us to explore further possibilities for utilizing heterocyclic aromatic ligands. Here we describe studies involving thiophene and indole rings. Our interest in thiophenes, which are cyclic R_4C_4S groups capable of formally replacing arenes as η^5 ligands in metal complexes,[7] grew partly from a desire to extend our earlier pyrrolyl/phospholyl metallacarborane studies to the chalcogen elements. A further point was the potential relationship of this chemistry to hydrodesulfurization,[8] an important commercial process for removing sulfur from petroleum feedstocks; thiophenes are among the most difficult components to desulfurize, and this has led to extensive studies of thiophene–metal complexes.

The indole ring system is closely related both to the pyrroles and to the hydrocarbon indene, the latter of which exhibits a complex and intriguing chemistry in combination with Fe(II)/Fe(III) and small carborane ligands.[9] Of particular interest is the ring migration exhibited by the η^6-indenylferracarborane upon

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Table II. 300-MHz ^{1}H FT NMR Data

compd	δ^{a-c}
2	2.61 m (CH_2), 2.46 m (CH_2), 2.18 s (CH_3), 2.11 s (CH_3), 1.27 t (ethyl CH_3)
3	2.12 m (CH_2), 2.06 s (CH_3), 1.99 m (CH_2), 1.96 s (CH_3), 1.13 t (ethyl CH_3), -6.18 s (B–H–B)
4	6.01 d (CH), 5.81 d (CH), 5.22 t (CH), 5.17 t (CH), 2.34 m (CH_2), 2.31 s (CH_3), 2.21 s (CH_3), 2.00 m (CH_3), 1.16 t (CH_3), 1.07 t (CH_3)
6	5.99 d (CH), 5.78 d (CH), 5.24 t (CH), 5.16 t (CH), 3.62 s (N–CH_3), 2.34 m (CH_2), 2.30 s (CH_3), 2.25 s (CH_3), 2.00 m (CH_3), 1.20 t (CH_3), 1.13 t (CH_3)

^{a}CH_2Cl_2 solution. ^{b}Shifts relative to $(CH_3)_4Si$. Integrated peak areas in all cases are consistent with the assignments given. Key: m = multiplet, s = singlet, d = doublet, t = triplet, q = quartet. ^{c}B–H-(terminal) resonances are broad quartets and mostly obscured by other signals.

Table III. Infrared Absorptions (cm^{-1}; Neat Films on KBr Plates)^{a,b}

compd	absorptions
2	2966 s, 2928 s, 2869 s, 2523 s, 2500 s, 1448 s, 1384 s, 1381 s, 1374 s, 1239 w, 1150 w, 1089 m, 1065 w, 1036 m, 894 w, 874 m, 811 w, 728 w
3	2959 s, 2921 s, 2866 s, 2506 s, 1860 m, 1845 w, 1576 w, 1521 w, 1517 w, 1512 w, 1507 w, 1499 w, 1497 m, 1491 w, 1465 m, 1457 s, 1448 s, 1420 w, 1380 s, 1373 m, 1086 w, 1078 w, 1053 w, 1031 m, 926 w, 779 w
4	2964 s, 2943 s, 2930 s, 2925 s, 2897 s, 2888 s, 2884 s, 2872 s, 2861 s, 2859 s, 2856 s, 2852 s, 2532 s, 2529 s, 1610 m, 1461 s, 1459 m, 1449 m, 1437 m, 1415 m, 1411 w, 1390 w, 1374 w, 1210 w
6	2961 s, 2926 s, 2872 s, 2870 s, 2855 s, 2517 s, 2513 s, 2509 s, 1596 w, 1508 w, 1468 s, 1411 m, 1402 m, 1388 m, 1377 m, 1367 w, 1346 w, 1326 w, 1304 w, 1223 w, 1195 w, 1141 w, 1123 w, 1097 w, 874 w

^{a}Microcrystalline films obtained by evaporation of solutions. ^{b}Key: s = strong, m = medium, w = weak.
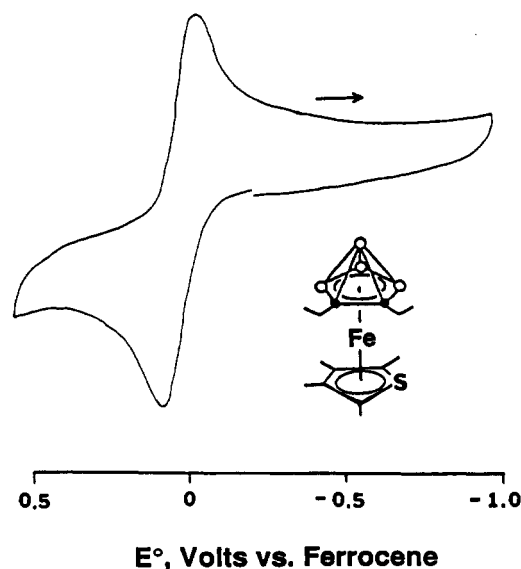

E°, Volts vs. Ferrocene

Figure 1. Cyclic voltammogram of **2** in dichloromethane.

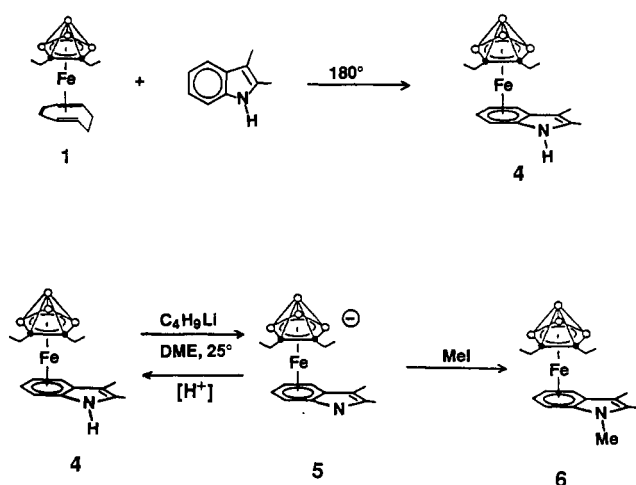deprotonation,[9] which raised the possibility that indolyl-ferracarborane species might behave similarly.

Results and Discussion

Tetramethylthiophene Complexes. Since thiophenes are electrically neutral species, the approach utilized previously to prepare sandwich complexes from the isoelectronic pyrrolide and phospholide ligands ($R_4C_4X^-$) in solution[1a,6] was not applicable here. Instead, we adopted the method developed in our laboratory[10] for

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Scheme II

preparing arene–iron–carborane complexes, in which the cyclo-octatriene ligand is thermally displaced from $(C_8H_{10})Fe(Et_2C_2B_4H_4)$ (1) by neutral arenes. As shown in Scheme I, 2,3,4,5-tetramethylthiophene (chosen for its facile preparation[11] and the assumption that the methyl groups would provide enhanced π-complexing ability) reacts with 1 at 180 °C in a sealed tube to generate the sandwich species $(Me_4C_4S)Fe(Et_2C_2B_4H_4)$ (2), isolated in moderate yield as a red air-stable solid. The proposed sandwich structure of 2 depicted in Scheme I (with arbitrary ring orientation) follows from its ^{11}B and ^{1}H FT NMR, infrared, and mass spectra (Tables I–III and Experimental Section) and is analogous to that of previously characterized (arene)Fe(Et_2C_2B_4H_4) complexes[10a] and their pyrrolyl and phospholyl analogues.[1a,6]

We believe 2 to be novel in two respects, as the first thiophene–metallacarborane sandwich and also, to our knowledge, the first example of a neutral η^5-thiophene–iron complex. Cyclic voltammetry of 2 in dichloromethane gave a reversible 1-electron oxidation at 0.05 V vs ferrocene (Figure 1). This finding can be compared to the oxidations of (arene)Fe(Et_2C_2B_4H_4), which occur reversibly at 0.52 V (for the C_6H_6 complex) and 0.19 V (for the C_6Me_6 species) under identical conditions.[4b] The fact that the iron center is more readily oxidized in 2 indicates that higher electron density resides on the metal in that species and that the thiophene ligand in 2 is a better electron donor than is even hexamethylbenzene in the corresponding arene–ferracarborane series.

Compound 2 is resistant to base-promoted decapitation (removal of the apex BH),[3] as shown by its essential inertness toward tetramethylethylenediamine (TMEDA) at room temperature. At 80 °C the reaction proceeds slowly, forming the open-faced complex $(Me_4C_4S)Fe(Et_2C_2B_3H_5)$ (3) in low yield (Scheme I). Although 3, a slightly air–sensitive orange solid, is readily deprotonated on treatment with NaH in tetrahydrofuran (THF), the anion exhibits no detectable reactivity toward $CoCl_2$ in the presence of the $C_5Me_5^-$ ion; hence, we were unable to prepare $(C_5Me_5)Co(Et_2C_2B_3H_3)Fe(Me_4C_4S)$ triple-decker sandwiches. This observation is in line with earlier work on (arene)Fe(R_2C_2B_3H_5) complexes which also failed to coordinate to a second metal–ligand unit[3a,12] and leaves $CpFe(Et_2C_2B_3H_3)CoCp$, a 29-valence-electron complex[12] (prepared by thermal displacement of cyclooctatriene, as in the formation of 2) as the only known C_2B_3-bridged iron triple-decker sandwich.

Indole Complexes. As noted in the introduction, the relationship of the indole ring system to pyrroles and to indene, both of which coordinate to metal–carborane groups to form families of stable sandwich species,[1a,6,9] led us to explore a possible role for this heterocycle in metallacarborane chemistry. The thermal reaction

of 1 with 2,3-dimethylindole formed the air-stable orange sandwich complex $(\eta^6\text{-HNMe}_2C_8H_4)Fe(Et_2C_2B_4H_4)$ (4) in excellent yield (Scheme II); however, the corresponding parent indole species was inaccessible by this method. It is clear from the ^{1}H FT NMR spectrum that the Fe atom in 4 is coordinated to the C_6 rather than the C_4N ring, in that the four carbocyclic ring protons are shifted upfield (5.2–6.0 ppm) relative to those of the uncomplexed ligand; moreover, the diamagnetism of 4 supports the presence of Fe(II) rather than Fe(III). An alternative possibility in which an Fe(II)–H center is bound to the five-membered ring (an analogue of which is known in the indenylferracarborane system[9]) is eliminated in 4 by the absence of a high-field metal hydride proton NMR signal and by the mass spectrum, which gives no indication of the presence of an extra hydrogen.

The reaction of 4 with n-butyllithium or KH in THF at 0 °C gave a scarlet anion (5), which reverted to the orange starting material on warming to room temperature; the reprotonating agent is assumed to be THF. In dimethoxyethane (DME) solution, the anion produced was stable at room temperature, but reprotonation of the anion occurred on exposure of the DME solution to moist air. No ring migration was observed, either on reprotonation or on heating the solution to 80 °C. This result is consistent with the reported behavior of $(CO)_3Cr(indole)$[13] but contrasts with the indenyl counterpart of 5, $(\eta^6\text{-}C_9H_7)Fe(Et_2C_2B_4H_4)^-$, which undergoes a haptotropic rearrangement above 0 °C to give the η^5-coordinated species.[9]

In 5, the nitrogen atom was found to retain sufficiently basic character to undergo alkylation on treatment with methyl iodide, forming 6 (Scheme II). The reaction is nearly quantitative and establishes that the deprotonation by butyllithium does indeed take place at the N–H group as shown. In summary, it appears from this investigation that the chemistry of the indole–ferracarborane species 4 is limited in comparison to that of the pyrrolyl/phospholyl counterparts as well as the indenyl-ferracarboranes.

Experimental Section

Synthesis of $(\eta^5\text{-Me}_4C_4S)Fe(Et_2C_2B_4H_4)$ (2). 2,3,4,5-Tetramethylthiophene (1.00 g, 7.14 mmol) and $(C_8H_{10})Fe(Et_2C_2B_4H_4)$ (1, 0.125 g, 0.43 mmol)[10] were sealed in a thick-walled Pyrex tube under vacuum, which was placed in an oven at 180 °C for 90 min. The tube was opened to the air and the contents extracted with dichloromethane. The red-orange solution was reduced in volume by rotary evaporation and suction-filtered through 2 cm of silica gel on a rotary glass disk with hexane as eluent to remove unreacted tetramethylthiophene. After the silica was washed with ca. 250 mL of hexane, the receiving flask was changed and the residue washed with dichloromethane, giving a red-orange filtrate, which was reduced in volume, placed on 20 × 20 cm preparative silica TLC plates, and eluted with 1:1 hexane/CH_2Cl_2. Three bands were obtained, the first of which was tetramethylthiophene, the second of which was 1 (0.43 g, 0.15 mmol), and the third of which was 2 (45 mg, 0.14 mmol, 50% yield based on 1 consumed). UV–visible wavelength maxima (nm, in CH_2Cl_2): 466, 316, 282, 246. Exact mass (m/z): calcd for $^{56}Fe^{32}S^{12}C_{14}{}^{11}B_4{}^1H_{26}{}^+$, 326.1477; found, 326.1483.

Synthesis of $(\eta^5\text{-Me}_4C_4S)Fe(Et_2C_2B_3H_5)$ (3). A 52-mg (0.16-mmol) sample of 2 was placed in a 50-mL round-bottom flask together with 3 mL of N,N,N',N'-tetramethylethylenediamine (TMEDA) and a stirring bar, and the flask was heated at 80 °C for 1 h, after which the TMEDA was removed by rotary evaporation. The residue was extracted with hexane, and the extract was suction-filtered through 2 cm of silica gel; the silica was then washed with hexane until the effluent was colorless. Subsequent washing with dichloromethane followed by evaporation of

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solvent afforded pure **3** (15 mg, 0.05 mmol, 30%) as a slightly air-sensitive orange solid. UV–visible wavelength maxima (nm, in CH_2Cl_2): 422, 310, 282. Exact mass (m/z): calcd for $^{56}Fe^{32}S^{12}C_{14}{}^{11}B_3{}^1H_{27}{}^+$, 316.1462; found, 316.1466.

Synthesis of $(\eta^6$-HNMe$_2C_8H_4)$Fe(Et$_2C_2B_4H_4$) (4). In a thick-walled Pyrex tube were placed 0.500 g (1.71 mmol) of **1** and ca. 1.0 g of 2,3-dimethylindole (Aldrich). The tube was sealed under vacuum and heated in an oven at 180 °C for 2.5 h, after which it was opened in air and the contents extracted with dichloromethane. The solvent was removed and the residue washed with a minimum volume of hexane and suction-filtered through silica gel with hexane as eluent, until all of the 2,3-dimethylindole was removed (ca. 1 L). Elution of the column with dichloromethane gave a red filtrate which upon evaporation gave **4** (0.49 g, 1.47 mmol, 86%). UV–visible wavelength maxima (nm, in CH_2Cl_2): 358, 278. Exact mass (m/z): calcd for $^{56}Fe^{14}N^{12}C_{16}{}^{11}B_4{}^1H_{25}{}^+$, 331.1709; found, 331.1709.

Deprotonation of 4 and Synthesis of $(\eta^6$-MeNMe$_2C_8H_4)$Fe(Et$_2C_2B_4H_4$) (6). A 74-mg (0.22-mmol) sample of **4** was placed in a 50-mL two-neck round-bottom flask equipped with a rubber septum and a vacuum line attachment. The flask was evacuated and placed in a liquid-nitrogen bath, and 40 mL of dry mL of dry DME was added via vacuum distillation, after which the reactor was warmed to ca. 0 °C, affording an orange solution. A 10-mL quantity of 2.5 M n-butyllithium was introduced via the septum, causing an immediate color change to dark red. The flask was warmed to room temperature, and 0.50 mL of methyl iodide was added via syringe, producing a color change to orange. The mixture was stirred for 10 min, the reactor was opened to air, and the solvent was removed by rotary evaporation. The residue was extracted with dichloromethane, and the extract was suction-filtered through silica gel with dichloromethane as eluent, affording a single orange band. Evaporation to dryness gave orange crystals of **6** (74 mg, 0.21 mmol, 96%). UV–visible wavelength maxima (nm, in CH_2Cl_2): 466, 294, 250. Exact mass (m/z): calcd for $^{56}Fe^{14}N^{12}C_{17}{}^{11}B_4{}^1H_{27}{}^+$, 345.1865; found, 345.1874.

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Structures and Spectroscopic Characteristics of Iron(III) Diethylenetriaminepentaacetic Acid Complexes. A Non-Heme Iron(III) Complex with Relevance to the Iron Environment in Lipoxygenases

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Certain enzymes, including lipoxygenase and phenylalanine hydroxylase, contain iron in an unusual non-heme environment. Solutions of the versions of these enzymes containing iron(III) display an EPR signal at $g = 6$.[1,2] While the $g = 6$ signal is usually associated with high-spin ferric heme,[3] the enzymes have none of the other distinguishing spectroscopic properties of heme proteins. The ligand environments of the iron atoms in these proteins are presently unknown in spite of substantial characterization efforts. In the case of lipoxygenase, the nature of the iron site has been probed in a number of investigations employing magnetic susceptibility,[4] paramagnetic NMR effects,[5] EXAFS,[6] EPR,[7] Mössbauer,[8] and MCD.[9] The enzyme isolated from soybeans (native) contains high-spin iron(II), probably in an octahedral field of six oxygen and/or nitrogen atoms. An evolutionarily conserved cluster of histidine residues has been proposed to be a part of the ligand field.[10] Treatment of the native enzyme

with 1 equiv of the hydroperoxide product of catalysis converts the iron site to the high-spin iron(III) species with the characteristic $g = 6$ EPR signal. There is evidence that water oxygen is one of the ligands to iron in the oxidized form of the enzyme.[11]

In a study of the incorporation of iron-57 into lipoxygenases by a tissue culture technique, we used iron as the diethylenetriaminepentaacetic acid (DTPA) chelate.[12] We were intrigued by the finding that this iron complex had Mössbauer spectroscopic properties similar to those of the iron in lipoxygenase and, like the metal in the enzyme, was resistant to oxidation by molecular oxygen.[8] While numerous investigations of the structures and spectroscopic properties of $Fe^{III}EDTA$ complexes have been carried out,[13] we could find only one structural study and limited spectroscopic characterization of the corresponding DTPA compounds.[14,15] The structures of $Fe^{III}EDTA$ complexes have been obtained under a wide variety of conditions. At low pH, the iron was found in a six-coordinate, roughly octahedral field, consisting of two nitrogen and three oxygen atoms from the ligand and one oxygen atom from water solvent.[16] At high pH, an additional ligand carboxyl was found to join the coordination sphere, making the iron seven coordinate and roughly pentagonal bipyramidal.[17] Like nearly all high-spin non-heme iron(III) species, the EDTA complexes displayed EPR signals at $g = 4.3$ irrespective of pH.[18] The single structure report on $Fe^{III}DTPA$ found the iron in a seven-coordinate pentagonal-bipyramidal geometry made up of three ligand nitrogen atoms and four ligand oxygens.[14] Like the EDTA complexes, $Fe^{III}DTPA$ has been characterized by the observation (at pH 9–10) of the $g = 4.3$ EPR feature.[15] This report describes the discovery of the interesting effect of conditions on both the solid-state (structural) and solution (spectroscopic) properties of the complexes of iron(III) with DTPA.

Experimental Section

Synthesis. H_5DTPA (Aldrich), $Fe(NO_3)_3\cdot 9H_2O$ (Fisher), $FeCl_3\cdot 6H_2O$ (Fisher), $NaHCO_3$ (Malinkrodt), and 40% aqueous $(C_2H_5)_4NOH$ (Alfa) were used as supplied without further purification. The $Fe^{III}DTPA$ complexes were prepared by a modification of the procedure of Sievers and Bailer.[19]

[FeH$_2$DTPA]$_2$·2H$_2$O (I). $Fe(NO_3)_3\cdot 9H_2O$ (4.04 g, 0.01 mol) was added to a solution of H_5DTPA (3.93 g, 0.01 mol) in deionized H_2O (20 mL), and the mixture was heated to 70 °C. The clear orange solution turned bright yellow and turbid during the heating process. The pH of

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