molecular structure of **2** is shown in Figure 1.[15] It contains an unusual vinylcarbene ligand. The bond distance between tungsten and the carbene carbon C(9) is characteristic of a tungsten–carbon double bond;[11,16,20b,c] the distances between tungsten and the vinyl carbon atoms C(16) and C(17) are very long for an olefinic group coordinated to tungsten[17] and even long compared to typical bond distances in tungsten–allyl complexes.[18] The C(9)–C(16) distance is close to the value expected for a single bond between two sp^2 carbon centers (1.48 Å) and the C(16)–C(17) distance is very close to values found in free olefins (1.35 Å).[19] The C(Ph)-CHCHMe ligand may, therefore, be described as an η^3-vinylcarbene ligand with a very weakly coordinated vinyl group.[20]

The characteristics of the vinylcarbene ligand in the present complex are intermediate between those of rigorously η^1-bonded vinylcarbene ligands, which are found in coordinatively saturated metal complexes,[3] and those of more strongly η^3-bonded ligands, which are found in low-valent iron complexes of the type [Fe-$(C_3R_4)(CO)_3$][9d,22] and which appropriately may be described as η^3-allylidene ligands. The difference in bonding clearly reflects better π-back-bonding of the electron-rich, low-valent iron center to the vinyl group. In more electropositive metal complex systems the transfer of electron density from the metal to the ligand proceeds even further, resulting in metallacyclobutenes as in titanocene cyclobutenes.[23]

Addition of 2 equiv of sodium diethyldithiocarbamate to a suspension of **2** in THF gives a red orange solution of a species with two infrared absorptions in the carbonyl region at 1931 and 1850 cm^{-1}. This initial product is formulated as the tungsten dicarbonyl complex $[W(C(Ph)CHCHMe)(S_2CNEt_2)_2(CO)_2]$ (**3**). Compound **3** is unstable; it is activated toward coupling of the vinylcarbene ligand with a carbonyl ligand and transforms into the vinylketene complex $[W(S_2CNEt_2)OCC(Ph)CHCHMe)(CO)]$ (**4**) (two diastereomers) within 1 h at 50 °C (eq 2).[24] Complex **4** is isolated in 90% yield after recrystallization from CH_2Cl_2/hexane.[25] The molecular structure of **4** is shown in Figure 2.[15] The vinylketene ligand is bonded to the metal center via four carbon atoms. The W–C distances and the respective C–C distances are comparable to values found in tungsten and molybdenum butadiene complexes,[26] with a somewhat shortened bond between tungsten and the ketene carbonyl carbon atom.

Carbonyl–vinylcarbene coupling in the present system occurs slowly only after addition of two strong, chelating donor ligands. In the related (η^3-allylidene)tricarbonyliron[9d,21] and dicyclopentadienyltitanacyclobutene systems[27] formation of vinylketene ligands occurs in the presence of carbon monoxide under atmospheric pressure. Good transfer of electron density from the metal center to the vinylcarbene moiety appears to be a crucial factor favoring the carbonyl–vinylcarbene coupling step.

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Supplementary Material Available: Tables of atomic coordinates, bond lengths, and bond angles for **2** and **4** (8 pages); tables of observed and calculated structure factors for **2** and **4** (33 pages). Ordering information is given on any current masthead page.

(14) **2**: ^1H NMR ($CDCl_3$) δ 5.61 (m, C*H*Me), 5.29 (d, $^3J_{CH}$ = 11.67 Hz, C*H*), 1,86 (d, $^3J_{CH}$ = 6.11 Hz, C*H*$_3$); ^{13}C NMR (DC_2Cl_2) δ 240.4 (*C*Ph), 122.9, 91.3 (*CH*CHMe); IR ν_{CO} (CH_2Cl_2) 2025 (m), 1944 (s) cm^{-1}.

(15) Crystal data for **2** and **4**. **2**: $C_{18}H_{17}Br_2NO_2W$, FW = 623.1, monoclinic, $P2_1$, a = 7.549 (3) Å, b = 12.64 (5) Å, c = 9.931 (4) Å, β = 90.65 (3)°, V = 948.2 (6) Å^3, Z = 2, ρ_{calcd} = 2.18 g cm^{-3}, μ(Mo Kα) = 109.2 cm^{-1}, 1663 unique observed date, $3 \le 2\theta \le 50°$, R = 0.036, R_w = 0.037. **4**: $C_{22}H_{30}N_2O_2S_4W \cdot CH_2Cl_2$, FW = 751.6, monoclinic, $P2_1/n$, a = 10.406 (2) Å, b = 12.929 (2) Å, c = 21.658 (4) Å, β = 94.30 (2)°, V = 2905.6 (9) Å, Z = 4, ρ_{calcd} = 1.72 g cm^{-3}, μ(Mo Kα) = 46.9 cm^{-1}, 3806 unique observed data, $3 \le 2\theta \le 50°$, R = 0.055. All intensity measurements were made at low temperature (−93 ± 3°C), using graphite-monochromated MoKα radiation (λ = 0.71069 Å) and a variable rate, ω-scan technique. Empirical absorption corrections were applied based on the azimuthal scans of suitable reflections. Data with [$|F_o| \ge 3\sigma(F_o)$] were considered observed. The structures were solved by conventional heavy atom methods and refined by blocked-cascade least squares. All calculations were performed by using the SHELXTL programs.

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(25) Major diastereomer: ^1H NMR (ppm, $CDCl_3$) δ 5.30(d, ^3J = 7.82 Hz, C*H*), 2.87 (m, C*H*Me), 2.01 (d, ^3J = 6.34 Hz, C*H*$_3$); ^{13}C NMR (ppm, $CDCl_3$) δ 234.9 (C=O), 204.7 (CO), 79.4 (*CH*), 68.9(*CH*Me), 56.1 (*C*Ph).

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Stereospecific Binding of *rac*-Iron(III) *N,N'*-Ethylenebis[(5-bromo-2-hydroxyphenyl)glycinate] to the Bilirubin Site on Human Serum Albumin

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Metal complexes that recognize specific sites on biological macromolecules have potential as drugs and molecular probes.[1-5] Our interest in paramagnetic chelates as liver-enhancing relaxation agents for NMR imaging has led us to study the interactions between chelates and relevant binding proteins.[6-11] In vivo, these

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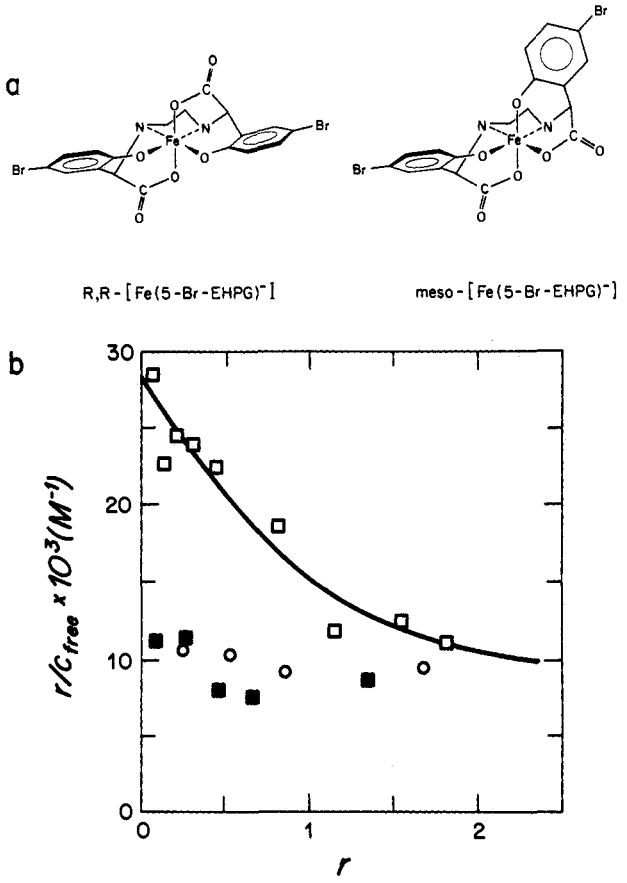

Figure 1. (a) Structures of the complexes. (b) Scatchard plot of the binding of racemic (□) and meso (○) forms of ^{59}Fe(5-BrEHPG)$^-$ to HSA as measured by equilibrium dialysis. Also shown are data obtained for the racemic complex after the addition of 1 mol of bilirubin IXα per mole of HSA (■). r represents the molar ratio of bound chelate to HSA; C_{free} is the molar concentration of free (unbound) chelate. Data were obtained at 5 °C with 100 μM HSA in 0.1 M sodium phosphate buffer, pH 7.4, containing 0.15 M NaCl. The curve through the data for the racemic complex represents the best fit[25] to a single high-affinity site (K = 2.2 × 10^4 M^{-1}) as well as to nonspecific sites.

agents may behave similarly to bilirubin, the heme breakdown product, which is transported to the liver bound to the blood protein albumin and then extracted by liver cells.[12,13] Since albumin possesses a remarkable capacity to bind structurally dissimiliar anionic and hydrophobic ligands,[14-17] strong binding of one such agent, iron(III) *N,N'*-ethylenebis[(5-bromo-2-hydroxyphenyl)-glycinate] [Fe(5-BrEHPG)$^-$], to human serum albumin (HSA) in vitro was not unexpected.[9] However, the structural basis for the binding is poorly understood. We have isolated diastereomeric forms of Fe(5-BrEHPG)$^-$ and report here that one form binds stereoselectively to the bilirubin site on HSA, indicating the importance of molecular shape in the binding interaction. The complexes thus serve as novel probes of this important binding site and provide a structural link toward understanding the common in vivo chemistry of bilirubin and various metal chelates.

The racemic (*RR* + *SS*) and meso (*RS*) diastereomers of Fe(5-BrEHPG)$^-$ (Na^+ salts) can be separated on the basis of solubility in methanol.[18,19] The structure of these isomers can

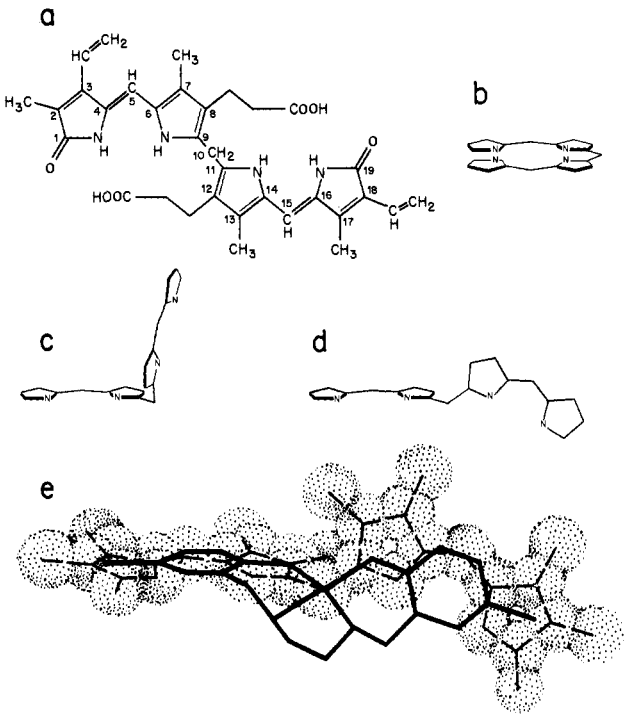

Figure 2. (a) Structure of bilirubin IXα. (b–d) Possible conformations of bilirubin as a function of the two torsional angles about the central methylene: ϕ_1, N–C9–C10–C11; ϕ_2, N–C11–C10–C9. (b) $\phi_1 = \phi_2 = 0°$ (porphyrin-like configuration); (c) $\phi_1 = \phi_2 = -60.8°$ (intramolecular hydrogen-bonded form exhibited in the crystal structure of the dianion[33]); (d) $\phi_1 = \phi_2 = -135°$ (example of an extended conformation); (e) superposition of a stick representation of (*R,R*)-Fe(5-BrEHPG)$^-$ (thick lines) within the van der Waals surface of bilirubin (dots and dashed lines) in the extended ($\phi_1 = \phi_2 = -135°$) conformation. The iron atom is placed at the central methylene of bilirubin and the complex is positioned to illustrate the similarity between the orientation of its bromophenolate rings with respect to the dipyrromethene moeities of bilirubin. In (b)–(e), selected peripheral atoms and all hydrogens have been omitted for clarity. In (e), the two carboxylates of the complex are not displayed.

be inferred from those of the parent compound on the basis of NMR evidence and similarity of TLC properties and visible spectra.[20-22] The racemic isomer (*RR* shown in Figure 1a) is a distorted octahedral complex with two equivalent phenolates coordinated to the metal in the equatorial plane but twisted relative to one another; a 2-fold axis of symmetry bisects the N–Fe–N angle. The meso isomer, on the other hand, lacks this symmetry since one phenolate (from the *S* carbon) coordinates to the iron at an axial site from above the equatorial plane. ^{1}H NMR spectra of the paramagnetically shifted ring proton resonances confirm the anticipated equivalence of the two rings in the racemic isomer and the inequivalence in the meso isomer.[18,23]

Equilibrium dialysis studies reveal that HSA has a distinct preference for binding the racemic isomer of Fe(5-BrEHPG)$^-$. Figure 1b displays Scatchard plots for both isomers. The meso isomer exhibits only nonspecific binding most likely to low affinity, high capacity sites as demonstrated by the flat appearance of the binding plot, whereas the racemic isomer binds additionally to

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a single high-affinity site with an estimated association constant of 2×10^4 M^{-1}.[18,25]

The specific binding site of *rac*-Fe(5-BrEHPG)$^-$ appears to be at or near the high-affinity site for bilirubin IXα (Figure 2a). One equivalent of bilirubin IXα added to HSA ($K \approx 10^8$ M^{-1}) completely inhibits the high-affinity binding of the racemic complex (Figure 1b). Other experiments show that the specific site does not appear to be one of the common drug-binding sites, denoted site I and site II, that were identified by Sudlow et al.[27] in displacement studies using the fluorescent probes dansylamide and dansylsarcosine, respectively. The addition of a large molar excess of the structurally analogous but colorless gallium(III) complex of 5-BrEHPG to both types of HSA-probe complexes results in only small reductions of fluorescence intensity in each case ($\sim$ 20%).[18] The lack of preferential displacement of either probe removes site I and II as candidates for the high-affinity site for *rac*-Fe(5-BrEHPG)$^-$. In addition, no significant degree of tryptophan-214 fluorescence quenching, seen for some site I binding drugs,[28,29] is observed with the gallium analogue.[18]

rac-Fe(5-BrEHPG)$^-$ shares certain chemical features in common with bilirubin, such as anionic charge, hydrogen-bonding groups, and hydrophobic regions, which, while prerequisite for binding, are insufficient by themselves in directing the complex to this specific site since the meso isomer exhibits these same features yet lacks the high-affinity binding. The stereoselectivity of the binding, therefore, suggests that the unique structure of *rac*-Fe(5-BrEHPG)$^-$ may be similar to that of HSA-bound bilirubin. The conformation of bilirubin when bound is still not known despite extensive study. Although circular dichroism studies suggest that the two dipyrromethene chromophores are held in a chiral configuration at some angle relative to one another, the flexibility inherent in the central methylene gives rise to a wide range of such conformers (Figure 2c,d).[30-32] Remarkable similarity exists between *rac*-Fe(5-BrEHPG)$^-$ and extended conformations of bilirubin in terms of the relative orientation of the planar groups with respect to each other and with respect to the central anionic region (Figure 2e).[18] Such a conformation of HSA-bound bilirubin seems reasonable since it would allow the dipyrromethene units to project into different regions of the HSA molecule, as suggested by others,[34] affording noncovalent contacts with both halves that would contribute collectively to the high association constant.

This work represents the first use of rigid metal complexes to explore the shape of a protein binding site for a potentially flexible ligand. The unique stereochemistry of metal complexes makes them well suited for probing macromolecules as shown in recent applications to DNA.[5] Further studies will determine if the binding of *rac*-Fe(5-BrEHPG)$^-$ to the bilirubin site on HSA is enantiomerically specific (i.e., preferential binding of either the *RR* or *SS* isomers).

Our results also point to the feasibility of metal-containing drugs, especially for diagnosis, which mimic the chemistry of endogenous substances. The binding of *rac*-Fe(5-BrEHPG)$^-$ to the bilirubin site on HSA illustrates how simple structural features of a complex, such as the relative placement of charged, hydrogen-bonding, and hydrophobic groups, can be sufficient for its recognition by in vivo binding sites. The utility of these iron(III) complexes as hepatobiliary imaging agents[8,9] most likely stems from hepatocellular binding interactions at sites involved in the transport of bilirubin.

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Supplementary Material Available: Information on the synthesis of the complexes, binding studies, fluorescence studies, and structural comparisons and NMR spectra of the complexes (4 pages). Ordering information is given on any current masthead page.

(25) The binding data for *rac*-Fe(5-BrEHPG)$^-$, in the form of a r (moles of complex bound per mole of HSA) vs. C_{free} (unbound complex concentration) plot, was fit to the following:

$$r = (KC_{free})/(1 + KC_{free}) + PC_{free}$$

A single high affinity site with association constant K was assumed. P represents a simple partition coefficient[26] to take into account the nonsaturable, nonspecific binding noted for the meso isomer. A least-squares fit yielded $K = 2.2 \times 10^4$ m^{-1} and $P = 6.2 \times 10^3$ M^{-1}. The calculated isotherm was recast into the Scatchard format for display in Figure 1.

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A New Room Temperature Molten Salt Solvent System: Organic Cation Tetrachloroborates

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In the past decade there has been considerable interest in $AlCl_3$-containing molten salts. These melts provide novel media for fundamental studies and are also of interest in high-energy batteries and for catalytic applications.[1] Relatively few molten salt systems are liquid at or below room temperature. The properties of these systems, mainly organic chloroaluminates, have been reviewed by Hussey;[2] several other room temperature molten salts have been described recently.[3] This paper describes tetrachloroborate salts that are stable liquids at room temperature; they are products of the reaction between *n*-butylpyridinium chloride or methylethylimidazolium chloride and boron trichloride.

N-Butylpyridinium chloride (BPC) and 1-methyl-3-ethylimidazolium chloride (MEIC) were prepared as described in ref 4-6. Melts were prepared by distillation of a measured volume of BCl_3 onto a weighed amount of BPC or MEIC in a glass tube cooled with liquid nitrogen. The tube was then sealed and warmed to room temperature. The composition of such melts is uncertain by about 15%.

Conductivity cells were calibrated with standard KCl; a YSI conductivity bridge was used for specific conductance measurements. PAR equipment was used for electrochemical measurements. Raman spectra were obtained with an ISA Ramanor 2000 spectrometer, an argon ion laser, and a photon-counting system.

Both solid chlorides react exothermically with gaseous BCl_3 to form droplets of colorless, viscous melt at room temperature. The reaction with MEIC is more exothermic. When the mole ratio of BCl_3 to the organic chloride is approximately 1:1, a single phase is formed; when the ratio is 2:1, two immiscible liquid phases

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