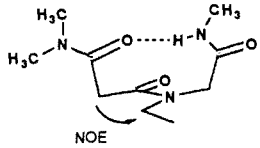
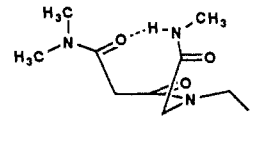
of **1c** as temperature decreases indicates that **1c** is enthalpically superior to **1a** and **1b**. The balance of non-covalent forces in **1** is sufficiently fine, however, that the entropic advantage of **1a** (and perhaps **1b**) becomes an important factor at higher temperatures.

The conformational equilibrium proposed in Scheme I is supported by the behavior of triamide **4**,[1] in which H_a of **1** is replaced by an ethyl group. This triamide has no option for a six-membered-ring hydrogen bond. IR spectroscopy shows triamide **4** to be virtually locked in an intramolecularly hydrogen bonded conformation in CH_2Cl_2 even at room temperature: the hydrogen bonded N-H stretch (3320 cm^{-1}) is dominant, and a tiny free N-H signal at 3445 cm^{-1} is just barely discernable in a 1 mM solution.[7] The proton NMR spectrum of **4** in CH_2Cl_2 shows that, despite the tertiary amide moiety, one conformer is predominant (>85%). Molecular models suggest that either stable rotamer about the central C-N bond (e.g., **4a** or **4b**) could allow a nine-membered-ring amide-amide hydrogen bond. We detect a positive NOE between the indicated methylenes, which implies that the major form has the *Z* conformation about the this C-N bond.



4a



4b

The observation that conformation **1c** (with or without the bifurcated hydrogen bond) is enthalpically superior to **1b** in a solvent that offers little or no hydrogen bonding competition demonstrates that the most stable folding patterns of oligoamides need not have the maximum pairing of hydrogen bond donors and acceptors. This conclusion is interesting in the context of protein tertiary structure, because one of the factors that specifies the compact, folded conformation of a globular protein is thought to be the drive to satisfy the hydrogen bonding potential of the largest possible number of the amide groups that are buried in the relatively nonpolar core of the macromolecule.[8]

We speculate that conformation **1c** is enthalpically more favorable than conformations containing hydrogen bonds in smaller rings because of the more linear N-H--O angle allowed by the larger ring. Ab initio calculations suggest that optimum amide-amide hydrogen bond strength is achieved when the N-H--O arrangement approaches linearity.[9] In protein crystal structures, deviations from hydrogen bond linearity are often observed, but it is impossible to know the extent to which such deviations result from competing non-covalent interactions within the biopolymer.[10] The conformational equilibrium observed for triamide **1** in nonpolar solution provides an opportunity to examine competition among hydrogen bonds of different geometries. These studies also suggest that multi-state conformational equilibria in oligoamides can be elucidated by comparisons with related molecules in which the number of conformational options is reduced.

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(7) The amide proton chemical shift temperature dependence measured for triamide **4** in CD_2Cl_2 is also consistent with nearly complete hydrogen bonding at all temperatures. The amide proton chemical shift occurs at 7.85 ppm at 298 K and at 8.36 ppm at 193 K, varying approximately linearly in between.

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Fluorine-Substituted Ferracyclopentadiene Complexes with an Unprecedented Fluorine Bridge between Boron and Carbon

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We recently reported the preparation of complexes **1a**,**b**, shown in Scheme I, which are derivatives of the well-known complex $Fe_2(\mu\text{-}CH_2)(CO)_8$.[1] Pettit has shown that the latter compound readily reacts with alkynes to form binuclear allyl complexes,[2] and it was thus of interest to determine if complex **1** would incorporate alkynes in a similar fashion. However, as reported herein, this reaction takes a most surprising course, to yield fluorine-substituted ferracyclopentadiene complexes that form by fluoride donation from BF_4^- and which have been crystallographically shown to possess an unprecedented fluorine atom bridge between carbon and boron atoms. Furthermore, it has been found that the fluorine substituent is readily abstracted by the BF_3 group when this complex is treated with nucleophiles.

Complex **1** rapidly reacts with PhC≡CH to give the fluorinated ferracyclopentadiene complexes **2a**,**b**,[3a] Scheme I, which were isolated as microcrystalline solids and have been crystallographically characterized, Figure 1 (**2b**).[3b] These complexes are derivatives of the well-known family of binuclear ferracyclopentadiene complexes (ferroles) prepared by the reaction of alkynes with iron carbonyls.[4,5] The surprising feature of this structure is the fluorine substituent on the ferracyclopentadiene ring and its bonding to both C(9) and the B atom in a bridging fashion [C(9)-F(1)-B(1) = 126.4 (4)°]. The short C(9)-F(1) distance of 1.329 (5) Å implies the presence of a C-F single bond (1.32-1.39 Å)[6] whereas the F(1)-B(1) distance of 1.528 (8) Å is quite long, especially when compared to the 1.37 (1) Å average bond length for the remaining three B-F bonds. The molecule appears best described as having a covalently bonded C-F group interacting in a donor-acceptor fashion with the Lewis acid BF_3, but to our knowledge, this is the first example of any type of compound with a fluorine atom bridging between carbon and boron atoms.

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(3) (a) **2b**: IR (CH_2Cl_2) ν_{CO} = 2078 (m), 2049 (vs), 2017 (m), 1997 (m), 1614 (w) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.94 (d, 1 H, J_{HF} = 15.8 Hz, C*H*), 7.32, 7.21 (m, 5 H, Ph) 6.62 (q, 1 H, C*H*, J_{H-F} = 1.2 Hz), 1.50 (s, 9 H, Bu^t); ^{13}C NMR (CD_2Cl_2) δ 210.1,209.0, 206.4, 205.6 (*C*O), 184.6 (dd, 4.1 Hz), 175.3 (d, $^1J_{CH}$ = 173.9 Hz, *C*H), 161.9 (*C*F), 149.8, 128.9, 128.5, 127.9 (Ph), 102.3 (d, $^1J_{CH}$ = 173.9 Hz, *C*H), 99.0, 60.3 (*C*(Me)$_3$), 28.6 (C(*C*H$_3$)$_3$). (b) $P2_1/c$, a = 21.188 (6) Å, b = 8.552 (2) Å, c = 13.429 (4) Å, β = 94.13 (2)°, V = 2427.0 (11) Å^3, Z = 4, $R(F)$ = 4.22%, R(wF) = 4.39% for 2360 reflections ($F_o \geq 5\sigma(F_o)$).

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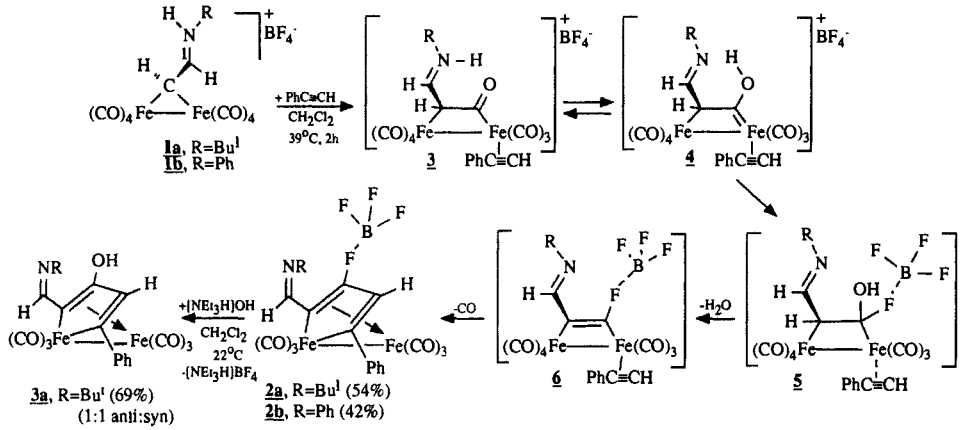
Scheme I



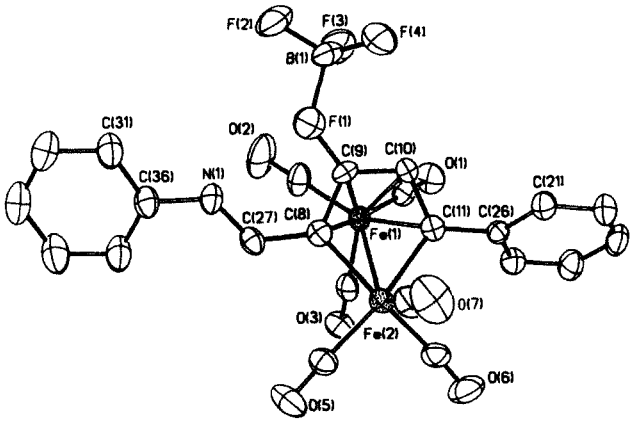


Figure 1. Molecular structure and labeling scheme for **2b** (40% thermal ellipsoids). Distances in angstroms: Fe(1)–Fe(2), 2.505 (1); Fe(1)–C(8), 2.066 (5); Fe(1)–C(9), 2.244 (5); Fe(1)–C(10), 2.171 (5); Fe(1)–C(11), 2.079 (5); Fe(2)–C(8), 1.989 (5); Fe(2)–C(11), 1.993 (5); C(8)–C(9), 1.438 (7); C(9)–C(10), 1.419 (7); C(10)–C(11), 1.422 (6); C(8)–C(27), 1.464 (7); C(27)–N(1), 1.294 (6); C(9)–F(1), 1.329 (5); F(1)–B(1), 1.528 (8); average B(1)–F(2,3,4), 1.37 (1).

The proposed mechanism for the formation of **2a,b** is shown in Scheme I. We suggest that coordination of the added alkyne induces CO insertion to form the ketene intermediate **3**, similar to the nucleophile-induced insertion of CO into the Fe–carbon bond of $Fe_2(\mu\text{-}CH_2)(CO)_8$.[7] Proton transfer from the iminium nitrogen of **3** to the carbonyl oxygen would give intermediate **4**, which could then add the BF_4^- ion to give **5**. Elimination of H_2O from **5** would form the bis(alkyne) complex **6**, which would yield the observed ferracyclopentadiene product by coupling of the two alkynes. Alternatively, water elimination could occur directly from **4** or after the ferracyclopentadiene ring had formed to give electrophilic intermediates capable of adding the BF_4^- anion. ^1H NMR analysis showed the formation of the H_2O byproduct, implying that free BF_3 is not released during the formation of **2** as otherwise this species would react with the water produced in the conversion of **1** into **2**. It was also observed that when the reaction was conducted with ^{13}CO-enriched **1a**, the product **2a** showed a significantly enhanced ^{13}C NMR resonance for the fluorine-substituted carbon atom, indicating that this carbon derived from a metal carbonyl ligand.

Although the crystal structures of **2a,b** clearly show short C–F bond lengths indicating a strong covalent bond between these atoms, preliminary reactivity studies indicate that the BF_4^- group is readily displaced by nucleophiles. When $[NEt_3H]OH$ was added to a CH_2Cl_2 solution of complex **2a**, an inseparable 1:1 mixture of syn and anti imino hydroxyferrole complexes **3a** formed, Scheme I. These complexes result from nucleophilic displacement of BF_4^- from **2a** by OH^- with subsequent imine isomerization by a tautomerization process involving proton transfer from the hydroxy group to the imine nitrogen. This reaction only occurs under basic conditions and not when just water is added to **2**. Given the apparent ease of nucleophilic displacement of the fluoride and the demonstrated transformation of ferracyclopentadiene complexes into a variety of organic products,[5a] it may prove possible to develop useful organic syntheses with complexes **2a,b**. Such studies are currently in progress.

Acknowledgment. We thank the Department of Energy, Office of Basic Energy Sciences, for support of this work and the National Science Foundation for contributing funds toward purchase of the X-ray diffractometer at the University of Delaware.

Supplementary Material Available: Tables of atomic positional parameters for **2b**, analytical data for **2a,b**, and spectroscopic data for **2b** and **3a** (2 pages). Ordering information is given on any current masthead page.

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New Trialkylsilyl Enol Ether Chemistry. Regiospecific and Stereospecific Sequential Electrophilic Addition

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In recent years much of the chemistry of enol derivatives has been dominated by the versatile reactivity of trimethylsilyl enol ethers.[1] Regiospecifically generated trimethylsilyl enol ether **1** reacts with electrophiles to give so-called kinetic products and concomitant loss of the trimethylsilyl group. The presumed oxonium intermediate **1a** is attacked by the counterion to give an "ate" complex **1b** (intermediate or transition state) leading to desilylation to give **2**. While these transformations proceed with excellent regiochemical control, the trimethylsilyl group is lost and cannot exert any further influence on the chemical fate of **2**. We have been interested in diverting the oxonium ion intermediate **1a** by proton loss rather than the usual nucleophilic attack on the silicon atom. Proton loss from **1a** should be stereospecific (axial) and result in a new regiospecifically generated trialkylsilyl enol ether. Here we report our preliminary results directed toward the above objective.[2] Treatment of the triisopropylsilyl enol ether

(1) Trialkylsilyl enol ethers have been treated with a wide range of electrophiles, see: Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York, 1983; pp 228–233. There are no examples of the direct amination of trialkylsilyl enol ethers.

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