L,

field is only ~ 14 ppm; the signal is centered at 12 ppm (Figure 1). These values are fairly characteristic of alkenes and alkanes in general: the former exhibit huge anisotropies, the latter much smaller ones. This is well understood in a qualitative sense. The NMR experiment probes the electronic structure around a nucleus, in the plane perpendicular to the field direction; thus, in a molecule of 3 whose plane is perpendicular to the magnetic field, it responds only to σ electrons and the corresponding component of the chemical shift tensor lies in the region characteristic of alkanes. In a molecule of 4, all tensor shielding components depend upon σ electrons so its anisotropy is small. On the other hand, when a molecule of 3 is oriented so that the axes of the atomic p orbitals of the carbons in its π system are perpendicular to the magnetic field, their very different involvement in chemical bonding is reflected in the observed chemical shift values. In this fashion, the anisotropy of the electronic structure of a carbon atom involved in a C=C bond compared with that involved in a C–C bond translates directly into the anisotropy of its chemical shift.

The three principal values of chemical shift can be read off the powder pattern spectra obtained on solid samples. This is shown in Figure 1, which illustrates very clearly the analogy between carbon and silicon. Just as in the case of the ¹³C NMR spectra of 3 vs. 4, the ²⁹Si NMR spectrum of disilene 1 displays a large anisotropy and that of 2 a small one. Computer line-shape fitting yields the values σ_{11} 180, σ_{22} 27, and σ_{33} -15 for 1 and σ_{11} -31, σ_{22} -56, and σ_{33}^{-73} for 2 (ppm downfield from Me₄Si). We conclude that the electronic structure of the Si=Si

double bond bears a close resemblance to that of the C=C double bond.

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Alkylation and Aldol Reactions of Iron Acyl Enolates

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Summary: Treatment of the acyliron complex CpFe-(CO)(PPh₃)COCH₃ with lithium diisopropylamide at low temperature in THF generates the corresponding enolate. Reaction of this enolate with alkyl halides gives high yields of C-alkylation products while aldol products result from reaction with carbonyl compounds. Oxidative cleavage of the acyl-iron bond occurs in high yield (NBS, CH₂Cl₂/EtOH) to give esters.

In order to expand the preparative chemistry of certain stoichiometric organometallics in conjunction with their utilization in organic synthesis, we have initiated a research program to explore the synthetic applications of organotransition-metal carbanions. Our first effort in this area has concerned the conversion of iron acyls into iron acyl enolates and their reaction with various electrophiles to produce derivatized iron acyls (eq 1).¹

$$Fe$$
 CH_3 L_nFe CH_2 L_nFe (1)

After our initial attempts to generate the enolate of $CpFe(CO)_2COCH_3^2$ 1a were thwarted by migration of the acyl group to the cyclopentadienyl ring,³ we found that slow addition of a THF solution of CpFe(CO)(PPh₃)-COCH₃⁴ 1b to a 0.15 M solution of lithium diisopropylamide (LDA) maintained under N_2 at -42 °C gave a deep red solution of the corresponding lithium enolate 2. After the mixture was stirred at -42 °C for 1.5 h, the enolate was quenched with various electrophiles to give good to excellent yields of products (Scheme I). For example, treatment of enolate 2b with MeI, EtBr, allyl bromide, and benzyl bromide gave C-alkylation products 3b-6b in isolated, purified yields of 78, 81, 78 and 91%, respectively.⁵ Aldol reactions with acetone, acetaldehyde, pivaldehyde, and benzaldehyde similarily occurred in good yields to give compounds 7b-10b with the latter three reactants each giving a ca. 1:1 mixture of diastereomeric products.⁵

In principle, the asymmetric iron atom of the enolate could influence the formation of the new asymmetric carbon atom in aldol products 8-10. To briefly probe this

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(4) Bibler, J. P.; Wojcicki, A. *Inorg. Chem.* 1966, 5, 889. (5) Spectral data and elemental analyses. 3b: orange solid; mp 158-161 °C (CHCl₃/petroleum ether); IR (CHCl₃, cm⁻¹) 3040, 3010, 2980, 1910, 1605, 1490, 1440, 1100, 1080, 880, 830; ¹H NMR (60 MHz, CDCl₃, δ) 7.50-7.13 (m, 15 H), 4.33 (br s, 5 H), 2.93-2.37 (m, 2 H), 0.56 (t, J = 7 Hz, 3 H). Anal. Calcd for C₂₇H₂₅FeO₂P: C, 69.25; H, 5.38. Found: C, 69.47; H, 5.48. 4b: orange solid; mp 157-159 °C (CHCl₃/petroleum ether); IR (CHCl₃, cm⁻¹) 3020, 2980, 1920, 1608, 1440, 1100; ¹H NMR (60 MHz, CDCl₃, δ) 7.50-7.13 (m, 15 H), 4.35 (br s, 5 H), 2.93-2.40 (m, 2 H), 1.43-0.87 (m, 2 H), 0.58 (t, J = 6 Hz, 3 H). Anal. Calcd for C₂₈H₂₇FeO₂H; C, 69.72; H, 5.64. Found: C, 69.82; H, 5.80. 5b: orange solid; mp 115-117 °C (CHCl₃/petroleum ether); IR (CHCl₃, cm⁻¹) 3040, 3005, 1910, 1600, 1485, 1440, 1100, 910, 820; ¹H NMR (60 MHz, CDCl₃, δ) 7.40-7.03 (m, 15 H), 5.70-5.07 (m, 1 H), 4.93-4.50 (m, 2 H), 4.30 (br s, 5 H), 3.00-2.47 (m, 2 H), 2.10-1.57 (m, 2 H). Anal. Calcd for C₂₉H₂₇FeO₂P: C, 70.46; H, 5.51. Found: C, 70.36; H, 5.73. 6b: orange solid; mp 128-131 °C (CHCl₃/ petroleum ether); IR (CHCl₃, cm⁻¹) 3070, 3010, 1920, 1600, 1440, 1100, 830; ¹H NMR (60 MHz, CDCl₃, δ) 7.70-6.70 (m, 20 H), 4.30 (br s, 5 H), 3.20-2.00 (m, 4 H). Anal. Calcd for C₃₃H₂₉FeO₂P: C, 72.81; H, 5.37. Found: C, 72.88; H, 5.55. 7b: yellow-orange solid; mp 130-132 °C (CHCl₃/petroleum ether); IR (CHCl₃, cm⁻¹) 3420, 3080, 2995, 1920, 1590, 1490, 1440, 1120, 1100, 950; ¹H NMR (60 MHz, CDCl₃, δ) 7.67-7.10 (m, 15 H), 4.30 (d, J_{P-H} = 1 Hz, 5 H), 4.00 (br s, 1 H), 3.17 (d, J = 17 Hz, 1 H), 2.70 (d, J = 17 Hz, 1 H), 1.00 (s, 3 H). Or0 (s, 3 H). Anal. Calcd for (5) Spectral data and elemental analyses. 3b: orange solid; mp C₂₉H₂₉FeO₃P: C, 67.98; H, 5.71. Found: C, 67.70; H, 5.69. 8b: yellow-orange solid; 50/50 mixture of diastereomers; IR (CHCl₃, cm⁻¹) 3395, 3078, 3060, 2998, 1918, 1583, 1481, 1435, 1120, 1093, 965, 825; ¹H NMR (60 MHz, $C_{e}D_{e}$, δ) 7.77–6.73 (m, 15 H), 4.16 (m, 5 H), 3.70 (br s, 1 H), (60) WH2, C₂D₆, 0 / 1.17–0.78 (m, 15 H), 4.16 (m, 5 H), 5.16 (b, 5, 1 H), 3.33–2.90 (m, 3 H), 1.03, 1.00 (two overlapping doublets, each J = 7 Hz, 3 H total, 50/50 ratio). Anal. Calcd for $C_{28}H_{27}FeO_3P$: C, 67.49; H, 5.46. Found: C, 67.70; H, 5.66. **9b**: yellow-orange solid; 50/50 mixture of diastereomers; IR (CHCl₃, cm⁻¹) 3440, 3080, 3020, 2980, 1920, 1585, 1480, 4000 (the case of the case of 1440, 1095, 1070, 1000, 825; ¹H NMR (60 MHz, $CDCl_3$, δ) 7.50–6.93 (m, 15 H), 4.23 (br s, 5 H), 3.60–2.50 (complex m, 3 H), 2.13 (br s, 1 H), 0.63, 0.60 (two singlets, 9 H total, 50/50 ratio). Anal. Calcd for $C_{31}H_{33}FeO_3F$: C, 68.80; H, 6.16. Found: C, 68.97; H, 5.90. 9d: yellow orange solid; 60/40 mixture of diastereomers; IR (CHCl₃, cm⁻¹) 3400, 2980, 2882, 1915, 1582, 1440, 1383, 1172, 1100, 1039, 1020, 935; ¹H NMR (270 MHz, CDCl₃, δ) 7.97-7.81 (m, 4 H), 7.62-7.38 (m, 6 H), 4.24 (m, 5 H), 3.46-2.22 (m, δ 6) $13^{1-7.81}$ (m, 4 H), $1.62^{-7.38}$ (m, 6 H), 4.24 (m, 5 H), $3.40^{-2.22}$ (m, 8 H), 1.10, 0.94 (two triplets, each J = 5 Hz, 6 H total, 40/60 ratio), 0.79, 0.75 (two singlets, 9 H total, 60/40 ratio). Anal. Calcd for $C_{29}H_{38}FeNO_3P$: C, 65.05; H, 7.15. Found: C, 65.23; H, 7.33. 10b: yellow-orange solid; 50/50 mixture of diastereomers; IR (CHCl₃, cm⁻¹) $3407, 3059, 3000, 1919, 1580, 1480, 1434, 1093, 998, 937, 824; ¹H NMR (60 MHz, CDCl₃, <math>\delta$) $7.73^{-7.07}$ (m, 20 H), $4.93^{-4.50}$ (m, 1 H), 4.40 (m, 5 H), 4.00 (m, 0.5 H, we have a right DO (2) 2.67 (m 2.5 H, 0.5 H, 0.5 H, 0.0) exchanges with D_2O), 3.33-2.67 (m, 2.5 H, 0.5 H exchanges with D_2O).

⁽¹⁾ After submission of our manuscript, Professor Bergman (Berkeley) reported the successful generation of the enolate of a cobaltacyclo-pentanone which underwent high yield aldol and alkylation reactions: Theopold, K. H.; Becker, P. N.; Bergman, R. G. J. Am. Chem. Soc. 1982, 104, 5250.



aspect of the chemistry, we prepared iron acyls $1c^4$ and $1d^6$ but found that 1c did not give a stable enolate and although 1d formed a stable enolate, reaction with pivaldehyde gave only a 60:40 mixture of diastereomeric aldol products 9d in 53% yield (31% recovered starting material).5

The acyl-iron bond is readily cleaved in these complexes to give high yields of esters. For example, slow addition of a CH_2Cl_2 solution of N-bromosuccinimide to a solution of iron acyl 6b in 1:1 CH₂Cl₂/ethanol at -42 °C resulted in oxidative cleavage, giving ethyl dihydrocinnamate in 89% yield (eq 2).

$$PPh_{3} \stackrel{\text{NBS}}{\underset{\text{CD}}{}} \stackrel{\text{NBS}}{\underset{\text{CH}_{2}Ci_{2}}{/}E + 0} \stackrel{\text{NBS}}{\underset{\text{E}}{} + 0} \stackrel{\text{CH}_{2}Ci_{2}}{\underset{\text{CH}_{2}Ci_{2}}{/}E + 0} (2)$$

The experimental procedures for the synthesis and subsequent cleavage or iron acyl 6b are typical. Diisopropylamine (190 μ L, 1.36 mmol) was added to a solution of *n*-butyllithium (825 μ L of 1.6 M hexane solution, 1.32 mmol) in THF (8 mL) maintained at 0 °C under N₂. After the mixture was stirred at 0 °C for 20 min, the flask was cooled in a dry ice/CH₃CN bath (ca. -42 °C). To this solution of LDA was added a solution of iron acyl 1b (500 mg, 1.10 mmol) in THF (4 mL) dropwise by syringe. During the addition the initial orange color of 1b turned to deep red. After the mixture was stirred at -42 °C for 90 min, the enolate was quenched by the addition of benzyl bromide (170 μ L, 1.43 mmol) that caused an immediate color change from red to dark orange. The reaction mixture was allowed to warm to room temperature, and after 30 min aqueous ammonium chloride (5%, 30 mL) was added followed by CH_2Cl_2 (30 mL) and 1.2 N HCl (20 mL). After the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (2 × 30 mL) and the CH_2Cl_2 extracts were combined and dried over Na₂SO₄. Filtration and removal of volatiles on a rotary evaporator left an orange oil that was chromatographed on activated alumina $(2 \times 15 \text{ cm}, \text{CH}_2\text{Cl}_2)$ and gave 542 mg (91%) of iron complex **6b** as a deep orange solid: mp 128-131 °C $(CH_2Cl_2/petroleum ether)$; IR $(CHCl_3, cm^{-1})$ 3050, 3010, 1920, 1600, 1490, 1440; 60-MHz ¹H NMR (CDCl₃, δ) 7.6-6.8 (m, 20 H), 4.3 (d, J = 2 Hz, 5 H), 3.2–2.0 (m, 4 H). Cleavage of the metal-acyl bond was effected by dissolving iron complex 6b (389 mg, 0.715 mmol) in CH₂Cl₂ (5 mL) and diluting with an equal volume of EtOH. After the solution was cooled in a dry ice/CH₃CN bath (ca. -42 °C), N-bromosuccinimide (142 mg, 0.793 mmol) dissolved in CH_2Cl_2 (5 mL) was added dropwise. The color of the solution slowly changed from orange to deep green. After the addition, the solution was allowed to warm to room temperature and after 45 min was transferred to a separatory funnel with the aid of CH_2Cl_2 and then washed with 1 N NaOH. After the aqueous solution was backextracted with CH_2Cl_2 , the combined CH_2Cl_2 layers were dried over Na_2SO_4 . Filtration followed by removal of volatiles on a rotary evaporator at room temperature left a green semi-solid residue that was triturated several times with Et_2O . The combined ether fractions were condensed to an oil which after filtration through a short alumina column with petroleum ether gave 114 mg (89%) of ethyl dihydrocinnamate, identical with an authentic sample.

The generation of these iron acyl enolates and their reaction with electrophiles are comparable to the formation and reaction of organic ester enolates under strongly basic, aprotic conditions. Although the chiral iron center, in the present work, did not significantly control the formation of any new asymmetric carbon atoms, further work with conformationally restricted iron acyl enolates may overcome this limitation.

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Octafluorocyclooctatetraene Transition-Metal Compounds. Novel Transannular Ring Closures and a Formal Intramolecular Redox Equilibrium between **1,2,5,6**- η and **1,2,3,6**- η Ligands

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Summary: Octafluorocyclooctatetraene (OFCOT) reacts with $[Co(CO)_2(\eta-C_5Me_5)]$ to give $[Co(\eta-C_5Me_5)(C_8F_8)]$, which is in dynamic redox equilibrium between the 1,2,5,6- η and 1,2,3,6- η forms of coordinated OFCOT. The molecular structure of a cobalt product derived from transannular ring closure of OFCOT is also reported, and structure reassignments for some Pt-OFCOT compounds are proposed.

The recent synthesis² and structural characterization³ of octafluorocyclooctatetraene (OFCOT) have allowed its organometallic chemistry to be compared to that of its thoroughly studied hydrocarbon analogue.⁴ We have

⁽⁶⁾ Prepared according to standard procedures⁴ from $CpFe(CO)_2CH_3$ and PhoPNEto

⁽¹⁾ Alfred P. Sloan Research Fellow, 1980-1984

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