

zation is observed in the H-H coupled components, as would be expected for para H₂ induced polarization. In addition, since each P split component exhibits an E/A phase compared with A/E phases in the trans and gem proton resonances of styrene, the sign of J_{HH} for IrH₂X(CO)(dppe) is opposite that of $^3J_{HH}$ in styrene and is therefore negative.

The results reported here demonstrate para H₂ induced polarization which should prove useful for the study of hydrogenations, H₂ oxidative additions, and, because of its amplification effect, the detection of catalytically significant hydrides. The effectiveness of the method depends on the pairwise transfer of H₂ to an organic substrate or a metal center and the rate at which this occurs relative to proton relaxation. Finally, unlike previous studies employing ortho/para H₂ conversion to follow hydrogenation and H₂ oxidative addition,^{15,16} the method described here monitors the products directly and is capable of much greater sensitivity.

Acknowledgment. We thank the National Science Foundation (CHE 86-05033) for partial support of this work and the Johnson Matthey Co., Inc. for a generous loan of rhodium salts. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank Prof. Robert G. Bergman, Prof. Dan Weitekamp, and Dr. Henry Bryndza for helpful discussions.

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Activation of Carbon-Fluorine Bonds by Oxidative Addition

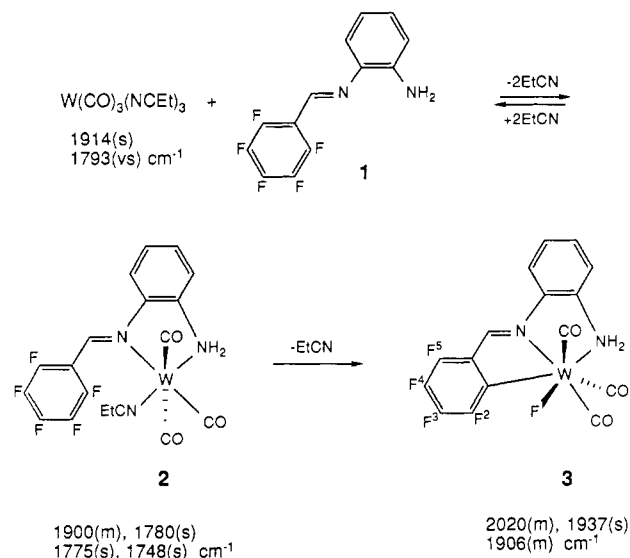
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The oxidative addition of carbon-heteroatom bonds to transition metals has been intensively investigated as a synthetic pathway to new organometallic complexes and employed for the catalytic functionalization of organic compounds.¹ Recent advances have extended the scope of this process to include carbon-hydrogen bond activation.² However, few examples of cleavage of carbon-fluorine bonds by oxidative addition to a metal center are known despite the continuing interest in fluoroorganometallic chemistry.³ The greater abundance of systems capable of activating C-H bonds relative to C-F bonds is perhaps not surprising given the great strength of the C-F bond (125 kcal/mol for Ph-F versus 110 kcal/mol for Ph-H).⁴ In this communication we report

Scheme I



that facile oxidative addition of an aromatic C-F bond takes place at tungsten(0).

Literature precedent for C-F bond cleavage includes the low yield synthesis of thermally unstable *trans*-Ni(PET₃)₂(C₆F₅)F from C₆F₆.⁵ Orthometalation of pentafluoroazobenzene by Mn₂(CO)₁₀^{6a} and of perfluoroazobenzene by CpRu(PPh₃)₂Me^{6b} has been observed as minor products in refluxing heptane. Photochemical activation of an aromatic C-F bond in a 1,4-bis(pentafluorophenyl)tetrazadiene ligand coordinated to cobalt has also been reported.⁷ In the latter three cases, the fate of the cleaved fluorine atom was not determined.

Recently we demonstrated that chelate-assisted oxidative addition of a Ph-X (X = Cl, Br, I) bond in appropriately designed ligands takes place at tungsten(0) under mild conditions.⁸ Extension of this chemistry has resulted in the discovery of a ligand in which oxidative addition of a Ph-F bond occurs in high yield to afford a stable tungsten(II) metallacycle with the cleaved fluorine atom bound to the metal center.

Reaction of pentafluorobenzaldehyde with 1.0 equiv of 1,2-diaminobenzene in ethanol affords the yellow crystalline 1:1 Schiff base (**1**) in 92% yield.⁹ Treatment of **1** with 1.0 equiv of $W(CO)_3(EtCN)_3$ ¹⁰ in THF at room temperature under nitrogen gives a deep red solution of **3**; IR monitoring (see Scheme I) indicates the reaction is complete in less than 10 min. Addition of hexanes and cooling to -10 °C affords red crystalline **3** in 69% yield as a THF solvate.¹¹

The structure **3** is assigned by interpretation of IR, ¹⁹F, and ¹H NMR spectroscopic data and confirmed by single-crystal X-ray diffraction. The ¹⁹F NMR spectrum exhibits four coupled aromatic C-F resonances at -111.44, -138.06, -151.61, and -162.06 ppm versus CCl₃F in acetone-*d*₆. A broad peak ($\nu_{1/2}$ = 23 Hz) at -225.97 ppm is assigned to the fluoride bound to tungsten. This resonance is slightly solvent dependent and shifts to -237.1 ppm when D₂O is added to the sample suggesting hydrogen bonding to the fluoride.¹² Although ¹⁸³W-¹⁹F coupling has been observed

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(9) NMR data for **1**: ¹⁹F (CDCl₃, CCl₃F reference) -142.87 (dd, 2 F), -151.16 (t, 1 F), -162.31 (m, 2 F); ¹H (CDCl₃) 8.68 (s, 1 H), 7.13 (m, 1 H), 6.78 (m, 3 H), 4.23 (br, 2 H). Anal. Calcd for C₁₃H₇N₂F₅: C, 54.56; H, 2.47; N, 9.79; F, 33.19. Found: C, 54.44; H, 2.30; N, 9.75; F, 33.36.

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(11) Anal for **3**·THF. Anal. Calcd for C₂₀H₁₅N₂F₅O₄W: C, 38.36; H, 2.41; N, 4.47; F, 15.17. Found: C, 38.03; H, 2.27; N, 4.63; F, 15.36.

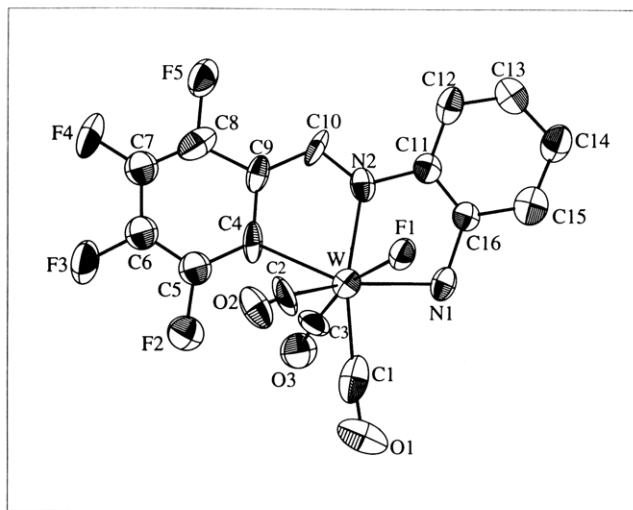


Figure 1. ORTEP representation of **3** with THF solvate omitted. Selected bond distances (Å) are as follows: W–N1, 2.250 (5); W–N2 2.182 (6); W–C1, 2.03 (1); W–C2, 1.947 (8); W–C3, 1.859 (7); N2–C10, 1.265 (8). Selected bond angles (deg) are as follows: F1–W–C4, 125.5 (2); N1–W–N2, 75.2 (2); N2–W–C4, 73.1; N2–W–C1, 164.6 (2); N1–W–C2; 155.1 (3); F1–W–C3, 165.1 (3).

in several higher oxidation state compounds,¹³ the width of the resonance hinders the detection of ¹⁸³W satellites. The strongly deshielded resonance at –111.44 ppm is assigned¹⁴ to F² (see Scheme I) and exhibits an additional coupling to the imine proton of the ligand (⁵J_{HF} = 1.9 Hz). Selective ¹⁹F decoupling of this resonance causes the imine to collapse to a singlet clearly revealing ¹⁸³W satellites (³J_{WH} = 8.8 Hz). This coupling is indicative of metallocycle formation in related ligand systems.⁸ Aside from the aromatic backbone of the ligand, diastereotopic NH protons are observed at 6.52 and 6.30 ppm. Addition of D₂O results in rapid proton exchange of the amine hydrogens as evidenced by ¹H NMR spectra.

The solid-state structure of **3** is illustrated in Figure 1.¹⁵ The geometry of the seven-coordinate complex can be approximated as a capped octahedron with C4 as the capping atom.¹⁶ The W–C4(2.232 (6) Å)⁸ and W–F1(2.032 (4) Å)¹⁷ bond lengths appear to be normal. The five-membered metallocycle is planar with the largest deviation from the least-squares plane being 0.09 Å. Indeed, the entire ligand (15 atoms) is planar within ±0.25 Å; the tungsten atom is located 0.72 Å from this plane.

The mechanism of this reaction is under investigation. Intermediate **2** can be isolated as a dark purple solid in 82% yield by conducting the reaction in CH₂Cl₂ followed by immediate precipitation with hexanes.¹⁸ Transformation of **2** to **3** is rapid in THF at room temperature. However, dissolution of **2** in CH₃CN affords **1** and W(CO)₃(NCCH₃)₃. Low-temperature ¹⁹F

NMR studies of **2** in acetone-*d*₆ did not provide any evidence for fluorocarbon binding to tungsten,¹⁹ but studies in less coordinating solvents proved difficult because of the low solubility and high reactivity of **2**.

Several factors probably account for the remarkably facile C–F oxidative addition process described above. The nitrogen donor atoms of **1** afford the very basic metal center (as judged by low ν_{CO} values in the IR spectrum) required for oxidative addition in the intermediate **2**. The chelating nature of the ligand reduces the entropic barrier to reaction and the planar, conjugated metallocycle is quite stable.⁸ In addition, the overall thermodynamic favorability of this transformation suggests that the tungsten(II)–fluoride bond is reasonably strong despite the low formal oxidation state of the metal.²⁰

These results suggest that metal-catalyzed transformations of heavily fluorinated organic molecules may be possible despite the great strength of the carbon–fluorine bond. We are continuing to explore other carbon–heteroatom bond activation reactions in this and related systems.

Acknowledgment. T.G.R. is the recipient of a Distinguished New Faculty Grant from the Camille & Henry Dreyfus Foundation Inc. We are grateful for support from the donors of the Petroleum Research Fund administered by the American Chemical Society. High field NMR spectrometers employed in this work were obtained through departmental grants from the National Science Foundation. We thank Dr. Alan E. Sopchik for recording 400 MHz ¹H{¹⁹F} NMR spectra.

Supplementary Material Available: Full crystallographic data for **3**·THF including tables of bond distances and angles and final positional and thermal parameters (14 pages); listing of calculated and observed structure factors (19 pages). Ordering information is given on any current masthead page.

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Free Energy Perturbation Method for Chemical Reactions in the Condensed Phase: A Dynamical Approach Based on a Combined Quantum and Molecular Mechanics Potential

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Received July 20, 1987

Dynamical simulations are necessary for a full understanding of the effect of the environment on the behavior of chemical reactions in solution^{1,2} and the active sites of enzymes.^{3,4} We have developed a molecular dynamics simulation methodology based on combined quantum and molecular mechanics potentials for addressing the general problem of chemical reactions in the condensed phase. In what follows we give a brief outline of the method and apply it to the S_N2 reaction Cl[–]+CH₃Cl in the gas phase and in solution.

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(18) NMR data for **2** at 0 °C: ¹⁹F (acetone-*d*₆, CCl₃F reference) –138.90 (d, 2 F), –154.65 (t, 1 F), –162.25 (m, 2 F); ¹H (acetone-*d*₆) 9.20 (s, 1 H), 7.71 (d, 1 H), 7.46 (m, 3 H), 6.21 (d, 1 H), 5.63 (d, 1 H).