zation is observed in the H-H coupled components, as would be expected for para H_2 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 $IrH_2X(CO)(dppe)$ is opposite that of $^3J_{HH}$ in styrene and is therefore negative.

The results reported here demonstrate para H_2 induced polarization which should prove useful for the study of hydrogenations, H_2 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 H_2 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 H_2 conversion to follow hydrogenation and H_2 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.

---

(15) Brown, J. M.; Canning, L. R.; Downs, A. J.; Forster, A. M. *J. Organomet. Chem.* **1983**, *255*, 103.

(16) Tadros, M. E.; Vaska, L. *J. Coll. Interfac. Sci.* **1982**, *85*, 389.

Activation of Carbon-Fluorine Bonds by Oxidative Addition

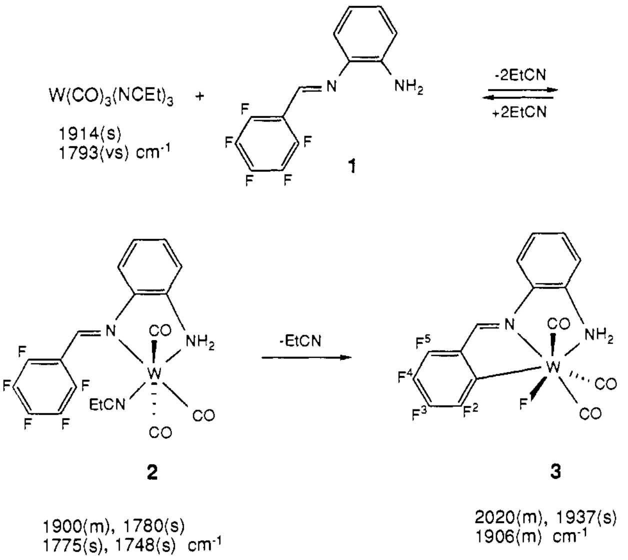
Thomas G. Richmond,* Carolyn E. Osterberg, and
Atta M. Arif

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

Received September 21, 1987

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

Scheme I



Literature precedent for C-F bond cleavage includes the low yield synthesis of thermally unstable *trans*-$Ni(PEt_3)_2(C_6F_5)F$ from C_6F_6.[5] Orthometalation of pentafluoroazobenzene by $Mn_2(CO)_{10}$[6a] and of perfluoroazobenzene by $CpRu(PPh_3)_2Me$[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, ^{19}F, and ^1H NMR spectroscopic data and confirmed by single-crystal X-ray diffraction. The ^{19}F NMR spectrum exhibits four coupled aromatic C-F resonances at -111.44, -138.06, -151.61, and -162.06 ppm versus CCl_3F 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 D_2O is added to the sample suggesting hydrogen bonding to the fluoride.[12] Although $^{183}W-^{19}F$ coupling has been observed

---

(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books, Mill Valley, CA 1987; pp 279-322. (b) Flood, T. C. *Top. Inorg. Organomet. Stereochem.* **1981**, *12*, 37-117. (c) Stille, J. K.; Lau, K. S. Y. *Acc. Chem. Res.* **1977**, *10*, 434-442.

(2) (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245-269. (b) Jones, W. D.; Foster, G. P.; Putinas, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 5047-5048, and references therein. (c) Nolan, S. P.; Hoff, C. D.; Stoutland, P. O.; Newman, L. J.; Buchanan, J. M.; Bergman, R. G.; Yang, G. K.; Peters, K. S. *J. Am. Chem. Soc.* **1987**, *109*, 3143-3145. (d) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1987**, *109*, 4726-4727.

(3) (a) Carl, R. T.; Doig, S. J.; Geiger, W. E.; Hemond, R. C.; Hughes, R. P.; Kelly, R. S.; Samkoff, D. E. *Organometallics* **1987**, *6*, 611-616, and references therein. (b) Burch, R. R.; Harlow, R. L.; Ittel, S. D. *Organometallics* **1987**, *6*, 982-987. (c) Stone, F. G. A. *Pure Appl. Chem.* **1972**, *30*, 551-573.

(4) Benson, S. W. *Thermochemical Kinetics*; John Wiley & Sons: NY, 1976; p 309.

(5) Fahey, D. R.; Mahan, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 2501-2508.

(6) (a) Bruce, M. I.; Goodall, B. L.; Sheppard, G. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1975**, 591-595. (b) Bruce, M. I.; Gardner, R. C. F.; Goodall, B. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1974**, 185-186.

(7) Gross, M. E.; Johnson, C. E.; Maroney, M. J.; Trogler, W. C. *Inorg. Chem.* **1984**, *23*, 2968-2973.

(8) Richmond, T. G.; King, M. A.; Kelson, E. P.; Arif, A. M. *Organometallics* **1987**, *6*, 1995-1996.

(9) NMR data for **1**: ^{19}F ($CDCl_3$, CCl_3F reference) -142.87 (dd, 2 F), -151.16 (t, 1 F), -162.31 (m, 2 F); ^1H ($CDCl_3$) 8.68 (s, 1 H), 7.13 (m, 1 H), 6.78 (m, 3 H), 4.23 (br, 2 H). Anal. for **1**. Anal. Calcd for $C_{13}H_7N_2F_5$: 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.

(10) Kubas, G. J. *Inorg. Chem.* **1983**, *22*, 692-694.

(11) Anal for **3**·THF. Anal. Calcd for $C_{20}H_{15}N_2F_5O_4W$: 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.

0002-7863/87/1509-8091$01.50/0 © 1987 American Chemical Society

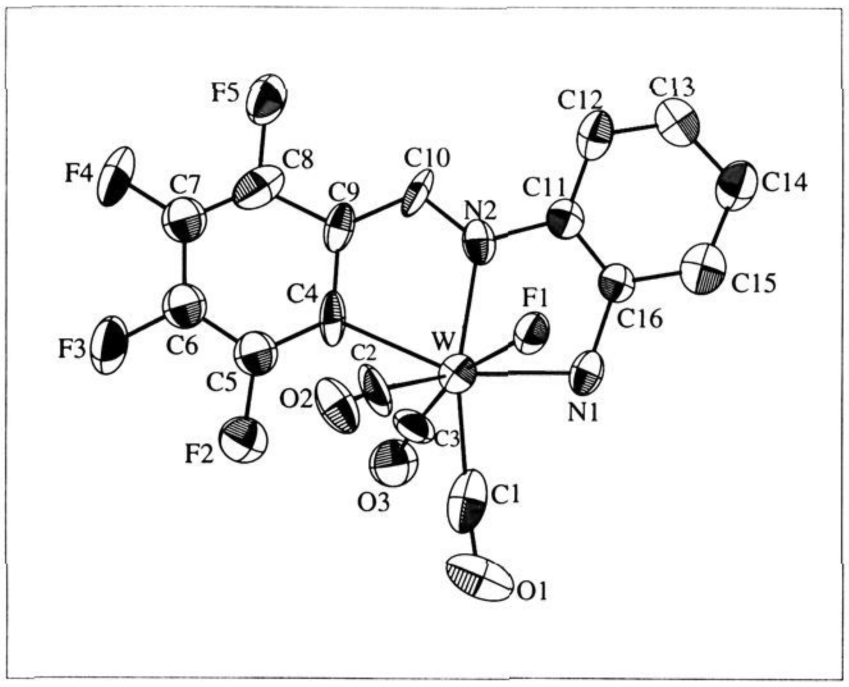


Figure 1. ORTEP representation of **3** with THF solvate omitted. Selected bond distances (Å) are as follows: W–N1, 2.250 (5); W–N2 2.182 (6); W–C1, 2.03 (1); W–C2, 1.947 (8); W–C3, 1.859 (7); N2–C10, 1.265 (8). Selected bond angles (deg) are as follows: F1–W–C4, 125.5 (2); N1–W–N2, 75.2 (2); N2–W–C4, 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 ^{183}W satellites. The strongly deshielded resonance at −111.44 ppm is assigned[14] to F^2 (see Scheme I) and exhibits an additional coupling to the imine proton of the ligand ($^5J_{HF}$ = 1.9 Hz). Selective ^{19}F decoupling of this resonance causes the imine to collapse to a singlet clearly revealing ^{183}W 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 D_2O results in rapid proton exchange of the amine hydrogens as evidenced by ^{1}H 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 metallacycle 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 CH_2Cl_2 followed by immediate precipitation with hexanes.[18] Transformation of **2** to **3** is rapid in THF at room temperature. However, dissolution of **2** in CH_3CN affords **1** and $W(CO)_3(NCCH_3)_3$. Low-temperature ^{19}F 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 metallacycle 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 $^1H\{^{19}F\}$ 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.

---

[12] (a) Nesmeyanov, A. N.; Nogina, O. V.; Fedin, E. I.; Dubovitskii, V. A.; Kvasov, B. A.; Petrovskii, P. V. *Dokl. Chem. Proc. Acad. Sci. USSR, Chemistry Section* **1972**, *205*, 632–636. *Dokl. Akad. Nark SSSR* **1972**, *205*, 857–860. (b) Buffin, B. P.; Richmond, T. G., unpublished results, **1987**.

[13] (a) Wray, V. *Ann. Rep. NMR Spec.* **1983**, *14*, 365. (b) Postel, U.; Riess, J. G.; Calves, J. Y.; Guerchais, J. *Inorg. Chim. Acta* **1979**, *32*, 175–180.

[14] Bruce, M. I. *J. Chem. Soc. A* **1968**, 1454–1464.

[15] Crystal data for **3**·THF: $WF_5O_4N_2C_{20}H_{15}$, yellow, monoclinic, $P2_1/a$, a = 9.228 (9) Å, b = 16.814 (13) Å, c = 13.800 (8) Å, β = 105.05 (6)°, V = 2067.9 Å^3, Z = 4, Mo Kα of 3030 reflections collected at ambient temperature (Syntex P$\bar{1}$, 3° < 2θ < 45°) were unique of which 1971 had $F^o > 2\sigma F^o$ and were used in the solution (Patterson) and refinement. Final refinement included all non-hydrogen atoms as anisotropic contributions except for C5 and C7 which were refined as isotropic contributions (279 variables). For parameters, R = 0.084 and R_w = 0.088, GOF = 2.7, and highest peak in the final map of 1.3 e Å^{-3} approximately 1.3 Å from W.

[16] Drew, M. G. B. *Prog. Inorg. Chem.* **1977**, *23*, 67–210. Hoffmann, R.; Beier, B. F.; Muetterties, E. L.; Rossi, A. R. *Inorg. Chem.* **1977**, *16*, 511–522.

[17] Hidai, M.; Mizobe, Y.; Sato, M.; Kodama, T.; Uchida, Y. *J. Am. Chem. Soc.* **1978**, *100*, 5740–5748.

[18] NMR data for **2** at 0 °C: ^{19}F (acetone-d_6, CCl_3F reference) −138.90 (d, 2 F), −154.65 (t, 1 F), −162.25 (m, 2 F); ^{1}H (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).

[19] (a) Kulawiec, R. J.; Holt, E. M.; Lavin, M.; Crabtree, R. H. *Inorg. Chem.* **1987**, *26*, 2559–2561. (b) Uson, R.; Fornies, J.; Tomas, M.; Cotton, F. A.; Falvello, L. R. *J. Am. Chem. Soc.* **1984**, *106*, 2482–2483. (c) Catala, R. M.; Cruz-Garritz, D.; Hills, A.; Hughes, D. L.; Richards, R. L.; Sosa, P.; Torrens, H. *J. Chem. Soc., Chem. Commun.* **1987**, 261–262.

[20] For a recent discussion of the stability of low valent metal fluorides, see: Branan, D. M.; Hoffman, N. W.; McElroy, E. A.; Miller, N. C.; Ramage, D. L.; Schott, A. F.; Young, S. H. *Inorg. Chem.* **1987**, *26*, 2915–2917.

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

Paul A. Bash,* Martin J. Field,* and Martin Karplus*

Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

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 $Cl^- + CH_3Cl$ in the gas phase and in solution.

---

[1] Chandrasekhar, J.; Smith, S. F.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 154.

[2] Bergsma, J. P; Gartner, B. J.; Wilson, K. R.; Hynes, J. T. *J. Chem. Phys.* **1987**, *86*, 1356.

[3] Northrup, S. H.; Pear, M. R.; Lee, C.-Y.; McCammon, J. A.; Karplus, M. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 4035.

[4] Brünger, A.; Brooks, C. B.; Karplus, M. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 8458.

0002-7863/87/1509-8092$01.50/0