Measurements were carried out both at a constant ionic strength of 0.5 M and also in the absence of any added electrolyte. The equilibrium constant increases with decreasing temperature. Lower ΔH^0 values are observed for the more acidic hydrides, while the negative values of ΔS^0 are expected due to greater solvation of the ionic products. Thermolysis of the iron vinylidene cation (BF_4^- counterion) in CH_3CN at 57 °C releases *tert*-butylacetylene and leads to the formation of $(C_5H_5)(CO)(PMe_3)Fe(CH_3CN)^+BF_4^-$, which was isolated as red needles in 78% yield.[3]

Acknowledgment. This research was carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences. I thank Drs. Carol Creutz, Mark Andrews, Ed Samsel, and Jack Norton for helpful discussions and Dr. Bruce Brunschwig for assistance with the stopped-flow kinetics.

Supplementary Material Available: Spectroscopic and analytical data for $\mathbf{1}^+$ (PF_6^-, Cr^-, Mo^-, W^- salts), $\mathbf{2}^+PF_6^-$, $\mathbf{3}^+PF_6^-$, $(C_5H_5)(CO)(PMe_3)Fe{-}C{\equiv}C{-}CMe_3$, $(C_5H_5)(CO)(PMe_3)Fe{=}C{=}C(H)CMe_3^+BF_4^-$, and $(C_5H_5)(CO)(PMe_3)Fe(CH_3CN)^+BF_4^-$ (3 pages). Ordering information is given on any current masthead page.

Para Hydrogen Induced Polarization in Hydrogenation Reactions

Thomas C. Eisenschmid, Rein U. Kirss, Paul P. Deutsch,
Sven I. Hommeltoft, and Richard Eisenberg*

Department of Chemistry, University of Rochester
Rochester, New York 14627

Joachim Bargon

Institut für Physikalische Chemie
Universität Bonn, 5300 Bonn, West Germany

Ronald G. Lawler

Department of Chemistry, Brown University
Providence, Rhode Island 02912

Alan L. Balch

Department of Chemistry, University of California at
Davis, Davis, California 95616

Received August 13, 1987

Since 1969, the occurrence of enhanced NMR absorptions and emissions known as CIDNP has been viewed as definitive evidence of a radical pair mechanism.[1-3] Recently, we reported that the binuclear complex $Rh_2H_2(CO)_2(dppm)_2$ hydrogenates alkynes with CIDNP observed in the product olefin resonances.[4] Through the use of ^{13}C and ^2H labeled substrates, we showed that the polarization process did *not* involve the intermediacy of organic radicals, thus differing from other observations of CIDNP in hydrogenations involving mononuclear organometallic hydrides.[5-8] We now report results with other complexes and substrates including simple olefins and show that the polarizations we observe, and those described earlier,[4] arise from para H_2. The notion that hydrogenation reactions using para H_2 can generate polarized products has recently been proposed and demonstrated by Weitekamp.[9] This means of developing polarization, which does not require radicals of any type, promises to be a highly useful tool for the study of hydrogenation reactions and H_2 oxidative additions.

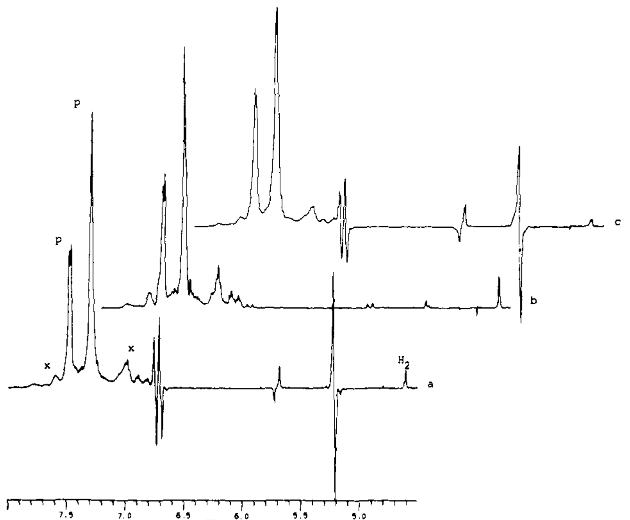
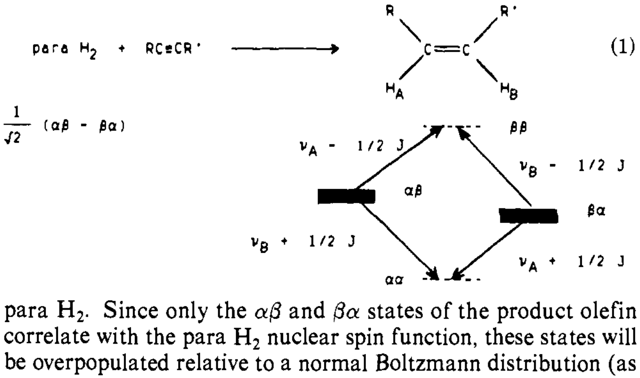


Figure 1. ^1H NMR spectra at 400 MHz showing para H_2 induced polarization in the resonances of styrene from the reaction of $[Rh_3Cl_2H_2(CO)_2((Ph_2PCH_2)_2PPh)_2]^+$ with $PhC{\equiv}CH$ in $CDCl_3$ under H_2: (a) after storage at −196 °C under H_2; (b) after storage at −196 °C under vacuum followed by addition of tank H_2; (c) after storage at −196 °C under vacuum followed by addition of para enriched H_2. The resonances marked "x" are due to the catalyst complex and those marked "p" are due to excess $PhC{\equiv}CH$.

According to the Weitekamp proposal,[9] para H_2 induced polarization can arise when H_2 is transferred pairwise to a substrate to yield a product in which the two transferred protons are magnetically distinct. If the reaction occurs fast relative to proton relaxation, then the transferred protons will initially reflect the nuclear spin populations of the starting dihydrogen. This is shown schematically in eq 1 for hydrogenation of an internal alkyne with para H_2. Since only the $\alpha\beta$ and $\beta\alpha$ states of the product olefin correlate with the para H_2 nuclear spin function, these states will be overpopulated relative to a normal Boltzmann distribution (as shown in the diagram of eq 1), giving rise to polarized A/E or



(1)

---

(1) (a) Kaptein, R.; Oosterhoff, L. J. *Chem. Phys. Lett.* **1969**, *4*, 195. (b) Kaptein, R.; Oosterhoff, L. J. *Chem. Phys. Lett.* **1969**, *4*, 214.

(2) Closs, G. L. *J. Am. Chem. Soc.* **1969**, *91*, 4552.

(3) (a) Lepley, A. R.; Closs, G. L. *Chemically Induced Magnetic Polarization*; J. Wiley and Sons: New York, 1973. (b) Salikhov, K. M.; Molin, Yu. N.; Sagdeev, R. Z. *Spin Polarization and Magnetic Effects in Radical Reactions*; Elsevier: New York, 1984. (c) Ward, H. R. *Acc. Chem. Res.* **1972**, *5*, 18–24. (d) Lawler, R. G. *Acc. Chem. Res.* **1972**, *5*, 25–31. (e) Kaptein, R. *Adv. Free Radical Chem.* **1975**, 5, 319. (f) Closs, G. L. *Adv. Magn. Reson.* **1974**, *7*, 157.

(4) Hommeltoft, S. I.; Berry, D. H.; Eisenberg, R. *J. Am. Chem. Soc.* **1986**, *108*, 5345.

(5) Halpern, J.; Sweany, R. L. *J. Am. Chem. Soc.* **1977**, *99*, 8335.

(6) (a) Nalesnik, T. E.; Orchin, M. *Organometallics* **1982**, *1*, 222–3. (b) Nalesnik, T. E.; Orchin, M. *J. Organomet. Chem.* **1981**, *222*, C5.

(7) (a) Connolly, J. W. *Organometallics* **1984**, *3*, 1333. (b) Thomas, M. J.; Shackleton, T. A.; Wright, S. C.; Gillis, D. J.; Colpa, J. P.; Baird, M. C. *J. Chem. Soc., Chem. Commun.* **1986**, *312*. (c) Wassink, B.; Thomas, M. J.; Wright, S. C.; Gillis, D. J.; Baird, M. C. *J. Am. Chem. Soc.* **1987**, *109*, 1995.

(8) (a) Bockman, T. M.; Garst, J. F.; King, R. B.; Marko, L.; Ungvary, F. *J. Organomet. Chem.* **1985**, *279*, 165. (b) Garst, J. F.; Bockman, T. M.; Batlaw, R. *J. Am. Chem. Soc.* **1986**, *108*, 1689.

(9) (a) Bowers, C. R.; Weitekamp, D. P. *Phys. Rev. Lett.* **1986**, *57*, 2645. (b) Bowers, C. R.; Weitekamp, D. P. *J. Am. Chem. Soc.* **1987**, *109*, 5541.

0002-7863/87/1509-8089$01.50/0

E/A transitions similar to a multiplet effect.

The procedure for generating para H_2 induced polarization is relatively simple. The sample for study is prepared under H_2 and stored for 8 h or more in liquid N_2 prior to reaction. While ortho/para H_2 conversion is slow in the gas phase, it is promoted, albeit inefficiently by many species including the platinum group element complexes used in the present study. At 80 K, the equilibrium composition of H_2 is 48.39% para and 51.61% ortho compared with 25.13% para and 74.87% ortho at 273 K.[10] Upon warming, the sample is shaken and inserted immediately into the NMR probe with data collection commencing within 20 s.

In one set of experiments, the trinuclear complex $[Rh_3Cl_2H_2(CO)_2((Ph_2PCH_2)_2\text{-}PPh)_2]^+$[11] (4.5 mM) was employed as the hydrogenation catalyst with $PhC{\equiv}CH$ as the substrate (150 mM) in $CDCl_3$ under 2–3 atm H_2. When the sample was introduced into the probe at 50 °C, styrene was produced which, as shown in Figure 1a, exhibited strong A/E polarization in the H resonance trans to phenyl (δ 5.06; J_{HH} = 11 Hz) and A/E/A/E polarization in the H resonance geminal to phenyl (δ 6.57; J_{HH} = 18, 11 Hz).[12] A weaker E/A polarization in the cis proton signal (δ 5.59; J_{HH} = 18 Hz) is also observed due to cross-polarization[9] since this proton was never part of the original H_2 molecule.[4,11] To verify that the polarization was indeed para H_2 induced, two other identical samples were prepared and stored under vacuum at −196 °C. To one sample was added H_2 (3 atm) just prior to insertion into the NMR spectrometer while to the other, a similar pressure of para enriched H_2, prepared separately,[12b] was added. The former showed no polarization (Figure 1b) while the latter (Figure 1c) exhibited polarizations essentially identical with that seen for the sample *stored* under H_2.

A second set of experiments used the complex $Pd_2Cl_2(Ph_2PCH_2PPh_2)_2$[13] as the catalyst. A sample containing the catalyst (2 mM) and $PhC{\equiv}CH$ (180 mM) in $CDCl_3$ under ~3 atm H_2 showed a small amount of styrene with *no* polarization when examined without prior storage at −196 °C. However, polarization similar to that in Figure 1a was seen when the sample was subsequently stored for 24 h in liquid N_2. After decay of the polarization which occurs within 10–12 min at 80 °C, the process was repeated. Through several cycles, large multiplet polarizations in the styrene resonances were observed when the sample was placed in the NMR probe.

Since the magnitude of the polarization relates in part to the relaxation time of the product protons, deuteriated substrates lead to more intense and longer lasting polarizations. This is particularly significant when olefins are used as the substrate, thus allowing for the observation of para H_2 induced polarization in the diproteo alkane products. These polarizations have been seen when styrene-d_8, propylene-d_6, and ethylene-d_4 have been employed with $[Rh_3Cl_2H_2(CO)_2((Ph_2PCH_2)_2PPh)_2]^+$ as the catalyst. Figure 2 shows the para H_2 induced polarization for CHD_2CHD_2 which, despite the equivalence of the two protons, is a complex $AA'X_2X'_2$ spin system due to H–D coupling. Thus this method can be used to study hydrogenation of simple olefins and assess whether the catalysis occurs via pairwise transfer of hydrogen atoms.

The activation of H_2 in homogeneously catalyzed hydrogenations occurs by oxidative addition. To determine whether para H_2 induced polarization can also be seen in the metal complex products of H_2 oxidative addition reactions, we have examined the reaction of IrX(CO)(dppe), X = CN and Br,[14] with para enriched H_2. These Ir(I) complexes undergo stereoselective H_2 oxidative additions to yield initially the cis dihydride products as shown in eq 2.[14] The results are shown in Figure 3. While each hydride resonance shows normal P coupling, impressive polari-

Figure 2. Para H_2 induced polarization in the ethane resonances of CHD_2CHD_2. Resonances marked s are due to impurities in the solvent. The separation between the absorption maxima (and between the emission minima) corresponds to 11.2 Hz while the separation between the central emission and absorption peaks is 3.4 Hz.

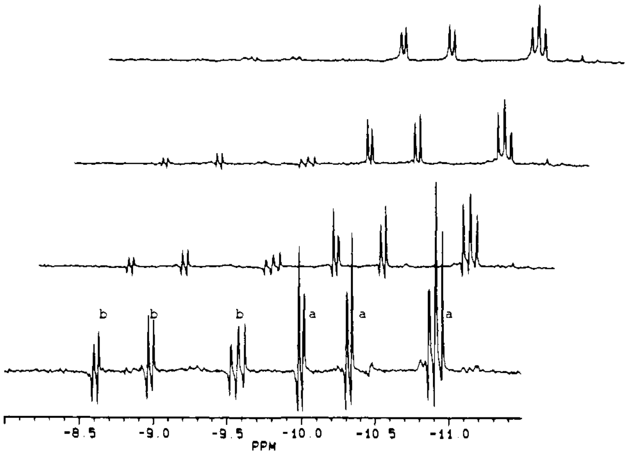
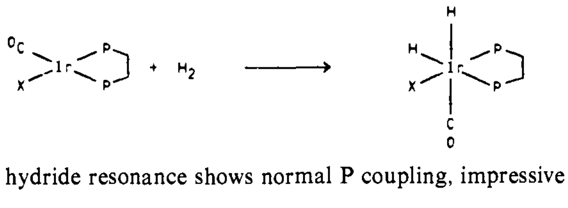


Figure 3. Para H_2 induced polarization in the hydride resonances of $IrH_2X(CO)(dppe)$ for X = CN labeled *a* and for X = Br labeled *b*. The times for the spectra correspond to 1, 2, 3 and 5 min after thawing the sample to commence reaction.



(2)

---

(10) Mackay, K. M. "The Element Hydrogen" In *Comprehensive Inorganic Chemistry*; Pergamon Press: Oxford, 1973; Vol. 1, pp 1–22, and references therein.

(11) Balch, A. L.; Linehan, J. C.; Olmstead, M. M. *Inorg. Chem.* **1985**, *24*, 3975.

(12) (a) In most cases 16 scans were collected which made the acquisition time for each spectrum 1 min. In some experiments only 8 scans were collected corresponding to an acquisition time of 30 s. A pulse width of 3 μs (~22° pulse angle) was used in all experiments. (b) Para enriched H_2 was prepared by pressurizing a 250-mL bulb to 1 atm H_2 at −196 °C over activated charcoal and iron oxide (rust) and allowing it to stand for 24 h at −196 °C.

(13) Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1983**, 889.

(14) Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 3148.

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

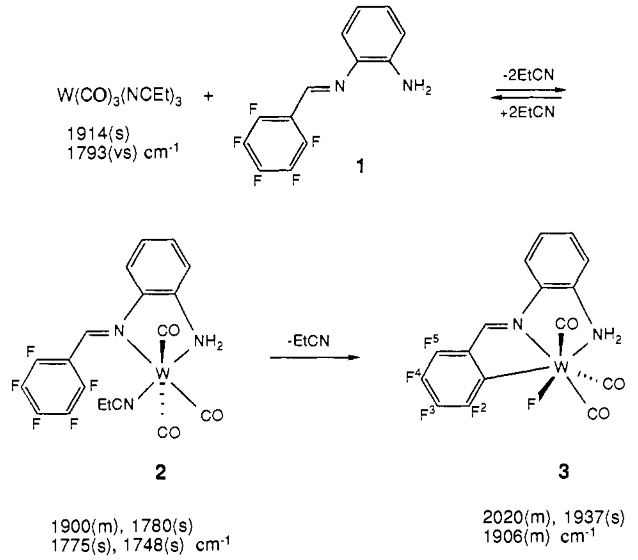
Thomas G. Richmond,* Carolyn E. Osterberg, and
Atta M. Arif

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