Table I. Hydrophilicity and Accessible Sulfonic Acid Groups in Sulfonated Polyethylene Films before and after Annealing[a]

sulfonation time,[b] min	annealing time, min: 0			15			60		
	$[SO_3H]$[c]	θ_a[d]	θ_r[d]	$[SO_3H]$[c]	θ_a[d]	θ_r[d]	$[SO_3H]$[c]	θ_a[d]	θ_r[d]
0.5	1.38×10^{14}	77	15	1.37×10^{14}	67	6	0.78×10^{14}	69	7
3.0	4.17×10^{14}	71	12	2.26×10^{14}	56	12	1.36×10^{14}	58	10
5.0	5.67×10^{14}	61	7	4.24×10^{14}	54	7	2.51×10^{14}	54	4

[a] Annealing was carried out in vacuum at 70 °C for 15-min or 60-min periods at a pressure of ca. 0.1 Torr. Annealing in air gave essentially the same results, but vacuum annealing was used to minimize the risk of autooxidation. Hydrophilicity was measured by using advancing water contact angles using doubly distilled water. [b] Sulfonations were carried out on commercial polyethylene films (cf. ref 11) according to the procedures described in the text. [c] Number of SO_3H groups/cm^2. [d] Degrees.

in size. More interesting was the behavior of films containing ammonium salts on annealing (Figure 1). As can be seen from these plots of θ_a versus annealing time, films with ammonium salts having longer organic groups annealed to form polyethylene-like surfaces while those having shorter chain alkylammonium salts annealed to form more hydrophilic surfaces.

Exchange of one alkylammonium salt for another indicated that these effects are reversible. For example, treatment of the octadecylammonium-containing film ($\theta_a = 81°$) with butylamine in ethanol for 1 h at 25 °C produced a film whose advancing contact angle after annealing in vacuum at 70 °C was 58° while treatment of a butylammonium film ($\theta_a = 62°$) with octadecylamine in ethanol for 1 h at 25 °C produced a film with $\theta_a = 85°$ after annealing.

There are a variety of possible explanations for the observed changes in hydrophilicity seen in the above experiments. First, it seems reasonable that the initial extent of sulfonation and advancing water contact angle both result from increasing amounts of surface sulfonation. Similarly, introduction of ammonium salts onto unannealed films produces a series of films whose contact angle varies in accord with the hydrophobicity of the introduced alkylammonium group. However, the explanation for the changes seen on annealing is less clear. Our experiments do however exclude some explanations. SEM and FT-IR measurements[11] before and after annealing show no change in the polymer's morphology though the SEM photographs showed that the surfaces were etched. The hysteresis seen in the contact angles (Table I) results, in part, because we are not dealing with smooth surfaces. All SO_3H-containing polymers had a decreased θ_a (water) after annealing. Receding contact angles were always low. The change in water contact angle roughly paralleled a decrease in the number of titratable SO_3H groups. The conclusion from the dyeing experiments that the $[SO_3H]_{surface}$ is diminished on annealing was confirmed by ESCA. ESCA showed that the area ratio for S/O/C was 0.19/1.34/1.00 initially and 0.10/0.45/1.00 after 60 min of annealing for a 5-min-sulfonated film. The change in the S/C ratio was approximately the same as noted in the dyeing experiment. The presence of sulfonated oligomers and the presence of other impurities seem unlikely explanations for the observed effects since similar changes were seen in vacuum and in refluxing solvent. Products of oxidative chain cleavage or other impurities should have been extracted by refluxing 2-propanol. An explanation for the decrease in θ_a invoking migration of SO_3H groups to the surface is also precluded by the *decrease* in $[SO_3H]$. One possible explanation for the observed *increase* in water wettability and the *decrease* in amount of sulfonic acid groups would be a morphological change in which the two-dimensional distribution of groups was altered. A broader distribution of sulfonic acid groups would plausibly produce a more hydrophilic surface even if the total number of sulfonic acid groups decreased. Such a change could occur if the initial sulfonated product contained areas with extensive sulfonation and areas with little sulfonation. Annealing could then have redistributed groups laterally in addition to redistribution of SO_3H groups into the subsurface. In qualitative agreement with this notion, a set of more heavily sulfonated films from one sulfonation experiment (2-, 3-, or 5-min sulfonation) all annealed in 1 h to form films with similar θ_a (56°, 58°, and 54°) and similar $[SO_3H]$ (0.9, 1.6, and 1.9×10^{14} groups/cm^2).

In conclusion, introduction of very polar sulfonic acid groups and salts onto surfaces of medium-density polyethylene films produces surfaces that do not thermally reorganize to a more hydrophobic surface unless they have been modified so as to contain a long-chain hydrocarbon group. Instead, these surfaces' hydrophilicity is retained or actually increased. This might be due to a change in the uniformity of distribution of sulfonic acid groups. Regardless of the explanation, these studies show that a judicious choice of functional groups and substrate polymer can be used to produce functionalized polymer films whose hydrophilicity can be controlled through synthesis.

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Nitrogen-15-Labeled Oligodeoxynucleotides. 2. Solvent Isotope Effects on the Chemical Shift of the Adenine N1 in an A·T Base Pair

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The ^{15}N chemical shift potentially is a valuable monitor of the H-bonding involved in nucleic acid–nucleic acid, protein–nucleic acid, and drug–nucleic acid interactions.[1,2] Experiments at both the monomer and polymer levels have succeeded in demonstrating chemical shift changes consistent with H-bonding between the nucleic acid bases.[3-7] There is, however, no direct evidence that H-bonding is the cause of the observed changes. In ^1H NMR studies using uniformly ^{15}N enriched tRNA, the low-field (H-bonded) ^{15}N–H resonances were observed as doublets only; there was no evidence of additional coupling to the ^{15}N acceptor in the partner base.[5] Similarly, in a hexameric DNA fragment containing a [1-^{15}N]adenine residue, d[CGT($^{15}N^1$)ACG], we observed an upfield ^{15}N chemical shift change of ~2.6 ppm in the duplex, but nevertheless could not detect coupling between the adenine $^{15}N1$ and the thymine H3 in either the ^{15}N or ^1H NMR.[7] We now report, using this same molecule in mixtures of D_2O and H_2O, evidence of a through-space interaction between these atoms.

A comparison of the ^{15}N NMR spectra of d[CGT($^{15}N^1$)ACG] in H_2O (95%) versus D_2O, using either broad-band or selective

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Table I. ^{15}N NMR Signal Intensities vs Solvent Composition[a]

Δδ, ppm (rel to 201.49)	20% D_2O, % obsd (calcd)	50% D_2O, % obsd (calcd)	80% D_2O, % obsd (calcd)	assignment A(N6)/T(N3)
+0.34	13 (13)	15 (13)	9 (3)	(HH)/(D)
+0.17	9 (6)	25 (25)	27 (26)	(HD)/(D)
0	47 (52)	22 (25)	41 (52)	(DD)/(D) or (HH)/(H)
-0.17	28 (26)	24 (25)	10 (6)	(HD)/(H)
-0.34	3 (3)	15 (13)	13 (13)	(DD)/(H)

[a] Determined from peak heights; estimated error ±3%.

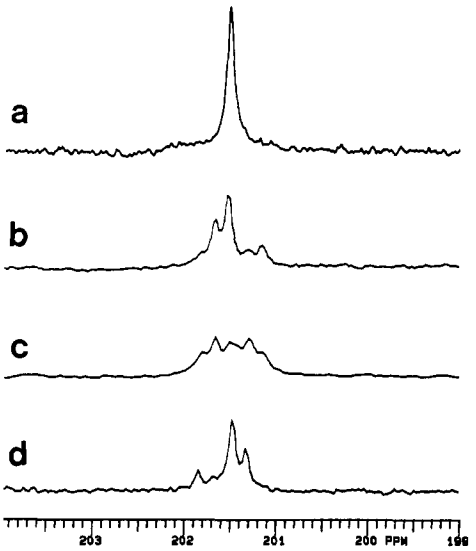
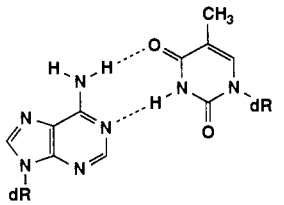


Figure 1. The 40.5-MHz ^{15}N NMR spectra of d[CGT($^{15}N^1$)ACG] acquired at 3.3 °C on a Varian XL-400 spectrometer equipped with a 10-mm broad-band probe. The solvent mixtures, number of scans acquired, and total acquisition times used were (a) 100% D_2O, 18 496, 16 h; (b) 80% D_2O, 75 872, 65 h; (c) 50% D_2O, 73 808, 63 h; and (d) 20% D_2O, 20 720, 18 h. Because of the small chemical shift differences, homogeneity of the magnetic field is critical. The homogeneity was determined by observation of the water signal using the ^1H decoupler coil of the 10-mm probe, with the coil detuned to minimize radiation damping. The ^{15}N NMR spectra were acquired under conditions where the water peak line width was less than 1.5 Hz, at a digital resolution of 1.2 Hz/point, and with low power selective H2 decoupling. To suppress NOE the H2 was irradiated only during acquisition (0.82 s). The recycle time was 2.3 s. The concentration of the single strand was 4.8 mM, in 0.1 M NaCl, 10 mM sodium phosphate, and 0.1 mM EDTA, at pH 7.0.

H2 decoupling, showed no detectable difference in the ^{15}N chemical shift. Yet if the 2.6 ppm chemical shift difference we observed in the ^{15}N NMR spectrum of the duplex form relative to the single strand were due in whole or in part to H-bonding, the ^{15}N chemical shift should differ depending on whether the ^{15}N H-bonding partner is ^1H or ^2H. Since in the duplex form



the exchange of these hydrogen atoms is slow, we then obtained ^{15}N NMR spectra in mixtures of D_2O and H_2O, so that both $^{15}N{\cdot}^1H$ and $^{15}N{\cdot}^2H$ pairs could be observed in the same sample. This type of experiment has been used successfully both with ^{13}C NMR[8] and with ^{15}N NMR.[9] Under these conditions, the single resonance became a group of five resonances (Figure 1). The additional resonances are displaceed ±0.17 and ±0.34 ppm,

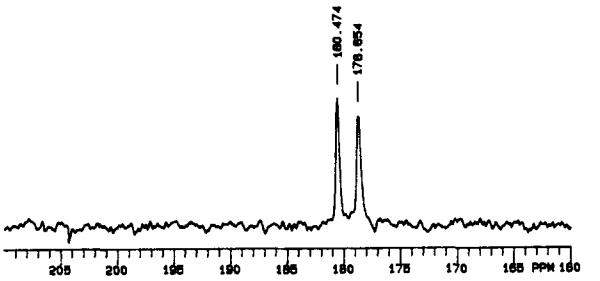


Figure 2. The natural-abundance 40.5-MHz ^{15}N NMR spectra of pyridine deuteriochloride (180.5 ppm) and pyridine hydrochloride (178.6 ppm). The samples were prepared by using a 1:2 ratio by volume of the pyridine to the 37% acid. The pyridine deuteriochloride was in a 10-mm tube with the pyridine hydrochloride in a coaxial insert. The spectrum was acquired by a single pulse experiment, with a recycle time of 2.2 s at a digital resolution of 4.9 Hz/point. The peaks were identified by comparison with the chemical shift observed for the pyridine deuteriochloride sample without the pyridine hydrochloride insert.

relative to the chemical shift in either solvent alone, with the relative intensities dependent on the composition of the mixture.

Secondary isotope shifts, defined as $\Delta\delta^{15}N(^2H,^1H) = \delta^{15}N(^2H) - \delta^{15}N(^1H)$, may be either positive (downfield) or negative (upfield). The spectra shown in Figure 1 suggest that there are two opposing (opposite sign) isotope effects on the adenine N1. Significantly, the two different kinds of exchangeable hydrogen atoms in an A·T base pair might be expected to affect the N1 differently. The thymine N3 hydrogen interacts with the adenine N1 via H-bonding, a through-space interaction, while for the adenine amino hydrogens a through-bond interaction is likely to predominate. The spectra shown in Figure 1, and the similarity of the chemical shift in neat H_2O or D_2O, could result from opposite-sign isotope effects where the magnitude of the isotope shift from each of the hydrogens on the 6-amino group is approximately half of the opposing shift from H-bonding. The effects would then cancel when both the 6-amino hydrogens and the thymine N3 hydrogen are either ^1H or ^2H. In contrast, in mixtures of H_2O and D_2O, up to five peaks would be expected, as is observed. The peak intensities observed for each mixture, shown in Table I, indicate a positive isotope effect from the H-bonding interaction and a negative isotope effect from each of the 6-amino hydrogens. Specifically, these data suggest that substitution of ^2H for ^1H at the thymine N3 position gives a downfield shift of ~0.34 ppm, while substitution of a ^2H atom for one of the 6-amino ^1H atoms gives an upfield shift of ~0.17 ppm. The observed peak intensities are in good agreement with intensities calculated on the basis of the statistical ratio of species to be expected from the solvent composition. Note that the two isotopomers with one ^1H and one ^2H on the 6-amino are degenerate.

Upfield isotope shifts resulting from substitution of ^2H for ^1H on the ^{15}N NMR chemical shift have been observed ranging from nearly 0.7 ppm over one bond (ammonia)[10] to 0.1 ppm over five bonds.[9] These shifts are consistent with an upfield shift on the adenine N1 from the 6-amino hydrogens. In addition, we compared the ^{15}N NMR chemical shifts of the pyridinium ions: pyr·$^1H^+$ and pyr·$^2H^+$. The ^{15}N chemical shift in the pyr·$^2H^+$ spectrum was shifted downfield by 1.8 ppm relative to the pyr·$^1H^+$ spectrum (Figure 2). This is, again, consistent with a (smaller)

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downfield shift for the adenine N1-thymine H3 H-bonding interaction.

The results presented above demonstrate that the nitrogen chemical shift for the adenine N1 in an A·T Watson-Crick base pair is influenced by the hydrogen isotope present in the H-bond. This is unequivocal observation by NMR of a through-space interaction between an imino nitrogen and the hydrogen to which it is H-bonded. This solvent isotope effect should be generally useful in probing the origin of ^{15}N chemical shifts observed in studying nucleic acid structure, particularly the structure of mismatched base pairs, as well as protein-nucleic acid and drug-nucleic acid interactions.

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Activation of Hydrocarbons by a Ruthenium(II) (Fluoroalkyl)phosphine Hydride Complex

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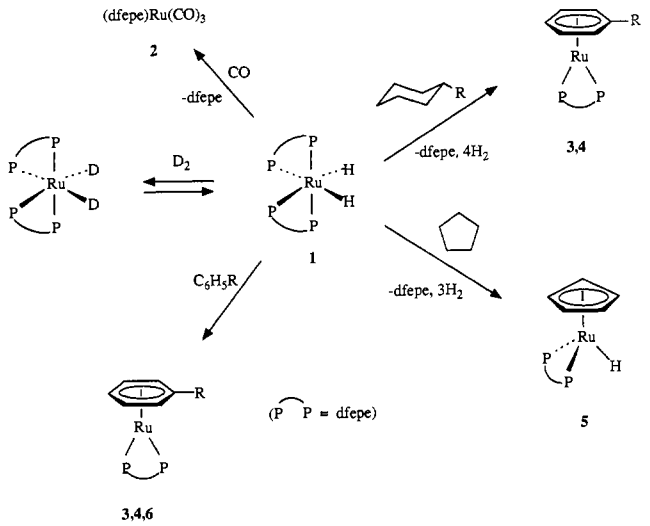
The selective functionalization of simple alkanes by transition-metal complexes in homogeneous media remains a goal of considerable practical and fundamental importance.[1] Substantial progress over the past decade has been made not only in the basic understanding of factors that influence the viability of the initial intra-[2] or intermolecular[1,3,4] addition of C-H bonds, but also in strategies for subsequent productive functionalization of unactivated hydrocarbons. In particular, catalytic photochemically driven systems for carbonylation of saturated[5] and unsaturated[6] hydrocarbons and dehydrogenation of cyclic[7] and acyclic[7c,8] alkanes have recently been demonstrated. Although these results are encouraging, a serious problem generally associated with these reactive systems that still needs to be overcome is catalyst deactivation via attack on ancillary ligand substituents.[1,7c,9]

Scheme I



We have recently begun to develop the (fluoroalkyl)phosphine chemistry of group VIII metals in an effort to design degradation-resistant electron-poor analogues to well-known $L_4M(R)_2$ (M = Fe, Ru, Os; L = PR_3, CO; R = H, alkyl) systems. C-H activation studies for this class of compounds to date have centered on electron-rich complexes such as $(dmpe)_2M(H)R$ (M = Fe, Ru; R = H, aryl)[10] and $(PMe_3)_4Os(H)R$,[11] with very little presently known concerning the comparable chemistry of electron-poor group VIII analogues.[12] Herein we report the synthesis of *cis*-$(dfepe)_2RuH_2$ (dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$)[13] and some initial observations concerning ligand substitution reactions and the unusual direct thermal dehydrogenation of cyclic alkanes by this electrophilic complex to give well-characterized polyene complexes.

cis-$(dfepe)_2RuH_2$ (**1**) is prepared in 41% yield as an air-stable sublimable white solid from the reaction of $(\eta^6\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})Ru$[14] with 2 equiv of dfepe under 1 atm H_2 in methanol.[15] The reaction chemistry of **1** is summarized in Scheme I.[17] With the exception of H_2/D_2 exchange,[18] a common feature in the

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(15) Spectroscopic data for **1**: ^1H NMR (50 °C, C_6D_6) δ 2.39 (m, 4 H, PCH_2), 1.38 (br s, 4 H, PCH_2), -10.79 (AA'MM'XX' pattern, $^2J_{PH}$(cis) ≈ 3 Hz, $^2J_{PH}$(trans) ≈ 50 Hz, 2 H, ReH_2); ^{31}P NMR (24 °C, $(CD_3)_2CO$) δ 109.4 (m), 91.2 (m); IR (Nujol) 1990 cm^{-1}. The crystal structure of **1** has been determined (see supplementary material) and shows that the coordination geometry about ruthenium is essentially equivalent to that reported for *cis*-$(dppe)_2RuH_2$.[16]

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(17) Thermolysis reactions of **1** were carried out in sealed NMR tubes or carius tubes fitted with Kontes Teflon high-vacuum valves. Cycloalkanes were treated with concentrated H_2SO_4 to remove traces of olefins, then distilled, and stored under N_2.

(18) H_2/D_2 exchange for **1** under 2 atm D_2 in benzene is quite slow, occuring to an appreciable extent only after several hours at 150 °C.

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