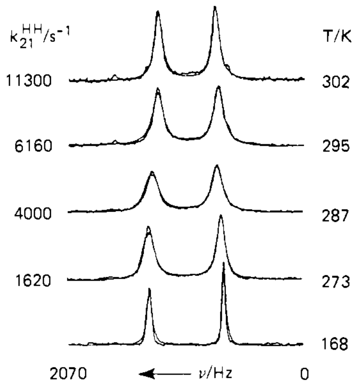

Figure 2. Superposed experimental and calculated ^{15}N CPMAS NMR spectra of 95% ^{15}N-enriched TPP. Experimental conditions as indicated in Figure 1. k_{21}^{HH} is the backward rate constant. The values of the equilibrium constant K are 0.149, 0.136, and 0.124, at 302, 295, and 287 K, respectively. Extrapolated values at 273 and 168 K are 0.111 and 0.015, respectively.

studies,[7] two singlets are obtained at low temperature which indicates that the proton migration shown in Scheme I is slow on the NMR time scale. At higher temperatures, the lines broaden and coalesce. The line shapes were simulated and the rate constants determined assuming a symmetric rearrangement with two tautomers of equal population. The resulting rate constants are shown in Figure 1. Since the line-shape analysis is not very accurate in the slow-exchange regime, we performed magnetization transfer experiments in the rotating frame on the two ^{15}N lines using a method described previously.[9] The method was easily adapted to the CPMAS experiment. The protons were decoupled during magnetization transfer. At 204 K, we obtained a value of $k = 4$ s^{-1}. A kinetic HH/DD isotope effect of 14 at 295 K was obtained by simulation of the ^{15}N spectra of TTP deuterated in the central proton sites. The rate constants and the kinetic isotope effect that we obtain are, within experimental error, identical with the solution rate constants of *meso*-tetraphenylporphine (TPP)[8,9] over the entire temperature range. In contrast, the corresponding solid-state spectra of TPP shown in Figure 2 exhibit very different temperature dependence. Although two singlets are observed at low temperature, the two signals do not coalesce at high temperatures. Nevertheless, as the temperature is increased, they do broaden and sharpen again, and the separation between them continuously decreases. The line shape was simulated in terms of two superposed asymmetrical two-site problems with the assumption that the chemical shifts of the NH in tautomer **1** and in tautomer **2** are equal. The same assumption was made for the chemical shifts of the nonprotonated nitrogen atoms. The assumption is justified, because no additional ^{15}N signals are observed in the slow-exchange region at low temperatures.[17,18] The population of the second tautomer is on the order of 10% at high temperatures where the populations are easily obtained from the line separation by using the assumption that the chemical shifts are independent of the temperature.[19]

These results suggest an explanation for the apparent contradiction, stemming from X-ray studies, between a proton disorder in tetragonal free base porphines on the one hand,[11,12] and proton localization on opposite nitrogen atoms in triclinic TPP on the other.[13,14] While X-ray analysis cannot distinguish between fixed protons and a rapid proton migration between two very unequally populated tautomers, the ^{15}N solid-state NMR data clearly show the latter to be the case for triclinic TPP. Although we have not yet studied tetragonal TPP by ^{15}N CPMAS NMR, it is likely that the situation is similar to TTP where the protons move rapidly at room temperature in a symmetric double-minimum potential. This would be consistent with the half hydrogens found in the crystal structure.[11]

Since TTP and TPP exhibit the same proton dynamics in solution,[20] the difference in behavior of the two compounds in the solid state may be due to induction of a more symmetric crystal structure by the methyl groups. Unfortunately, an X-ray analysis has not yet been carried out for TTP. Nonetheless, it appears that appropriate substitution, even at a site that is remote from the migrating protons, can alter the symmetry of the double-minimum potential. For example, preliminary experiments show that proton migration also occurs in phthalocyanine where the degree of asymmetry of the rearrangement is intermediate between that found in TTP and TPP.[21] We are also studying the influence of asymmetry on the kinetic isotope effect, as well as the effect of adding metal–TPP to TPP in order to make the hydrogen migration symmetric.[14] A complete account of our results will be described in a subsequent paper.

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Registry No. D_2, 7782-39-0; ^{15}N, 14390-96-6; TTP, 14527-51-6; TPP, 917-23-7.

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(17) It is interesting to note the k_{21} for the asymmetric TPP tautomerism found in the solid (see Figure 2) is close to the symmetric rate constant k found in solution.[8] Since $K \sim 0.1$ (vide infra), this result is not in agreement with the value of $k_{21} = kK^{-1/2}$ predicted by simple Marcus theory.[18]

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(19) This assumption was confirmed by measuring ^{15}N spectra of TPP deuterated in the inner-proton sites where the slow-exchange limit is observed at 295 K. A reaction enthalpy of about 6 kJ M^{-1} was obtained. It is important to note that the rate constants increase continuously with temperature indicating the absence of a phase transition.

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Perfluorocyclopentadienyl Anion, $C_5F_5^-$

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The cyclopentadienyl anion is a classic aromatic ring system with major importance in organometallic chemistry. The pentachloro derivative, $C_5Cl_5^-$, is known,[1,2] including some organometallic compounds of it.[3] Some effort to achieve $C_5F_5^-$ has become known.[4-6] Here we report the synthesis of this novel anion.

Hexachlorocyclopentadiene, C_5Cl_6, is fluorinated at the saturated carbon atom by heating it to 280 °C with HgF_2. Products are 10% C_5Cl_5F (bp 80 °C 19 mbar; NMR δ_F −131.4) and 20% of its Diels–Alder dimer $(C_5Cl_5F)_2$ (mp 170 °C, sublimation 100 °C (10^{-2} mbar); NMR δ_F −97.3, 102.9). The dimer is monomerized by subliming it in vacuum through a 350 °C hot Pyrex tube. The overall yield of C_5Cl_5F so obtained is close to 30%. This is fluorinated with increasing concentration of elemental fluorine

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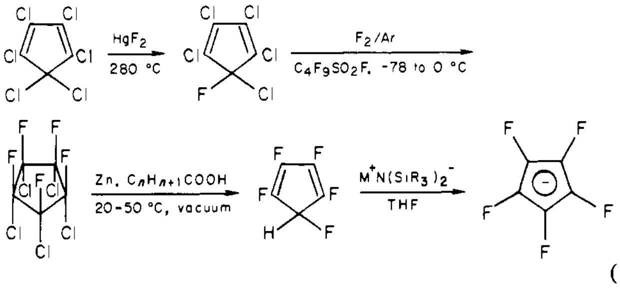
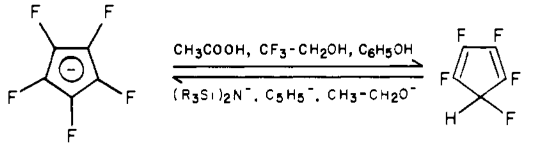
in argon and increasing temperature to give $C_5Cl_5F_5$ in one step. This wax-type material, mp 60–75 °C, is purified by a spinning band distillation, 117 °C (20 mbar), yield 49%. $C_5Cl_5F_5$ is a mixture of four isomers, as expected, which can be separated by gas chromatography. The all-cis compound shows one sharp singlet in the NMR, δ_F −121.3 ppm; the other isomers have AA'BB'C spectra as expected. Reduction of $C_5Cl_5F_5$ with zinc in medium-long carbonic acids, such as $C_6H_{13}COOH$ or $C_7H_{15}COOH$, at 10–50 °C in vacuum affords 45% of crude C_5F_5H. This 1,2,3,4,5-pentafluorocyclopentadiene is purified on a squalane/silica gel column, 55–110 °C, by gas chromatography (NMR AA'BB'CX spectra with δ_A −153.3 δ_B −162.9, δ_C −220.7, δ_H 3.8) and has to be stored at −196 °C to avoid Diels–Alder dimerization. The yield of pure material is only 22%, mainly due to losses by dimerization. The dimer $(C_5F_5H)_2$, a mixture of at least two isomers, can be converted to the monomer only at 700 °C in 5% yield (eq 1).



(1)

Metalation of the proton preferably with $M^+N(SiR_3)_2^-$ affords the title anion. THF solutions of the metal salts are unstable. The lithium salt decomposes within minutes at −110 °C, the sodium salt within hours at −78 °C, and the thallium and caesium salts at −30 °C. The $Na^+[18\text{-crown-6}]C_5F_5^-$ in THF is the most stable so far. It can be observed at 22 °C for a few hours and exhibits like the others a singlet NMR resonance at δ_F −209.0. The typical decomposition reaction is loss of metal fluoride, catalyzed especially by smaller cations, and polymerization. The instability of the metal salts and the bad crystallization behavior of crown ether complexes prevented the isolation of the pure salts so far.

The acidity of C_5F_5H has been estimated by the equilibrium eq 2, which was followed by NMR measurements. It was found



(2)

to be more acidic than cyclopentadiene (p*K*s = 15.5) but less than $CF_3\text{–}CH_2OH$ (p*K*s = 12.8).

The small effect of perfluorination on the acidity is explained by the dual effect of fluorine in aromatic systems: electron-acceptor qualities via σ bonds and donor qualities via π bonds. This is in marked contrast to 5*H*-Perfluorpentamethylcyclopentadiene, $C_5(CF_3)_5H$, which has been recently described and shows an acidity increase of about 18 orders of magnitude as compared with cyclopentadiene.[7] But this difference is conceivable since the CF_3 groups have electron-acceptor qualities only.

At present the effect of perfluorination in metallocene chemistry is unknown. We have not yet obtained any such material from C_5F_5H or $C_5F_5^-$. As seen from its acid–base behavior as compared with cyclopentadiene, it may well serve as a similar good π ligand.

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Ab Initio CI Study of the Hydrogen Abstraction by $NH(a^1\Delta)$

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The NH radical as a monocentric divalent species exhibits different modes of chemical reaction, depending on its electronic state. Thus, the NH radical in the lowest singlet state ($a^1\Delta$) inserts into a covalent bond most efficiently, while the ground-state triplet ($X^3\Sigma^-$) tends to add to an unsaturated atomic center or abstract an atom from a saturated bond.[2] However, the $^1\Delta$ state can in cases manifest a radical character as well.[3] In fact, clear-cut evidence exists indicating that $NH(a^1\Delta)$ directly abstracts a hydrogen atom from paraffins to give NH_2 in a manner more or less competitive to the insertion reaction giving amines.[4] We herein wish to demonstrate theoretically how $NH(a^1\Delta)$ can enter into hydrogen abstraction reaction.

The lowest singlet state ($^1\Delta$) of NH can be represented by either a combination of two *closed-shell* configurations $(1\sigma)^2(2\sigma)^2(3\sigma)^2[(x)^2 - (y)^2)]$ or a single *open-shell* configuration $(1\sigma)^2(2\sigma)^2(3\sigma)^2(x)(y)$, where x and y denote the degenerate $p\pi$-type real-function atomic orbitals (AO) orthogonal to the NH σ bond.[3,5] The two singlet states involving these leading configurations are degenerate to each other. Obviously, it is the latter configuration that is responsible to the abstraction reaction of our concern.

We have first examined

$$NH(a^1\Delta) + H_2 \rightarrow NH_2(\tilde{X}^2B_1) + H \qquad (1)$$

as a prototype of the $NH(a^1\Delta)$ abstraction reactions. The AO basis set used is the conventional split-valence 4-31G functions.[6a] For the sake of convenience, the reaction path was traced by the singlet UHF SCF geometry optimization of the entire system for fixed interatomic distances R(N–H) or r(H–H). It has been proven that the reaction proceeds, maintaining the planar $A''(C_s)$ structure throughout. The multireference double-excitation configuration-interaction (MRD-CI) calculations[7] were then conducted at several points on the SCF minimum-energy path. The configuration selection threshold T was set strictly equal to 0 μhartree to obtain the CI energy $E_{CI,T=0}$. Three-reference (3M) calculations were adopted as a standard procedure. The dimension of the configurational space used was 2678.

Figure 1 shows the change in $E_{CI,T=0}$ calculated as the function of $(r - R)$ chosen as a principal reaction coordinate. For the sake of comparison, a similar potential-energy profile calculated for the case of $NH(X^3\Sigma^-)$ is illustrated with it. For either case, we define the structure giving the maximal $E_{CI,T=0}$ value on the

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