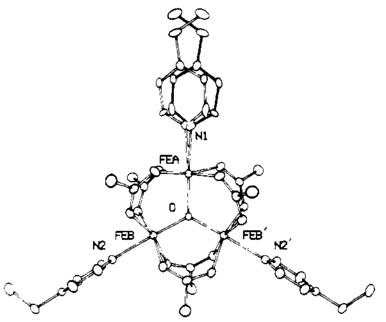

Figure 2. Molecular structure at 163 K of the mixed-valence Fe_3O complex in Figure 1. The two positions of the disordered 4-Etpy ligand at the unique iron ion (FeA) are shown.

perature is increased. Above 200 K only one average quadrupole-split doublet is seen and the electron-transfer rate is greater than $\sim 10^8\ s^{-1}$. If the solvate is benzene, a different temperature dependence is observed.

The significance of our second major observation on the mixed-valence iron complexes is more subtle. We have found for many of the mixed-valence complexes exhibiting temperature-dependent Mössbauer spectra that there is no evidence of line broadening. The "Fe^{II}" and "Fe^{III}" doublets gradually move together without broadening, giving an average doublet as the sample temperature is increased, eventually becoming a single doublet. The dynamic process that leads to the averaging of the Fe^{II} and Fe^{III} doublets is always occurring faster than the Mössbauer technique can sense.

We propose that it is a transformation in certain ligands and/or solvate molecules from a statically disordered to a dynamically disordered state that indirectly controls the rate of electron transfer in these solid-state, mixed-valence complexes. At low temperatures the solid is statically disordered, and the environment about the mixed-valence core is probably asymmetric. We suggest that solvate and/or certain parts of ligands become dynamically disordered as the temperature of the solid is increased. This dynamic disorder would tend to symmetrize the environment of the mixed-valence complex. In effect, if the intermetal electronic coupling were constant as a function of temperature, the symmetrizing effect of the dynamic disorder reduces the potential barrier for electron transfer and the electron-transfer rate would be increased dramatically. No Mössbauer line broadening would be expected because the librations (phonons) operative in the dynamic disorder could well be occurring at a frequency greatly in excess of $10^8\ s^{-1}$.

The molecular and solid-state structures of **1** have been determined at 163 and 298 K by single-crystal X-ray diffraction techniques.[12] An oxo-centered triangular arrangement of three iron ions is present (Figure 2). The space group does *not* change from 298 to 163 K. There are two elements of disorder in the solid. The 4-Etpy solvate molecule is disordered about a center of inversion. There is a 2-fold axis of symmetry in the Fe_3O plane and the 4-Etpy ligand bonded to the unique iron ion is disordered about this axis. Large thermal parameters associated with the atoms of this disordered ligand are consistent with dynamic disorder. The ordered 4-Etpy ligands are firmly held (four intermolecular non-H contacts less than 3.5 Å), while the disordered ligand is loosely surrounded (shortest non-H contact greater than 3.7 Å, to solvate). Significantly, the Fe_3 triangle becomes more equilateral as the crystal is heated from 163 to 298 K. At 163 K the bond distances to the central oxide ion are Fe^{II}–O = 2.011 (4) and Fe^{III}–O = 1.856 (1) Å, whereas at 298 K they become "Fe^{II}"–O = 1.954 (5) and "Fe^{III}"–O = 1.880 (1) Å.

At 298 K the two Mössbauer doublets for **1** are close to, but still have not become, a single average doublet. Additional convincing evidence for the presence of dynamic disorder comes from the areas (recoilless fractions) of these doublets. At temperatures below ~100 K the area ratio of the two doublets is 2:1, in keeping with the ratio of Fe^{III} and Fe^{II} ions in the molecule. As the sample, temperature is increased above ~100 K, the Fe^{III}/Fe^{II} doublet area ratio increases until at 298 K it is 3.5:1. In order words, the dynamic disorder of the 4-Etpy ligand bonded to the "Fe^{II}" ion reduces the recoilless fraction of this iron site.

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Supplementary Material Available: Crystallographic summaries, listings of atomic positional parameters and thermal parameters, and selected bond lengths and angles for both structure determinations of **1** (7 pages). Ordering information is given on any current masthead page.

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[12] Monoclinic, $C2/c$, $Z = 4$: at 163 K, $a = 17.060$ (6) Å, $b = 16.934$ (7) Å, $c = 16.183$ (8) Å, $\beta = 104.49$ (4)°, $V = 4526.6$ Å^3, $D_{calcd} = 1.418$, $R = 0.045$, $R_w = 0.042$ for 2847 observed reflections ($|F_o| \geq 6.0\sigma|F_o|$); at 298 K, $a = 17.142$ (3) Å, $b = 17.004$ (1) Å, $c = 16.571$ (4) Å, $\beta = 104.27$ (2)°, $V = 4681.1$ Å^3, $D_{calcd} = 1.371$, $R = 0.052$, $R_w = 0.055$ for 2809 observed reflections ($|F_o| \geq 6.0\sigma|F_o|$).

First Stable Compound with a Protonated Phosphorus-Bound Nitrogen Atom

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Compounds containing quaternarized, phosphorus-bound nitrogen atoms are scarce[1-5] and no example of a compound with a protonated nitrogen of this type appears to have been isolated so far. As a rule, the haloacids readily cleave the P–N "single" bond of aminophosphanes, phosphine oxides, and related compounds, to give the corresponding halophosphine derivatives and ammonium halides. This well-documented reaction is rapid and complete at or below room temperature.[6-8] It has been extensively used as a commodious, smooth access to mixed halophosphanes and to many of their derivatives, which often cannot be isolated conveniently by other routes.[7] Coordination of the phosphorus atom to transition metals does not alter the issue of the reaction, which has also provided routes to new adducts of mixed P(III) ligands, many of which are not accessible through direct substitution.[8] Protonation of the nitrogen atom with preservation of the P–N bond seems never to have been achieved. Although such species have been postulated as reaction intermediates,[9] no direct

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[1] They consist essentially of two phosphatranes,[2] some borane aminophosphane or phosphorane adducts[3] and some transition-metal phosphoranides.[4] Evidence has also been presented for $SP(\overline{NCH_2CH_2})_3 \cdot BH_3$ in which at least one of the BH_3 groups is expected to be bonded to a nitrogen.[5]

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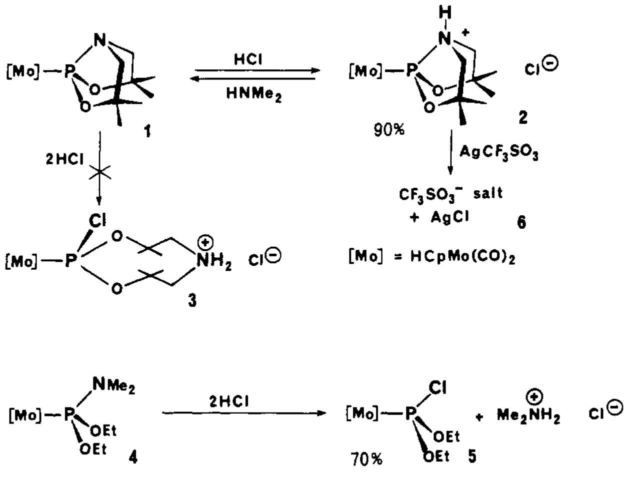
Scheme I



evidence for their formation could be produced.

We therefore wish to report the isolation and unexpected stability of compound **2**, a phosphorammonium salt with a constrained bicyclic structure. The aminophosphine ligand symmetrically tetramethylated at the carbon α to the oxygen atoms was selected for the simplicity expected of its ^{1}H NMR spectra (Scheme I).

Compound **2** precipitated instantaneously when dry gaseous HCl was bubbled through a solution of the aminophosphane adduct **1**[10] in toluene at −20 °C and was isolated in close to quantitative yields as an unexpectedly stable (dec ~135 °C as compared to ~75 °C for **1**), but highly air-sensitive N-protonated salt, soluble in CH_3CN, $CHCl_3$, and THF, sparingly soluble in ether and toluene. By contrast, when compound **4**–a close, but *non*cyclic analogue of **1**–was treated with HCl in similar experimental conditions, it readily led to the toluene- and ether-soluble chloro phosphite adduct **5** (identified by elemental analysis, IR, NMR, and mass spectroscopy), together with $Me_2NH_2^+Cl^-$, which were isolated in 70% and 90% yields, respectively, thus attesting that the usual P–N bond cleavage reaction took place in this case.

Compound **2** was identified unambiguously. First, its formulation was ascertained by elemental analysis (C, H, Cl, Mo, N, P) and mass spectrometry, which also exclude the formation of the P–N cleavage product **3**. The obtaining of **2** rather than **3** was also established by using a titrated solution of HCl in ether to effect the protonation, which showed that only 1 molar equiv of HCl is needed to convert **1** integrally into **2**. The anion is readily exchanged at −25 °C in MeCN under the action of $AgCF_3SO_3$. The ionic nature of the resulting species **6** is shown by the conductivity of its solutions ($\Lambda = 19.6\ \Omega\ cm^2\ mol^{-1}$ in nitrobenzene) compared to that of the starting material **1** ($\Lambda = 0.97\ \Omega\ cm^2\ mol^{-1}$).

Among the most pertinent evidence for the preservation of the P–N bond is the ^{1}H NMR spectrum (CD_3CN), which at room temperature exhibits an eight-line phosphorus-coupled AB system for the CH_2 groups of the five-membered cycles ($\delta_A = 3.82$, $\delta_B = 3.44$; $J_{AB} = 13$, $^1/_2(J_{H_AP} + J_{H_BP}) = 0.4$ Hz, a system analogous to, but with chemical shift and coupling parameters slightly different from, those of the free ligand ($\delta_A = 3.08$, $\delta_B = 2.75$; $J_{AB} = 12$, $^1/_2(J_{H_AP} + J_{H_BP}) = 0.3$ Hz, C_6D_6).

The ^{1}H spectrum also shows a singlet at 5.53 ppm for the cyclopentadienyl protons, a doublet at −6.73 ppm ($J_{HP} = 61.7$ Hz) for the MoH hydride proton, and two signals at 1.55 and 1.31 ppm for the nonequivalent methyl groups. Contrary to what is observed with the unprotonated complex **1** no splitting of the signals, attributable to cis and trans isomers at molybdenum, was observed upon cooling at −80 °C in CD_2Cl_2. This means either that only one isomer is present for **2** in these conditions or that the cis–trans interchange is still rapid on the NMR time scale. The significantly smaller apparent coupling observed for **2** at −80 °C in CD_2Cl_2 (54 Hz) compared to that measured at room temperature in CD_3CN (61.7 Hz) points rather to a fast temperature-dependent equilibrium between the two isomers, with predominance of the cis isomer in view of the larger J_{HP} coupling expected,[11] comparable to that found for *cis*-**1** (61.0 compared to 27.1 Hz for *trans*-**1** in toluene-d_8 at −40 °C).

The retention of the bicyclic structure is further ascertained by the close resemblance of the mass and infrared spectra of **2** to those of **1** and their difference with respect to those of **5**. The modification undergone by the ligand is nevertheless evidenced by the presence of the broad signal (~100 Hz) at 11.55 ppm in the ^{1}H NMR spectrum, as expected for an ammonium proton, and by a slight displacement, by ca. 5 ppm, of the ^{31}P signal (δ 209.5, $J_{PH} = 62.5$ Hz in CD_2Cl_2) toward higher fields, smaller than would be expected for **3**. Comparable NMR patterns are observed for the trifluoromethanesulfonate salt **6**. Also noteworthy is the absence in the IR spectrum of **2** of the characteristic ν(PCl) stretching vibration found around 535 cm^{-1} for **5**.[12]

Protonation causes a decrease in electron density on phosphorus, both because of the presence of the positively charged quaternarized nitrogen and because N(pπ)–P(dπ) donation is no longer possible. The decrease (by 10 and 16 cm^{-1}) in frequency of the two ν(CO) vibrations upon protonation is interpreted to mean that the diminution in electron density in the bonding orbitals of the CO groups outweighs that which occurs in their π^* orbitals.

Compound **2** can be deprotonated under the action of diethylamine (1 equiv is required to complete the process) to restore adduct **1** (80% isolated) and the ammonium salt H_2NEt_2Cl (85% isolated).

Attempts to protonate the uncomplexed bicyclic aminophosphane ligand led to the immediate formation, even at −80 °C, of a white precipitate, whose ^{31}P spectrum exhibited numerous signals.

These results illustrate the drastic changes in behavior of the P–N entity when subjected to constraints that force the nitrogen atom to keep a pyramidal configuration.

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Determination of Molecular Structure in Solution via Two-Dimensional Nuclear Overhauser Effect Experiments: Proflavine as a Rigid Molecule Test Case

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The two-dimensional NMR nuclear Overhauser effect (2D NOE) experiment is potentially the most powerful method for determining molecular structures in solution.[1,2] Wüthrich's lab has elegantly exploited the 2D NOE technique semiquantitatively in studies of small protein structure.[3,4] We have recently examined some aspects of molecular structure determination via 2D NOE theoretically.[5] Proflavine, a rigid molecule with X-ray crystal structure determined, was studied here as a test case. The in-

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