precursor **2b** from **1** (Scheme I, 14% yield, orange crystals[9]). The permethylation stabilizes the highly reduced oxidation states as can be seen on the voltammogram of **2b** (Figure 1). Whereas the Na–Hg reduction of **2a** in THF at 20 °C led to decomposition, the analogous reaction with **2b** gave, after 1 h, a deep purple, thermally stable, air-sensitive complex which could be extracted with acetone, precipitated by ether, and recrystallized from acetone at −40 °C (80% yield of **3b**, purple crystals).[10] Contact with air and water, followed by metathesis with $H^+PF_6^-$, gave back **2b**. The EPR spectra of the samples of **3a,b** in frozen THF solutions at 77 K showed three g values close to 2 (**3a** $g_x = 2{,}005$, $g_y = 2.072$, $g_z = 1.911$; **3b** $g_x = 2.005$, $g_y = 2.071$, $g_z = 1.906$) corresponding to a rhombic distortion.[11] The magnetic susceptibility of **3b** (Gouy method: $m = 1.7\ \mu_B$) indicated the presence of a single electron per bis sandwich. This result was confirmed by the Mössbauer spectra under 6 T: the contact (Fermi) term found was 5.5 T, corresponding to 42% electron on each Fe (13 T per electron). Since the HOMO has 83% metal character (vide supra), it means that each sandwich carries only half of an extra electron. The zero field Mössbauer spectra of **3a,b** at 4.2, 77, and 293 K showed a single doublet[10] indicating that only one type of iron is detectable at the Mössbauer frequency ($10^9\ s^{-1}$).

Thus, electron exchange between the two iron centers is faster than $10^9\ s^{-1}$ at 4.2 K, and therefore **3a,b** belong to the class III of the mixed-valence complexes.[2c] Since the bulky C_6Me_6 ligands prevent the two iron centers from coming close to each other—they must remain on opposite sides of the fulvalene bridge—the electron jump must proceed through it.[12] An outstanding feature of the Mössbauer doublet observed for **3a,b** is that the quadrupole *splitting is independent of the temperature*, contrasting sharply with temperature dependences observed for all Fe^I monomers.[3] This property of the delocalized mixed-valence system **3a,b** suggests a modified electronic structure, e.g., strong electronic coupling between the two sandwiches. We believe that it is due to the fact that, in Fe^I monomers, the e_1^*(Fe) and e_1(Cp) orbitals have close energy levels, a characteristic that was actually the source of the concept leading to the design of such average valence substrates. This coupling is corroborated by preliminary SCC EHT calculations effected with trans Fe units: the thermal population of the upper Kramers' doublet, which causes the variation QS = $f(T)^3$, is no longer involved since the 37th electron occupies a single orbital of 83% metal character. The purple color of **3** (**3b**: λ = 554 nm, ϵ 7660 L $mol^{-1}\ cm^{-1}$) is also at variance with the usual dark green found in Fe^I monomers, a color attributed to the $e_1^* \rightarrow e_2$ transition.[3b] The 38-electron complexes **4** can be generated from **2a–b** and Na–Hg (**4a**) or potassium mirrors (**4b**) in THF.[13] It is interesting that, as Fe^I monomers, they are also dark green (at −50 °C, λ = 725 nm, ϵ 1400 L $mol^{-1}\ cm^{-1}$), which suggests an Fe^IFe^I formulation. Another indication along this line is given by EPR spectra, recorded at 77 K in frozen THF, which show the absence of Cp–Cp coupling to diamagnetic Fe^OFe^O fulvalene.[14] The rhombic distortion in **4a** ($g_\perp = 1.994$, $g_\parallel = 2.076$) and **4b** ($g_\perp = 2.019$, $g_\parallel = 1.921$) is different from that in **3a–b** or in Fe^I monomers. Despite its thermal instability above −10 °C, **4a** was synthesized by Na–Hg reduction (THF, 4 h, −20 °C) of **2a** followed by filtration at −20 °C; green-black microcrystals were obtained by addition of pentane at −80 °C; they burn explosively upon contact with air. The Mössbauer spectra were recorded under Ar and fitted between 4.2 and 220 K. The values of the parameters (IS = 0.8 mm s^{-1} vs. Fe; QS = 1.43 mm s^{-1} at 4.2 K and 0.6 mm s^{-1} at 220 K) as well as the sharp QS variation (suplementary material, i.e., 0.80 mm s^{-1} at 80 K) are definitive evidence for d^7 Fe^I complexes such as $CpFe^IC_6R_6$ (R = H, Me).[15] These data emphasize the specificity of the electronic structure of the average valence complexes containing Fe^I.

Acknowledgment. We thank Drs. J.-J. Girerd (Orsay), B. Nickel, and A. Jeunet (Grenoble) for EPR assistance, Dr. M. Lamotte (Bordeaux) for designing low-temperature UV–vis experiments, and the DGRST for grants to M.H.D. and J.G.

Registry No. 1, 1287-38-3; **2a**, 53702-58-2; **2b**, 97431-19-1; **3a**, 97431-21-5; **3b**, 97431-20-4; **4a**, 78398-48-8; **4b**, 97431-22-6; **7**, 51539-79-8; C_6Me_6, 87-85-4.

Supplementary Material Available: Mössbauer spectra of **4a**—variation of the quadrupole splitting with the temperature between 4.2 and 220 K (1 page). Ordering information is given on any current masthead page.

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[10] **3b**: Anal. Calcd for $C_{34}H_{44}Fe_2PF_6$: C, 57.54; H; 6.20; Fe, 15.79; P, 4.37. Found: C, 57.98; H, 6.27; Fe, 15.75; P, 4.36. Mössbauer (mm/s vs. Fe, 4 K) IS 0.47, QS 1.38. Near-infrared (acetone) λ = 989 nm (ϵ 170 L $mol^{-1}\ cm^{-1}$). Given the low ϵ value, there is little chance this be the intervalence band.

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[12] For a controversy on this question in biferrocenylenium cation see: Watanabe, M.; Ijima, S.; Motoyama, I.; Sano, H. *J. Phys.* (*Les. Vlis, Fr.*) **1979**, *40*, Suppl. C2-392.

[13] These dark-green THF solutions of Fe^IFe^I complexes **4a,b** were chemically and electrochemically characterized and titrated as follows: addition of $^1/_2$ mol of I_2 or $^1/_4$ mol of O_2 at −20 °C gave back (fast) purple precipitates of **3a,b** and 1 mol of NaI or $^1/_2$ mol of Na_2O_2, respectively (for salt effects due to $NaPF_6$ upon formation of $[Fe^{II},O_2^{-}\cdot]$ from $Fe^I + O_2$, see: Hamon, J.-R.; Astruc, D. *J. Am. Chem. Soc.* **1983**, *105*, 5951). Further reaction with $^1/_2$ mol of I_2 or $^1/_4$ mol of O_2 was slower ($^1/_2$ h for completion at -20 °C) and gives back the orange solids **2a,b**. Cyclic voltammograms of **4a,b** (THF + DMF, −30 °C, n-Bu_4NBF_4, Hg) also show the oxidation waves to Fe^IFe^{II} and further to $Fe^{II}Fe^{II}$, as in Figure 1.

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Intermediacy of the Parent Diazonium Ion (Protonated Dinitrogen, $N_2{}^+H$) in the Diazotization of Ammonia and Its Derivatives with $^{15}NO^+BF_4^-$ Giving $^{15}N^{14}N$[†,1]

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Protonated dinitrogen **1**, the parent diazonium ion $HN_2{}^+$, remains elusive in the condensed state. All attempts, including our own,[2] to effect protonation of dinitrogen even in the strongest superacids (HF–SbF_5) were inconclusive. Direct spectroscopic observation of diazonium ion was not achieved nor was there any effect observed of added nitrogen on the rate of H_2 and D^+ exchange reaction (the change in the exchange rate was used as a probe to detect possible protonation of nitrogen).[3] In contrast to the condensed state $HN_2{}^+$, **1** has been observed in the gas phase mass spectrometric and ICR studies.[4,5] Recently by use of Laser magnetic resonance rotational spectroscopy[6] the N–H vibration–rotation band of **1** has been detected in ac glow discharge.[7a] More recently even the N–N stretch has been observed.[7b] Significantly **1** was also detected in extraterestial space indicative of ion–molecular reactions taking place in interstellar cloud chemistry. Theoretical calculation on **1** at STO-3G basis set level

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[†] Dedicated to Professor Rolf Huisgen on occasion of his 65th birthday.

[1] Onium Ions. 32. For part 31, see: Olah, G. A.; Prakash, G. K. S.; Barzaghi, M.; Lammertsma, K.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.*, in press.

[2] Olah, G. A., unpublished results.

[3] Olah, G. A.; Shen, J. *J. Am. Chem. Soc.* **1973**, *95*, 3582.

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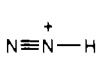
[6] Saykally, R. J. *Chem. Brit.* **1985**, 159.

[7] Gudeman, C. S.; Begemann, M. H.; Pfaff, J.; Saykally, R. J. *J. Chem. Phys.* **1983**, *78*, (9), 5837. Also see: Foster, S. C.; McKellar, A. R. W. *J. Chem. Phys.* **1984**, *81* (8), 3424.

0002-7863/85/1507-5282$01.50/0

by Pople and co-workers[8] has shown that linear structure **2** is more stable than the bridged one **3**. In the course of nitrogen fixation[9,10]



$N{\equiv}\overset{+}{N}{-}H$

2

3

it is highly unlikely that proton transfer to free nitrogen occurs. Instead, such proton transfer probably occurs on to coordinated dinitrogen on a suitable transition-metal site such as molybdenum. In continuation of our studies on substituted diazonium ions (such as $N_2^+NH_2$,[11] $N_2^+NO_2$,[12] N_2^+CN,[12] N_2^+F[12], etc.) we would like to report new results on our attempts to generate diazonium ion **1** not by direct protonation but by diazotization of ammonia and some of its derivatives using nitrosonium tetrafluoroborate salt.

It is known that aromatic as well as aliphatic amines and isocyanates react with NO^+ salts, such as $NO^+BF_4^-$ to form the corresponding diazonium ions.[13] Weiss recently reported[14] a useful

$$RNH_2 + NO^+BF_4^- \rightarrow RN^+ \equiv NBF_4^- + H_2O$$

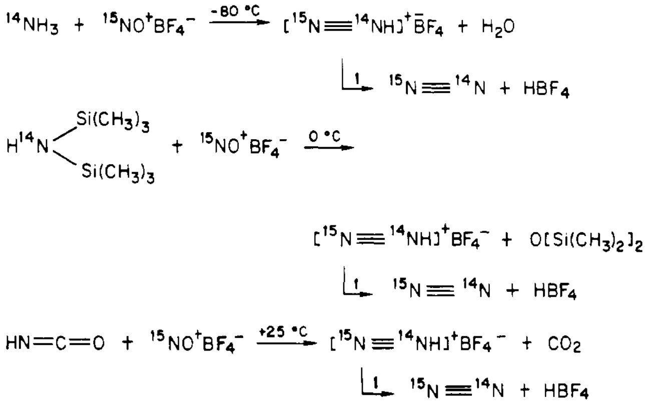
$$RN{=}C{=}O + NO^+BF_4^- \rightarrow RN^+ \equiv NBF_4^- + CO_2$$

additional anhydrous diazotization method by reacting bissilylated amines with NO^+ salt.

$$R{-}N(Si(CH_3)_3)_2 + NO^+X^- \rightarrow RN^+ \equiv N\ X^- + [(CH_3)_3Si]_2O$$

As the direct protonation of nitrogen could not be achieved in solution, it occurred to us that the problem could be attacked by generating protonated dinitrogen, i.e., the parent diazonium ion via diazotizing ammonia and some of its derivatives.

Using 96% enriched $^{15}NO^+BF_4^-$ salt[15] we have indeed succeeded with diazotization of ammonia, bis(trimethylsilyl)amine, and isocyanic acid, respectively, resulting in the formation of $^{14}N{\equiv}^{15}N$. The mono ^{15}N-labeled nitrogen gas obtained can be produced only through the intermediacy of the parent diazonium ion **1**.



All reactions were carried out in dichloromethane solution and the nitrogen evolved during the reaction was analyzed by GC-MS.[16] Ammonia itself reacts with nitrosonium tetrafluoroborate rather violently even at −80 °C to give 89% monolabeled and 11% unlabeled dinitrogen. In reaction of bis(trimethylsilyl)amine 94% monolabeled nitrogen was formed, the reaction being somewhat sluggish at −80 °C. Isocyanic acid reacted very slowly with the nitrosonium ion even at room temperature. A competing polymerization of isocyanic acid seem to occur along with the diazotization and it was not possible to determine the exact isotope distribution of the evolved nitrogen although it is estimated to be ⩾90% monolabeled.

Attempts were made to directly detect the monolabeled diazonium ion **1** using ^{15}N NMR spectroscopy.[17] In a typical experiments ≈50 mg of bis(trimethylsilyl)amine was treated with ≈100 mg of 95% $^{15}NOBF_4^-$ in 2 mL of dichloromethane in a 10-mm NMR tube at −80 °C in the NMR probe. The probe temperature when raised to −40 °C resulted in slow evolution of nitrogen gas. Accumulation of ^{15}N data over a period of 30 min detected, however, the presence of only $^{15}NO^+$ salt and no signal for **1** could be observed. The failure to detect HN_2^+ in the described stop-flow experiment seems to indicate that **1** is unstable under the reaction conditions. This is in accordance with the known low proton affinity of dinitrogen.

Our studies reported indicate that the parent diazonium ion **1** was in situ formed in the diazotization of ammonia and its derivatives with $^{15}NO^+BF_4^-$. However, **1** once formed has very short lifetime to be observed by NMR spectroscopy and spontaneously deprotonates to $^{15}N{\equiv}^{14}N$.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged. R. Herges is grateful for the financial support by a Feodor Lynen grant of the Alexander von Humbold Foundation.

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[15] 96% ^{15}N enriched $NO^+BF_4^-$ was prepared by treating 96% $^{15}NOCl$ with $HF{-}BF_3$ in nitromethane solution at −78 °C. The 96% $^{16}NOCl$ was generated by treating 96% $Na^{15}NO_2$ with dry HCl in nitromethane solvent with $CaCl_2$ drying.

[16] GC-MS analysis was performed on a Hewlett-Packard 5985 A GC-MS spectrometer.

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Total Synthesis of the Cytochrome P-450 Epoxygenase Metabolites 5(*R*),6(*S*)-, 5(*S*),6(*R*)-, and 14(*R*),15(*S*)-Epoxyeicosatrienoic Acid (EET) and Hydration Products 5(*R*),6(*R*)- and 14(*R*),15(*R*)-Dihydroxyeicosatrienoic Acid (DHET)[1]

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Received May 9, 1985

Recent reports[3] have elucidated an alternative mode of eicosanoid production,[4] designated the epoxygenase pathway,[5a] that

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