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Tricarbonyl(4–7-η-1(1*H*),2-diazepine)iron(0). Fluxional Pathways

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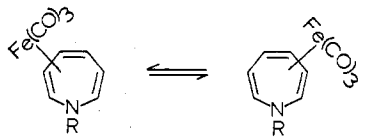
The synthesis and characterization of tricarbonyl(4–7-η-1(1*H*),2-diazepine)iron(0) and the related complexes tricarbonyl(4–7-η-3-methyl-1(1*H*),2-diazepine)iron(0) and tricarbonyl(4–7-η-1-methyl-1(1*H*),2-diazepine)iron(0) are described. Solvent- and concentration-dependent ^{1}H NMR and ir studies of the fluxional parent complex tricarbonyl(4–7-η-1-(1*H*),2-diazepine)iron(0) indicate that the fluxional pathway involves intermolecular proton transfer. The fluxional process is strongly acid catalyzed and proceeds through a fluxional η^4 imminium ion complex which can be directly observed in the ^{1}H NMR spectrum. A crystalline trifluoroacetate salt of this η^4 imminium ion has been isolated and structurally characterized. Protonation of nonfluxional diazepine derivatives leads to static N_2-protonated η^4 imminium ion complexes. Tricarbonyl(4–7-η-1-methyl-1(1*H*),2-diazepine)iron protonates with rearrangement to give the same ion as that obtained from reaction of tricarbonyl(4–7-η-1(1*H*),2-diazepine)iron with methyl fluorosulfonate.

Introduction

Substituted 1(1*H*),2-diazepines,[1–3] like other seven-membered rings[4–8] with three sites of unsaturation, readily form η^4 tricarbonyliron complexes. Crystallographic evidence indicates that a change from a "tub" to a folded "envelope" conformation is a common feature accompanying complexation (cf. Figure 1). In spite of the fairly extensive geometrical reorganization required, processes leading to a time-averaged symmetry plane can occur and both tricarbonyl(4–7-η-*N*-ethoxycarbonyl-1*H*-azepine)iron **2c** (R = CO_2Et)[5,6] and tricarbonyl(4–7-η-1(1*H*),2-diazepine)iron **2d** (R = H)[3] are fluxional on the ^{1}H NMR time scale at or near room temperature.[1,2] Fluxional pathways[5,6] leading to the time-averaged symmetry plane for the azepine complexes **2c** require a simple shift of the $Fe(CO)_3$ moiety to an alternate η^4 bonding site (**3** ⇄ **3'**) in a fashion similar to that found for tricarbonyl-(1–4-η-cyclooctatetraene)iron[15] and characteristic of cycloolefin complexes in general. The nature of the N substituent appears to have little effect on the fluxional character although this aspect has not been studied in detail.[5,6] A different situation persists for the 1(1*H*),2-diazepine complexes **2d** for which a time-averaged symmetry plane cannot be achieved via a simple $Fe(CO)_3$ migration. The fluxional behavior observed[3] for **2d** (R = H) must involve prototropy as well as valence isomerization. The as yet unknown and potentially antiaromatic 1(1*H*),2-diazepine **1d** (R = H) bears a vinylogous relationship to pyrazole which also shows a ^{1}H NMR spectrum characteristic of a symmetrical structure resulting from rapid valence tautomerism.[16] In the case of the N-substituted 1(1*H*),2-diazepine(tricarbonyl)iron complexes (**2d**, R = alkyl, acyl), prototropy is impossible and static structures result.[1–3] Analogous pyrazole complexes are not available for comparison.[17]

We were interested in obtaining more detailed information concerning the nature of the fluxional process described by **4** ⇄ **4'**. In particular we wished to establish (i) whether the prototropy required in the fluxional process was *inter-* or *intra*molecular and (ii) the effects of protonation. Presently we report findings relevant to (i) and (ii) together with details of some of our previous results.[3]



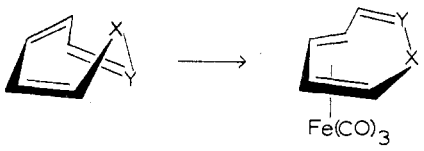
3 **3'**

Results and Discussion

The synthesis of tricarbonyl(4–7-η-1(1*H*),2-diazepine)iron (**2d**, R = H) in high yield was accomplished via sodium ethoxide promoted deacetylation of tricarbonyl(4–7-η-1-acetyl-1(1*H*),2-diazepine) (**2d**, R = $COCH_3$). A similar reaction afforded complex **11** in good yield from tricarbonyl(4–7-η-1-acetyl-3-methyl-1(1*H*),2-diazepine)iron. The *N*-methyl complex **7** was prepared from **4** by treatment with methyl bromide in the presence of sodium carbonate.[18]

The infrared spectrum of **2d** in the carbonyl region in the solid state and in solution shows three bands characteristic of a diene(tricarbonyl)iron complex with an overall molecular symmetry lower than C_{3v}.[2] The molecule fragments as expected in the mass spectrometer, consecutive loss of three molecules of CO giving the base ion $(C_5H_6N_2)Fe^+$. A significant feature of the mass spectrum is the ion at *m/e* 94 which was unequivocally identified by accurate mass measurements as the molecular ion of the unknown parent 1-(1*H*),2-diazepine. The stability of this ion in the mass spectrometer is notable, considering the likelihood that the neutral molecule possesses antiaromatic properties. Analytical, infrared, and mass spectrometric data for complexes **7** and **11** confirm their identity as typical η^4-diene(tricarbonyl)iron derivatives.

The novel fluxional properties of **2d** were described in a preliminary communication.[3] Further information concerning the fluxional process **4** ⇄ **4'** was obtained from detailed ir and ^{1}H NMR studies. Figure 2 shows the results of a concentration-dependent infrared study of tricarbonyl(4–7-η-1(1*H*),2-diazepine)iron (**4**) in carbon tetrachloride. Saturated solutions (ca. 0.1 M) in CCl_4 showed a sharp ν(N–H) absorption at 3418 cm^{-1} assigned to free N–H as well as broad bands at 3280 and 3180 cm^{-1} characteristic of



1 2

1a, 2a; X = CH_2, Y = CH [8]
1b, 2b; X = CO, Y = CH [9]
1c, 2c; X = NR, Y = CH [10]
1d, 2d; X = NR, Y = N: [11]

Figure 1. Conformation of cyclic trienes and their tricarbonyliron complexes.

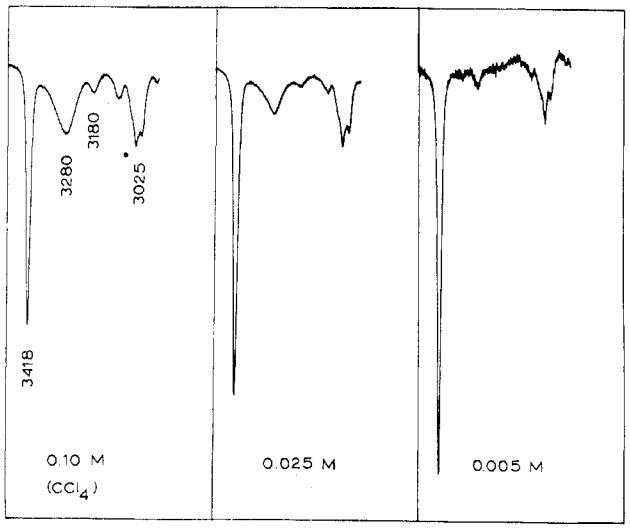
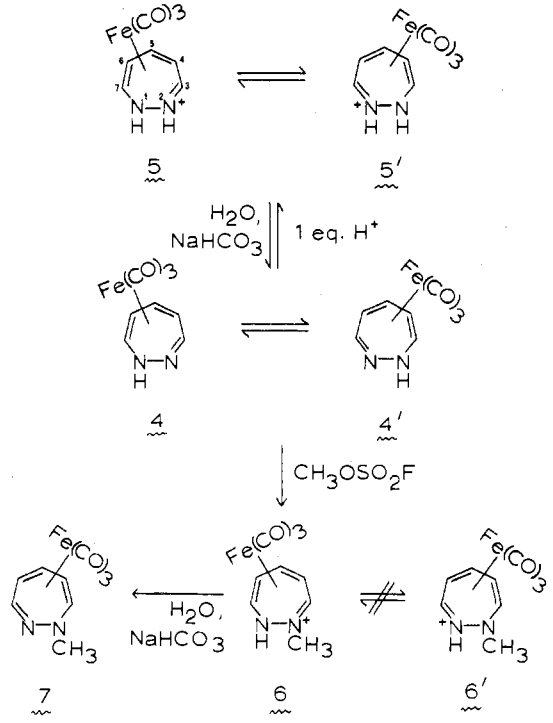


Figure 2. Concentration-dependent infrared spectra of **4** in carbon tetrachloride solution. Frequencies refer to ν(N–H) with the exception of the band labeled with a dot which is due to ν(C–H).



hydrogen-bonded species. As the concentration of **4** decreased, the relative intensity of the monomer band increased at the expense of absorptions due to the hydrogen-bonded species in a fashion analogous to that found for pyrazole under similar conditions.[19] These observations are diagnostic and sufficient to establish that hydrogen bonding is an *inter*molecular process.[20]

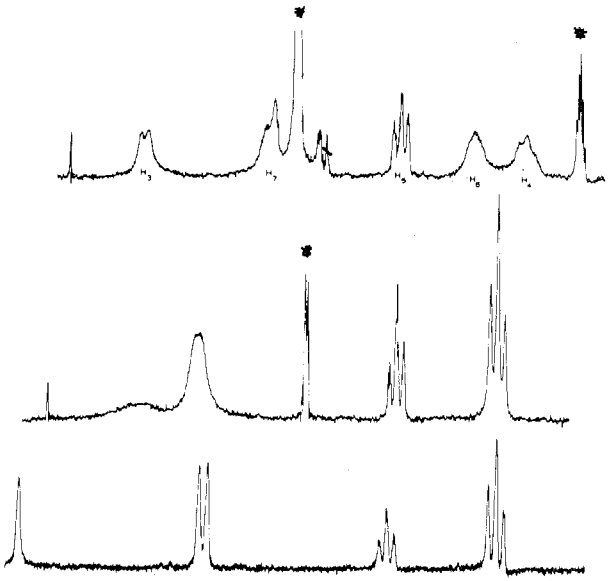
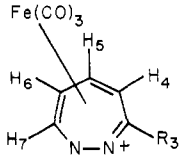


Figure 3. Solvent-dependent ^{1}H NMR (100 MHz) spectra of **4**: top, methanol-d_4; middle, methylene-d_2 chloride; bottom, liquid sulfur dioxide. Peaks marked with asterisks originate from the solvent.

^{1}H NMR studies in media of different hydrogen-bonding properties revealed significant differences in the rate of fluxional processes leading to a time-averaged symmetry plane, **4** $\rightleftarrows$ **4'**. Figure 3 shows the results obtained at −50°C for equal concentrations of **4** in methanol-d_4, methylene-d_2 chloride, and liquid sulfur dioxide. Comparison of the three spectra shows that the relative rates decrease along the series SO_2 > CD_2Cl_2 > CD_3OD. In liquid SO_2 complete averaging of H_3 = H_7 and H_4 = H_6 is observed while in methanol-d_4 distinct signals remain for all five nonequivalent ring protons described by the static structures **4** or **4'**. Although the N–H proton is not visible in methanol-d_4 due to slow exchange with solvent, the chemical shift of N–H in SO_2 lies to lower fields than in methylene-d_2 chloride. Decreased shielding for N–H protons is indicative of extensive hydrogen bonding[21] which facilitates prototropy as evidenced by the relatively sharp N–H signal in SO_2.

When the requirement for *inter*molecular proton transfer within hydrogen-bonded species is eliminated by the addition of traces of acid which rapidly exchange on nitrogen sites,[3] fluxional rates are greatly increased. Figure 4 shows the ^{1}H NMR spectrum (60 MHz) obtained by adding traces of trifluoroacetic acid (TFA) to a methylene-d_2 chloride solution of **4**. Well-resolved coupling indicative of fast exchange is observed. Incremental addition of TFA gave monotonic changes in chemical shift with retention of the overall splitting pattern, until 1 equiv had been added. Continued additions of TFA gave no further changes and the N–H signal now integrated for two protons indicating that monoprotonation on nitrogen had occurred. Use of TFA-*d* gave identical results except that the low-field absorption corresponding to two protons was absent. Similar results were obtained in liquid SO_2 by adding anhydrous HCl. On the basis of the smooth changes in chemical shifts and the retention of the overall coupling pattern (cf. the ^{1}H NMR spectrum of **4** in SO_2 (Figure 3) where the fluxional rate is fast), structure **5** can be assigned to the monoprotonated species. The resulting η^4 imminium ion is fluxional, with rates greater than those found

Table I. ^{1}H NMR Spectra of the η^4 Ions



	Solvent	Temp, °C	Chem shift, τ							Coupling const, Hz						
			R_1	R_2	R_3	H_4	H_5	H_6	H_7	J_{17}	J_{34}	J_{45}	J_{46}	J_{56}	J_{57}	J_{67}
$R_1 = R_2 = R_3 = H$ (**5**)	SO_2	−10	−0.60	−0.60	3.07	5.75	4.85	5.75	3.07							
	95% TFA-*d*	0			2.96	5.75	4.85	5.79	2.96		6.7[d]	6.0[d]		6.0[d]		6.7[d]
$R_1 = R_3 = H$, $R_2 = CH_3$ (**6**)	SO_2[a]	−10	1.71	6.33	2.72	5.98	4.77	5.49	3.79		7.8	6.7	1.5	5.5	1.8	6.7
	95% TFA[b]	0	2.90	0.27	2.35	6.07	4.67	5.29	4.05	4.7	7.6	6.5	1.5	5.5	1.5	6.7
$R_1 = COCH_3$, $R_2 = R_3 = H$ (**10**)	100% TFA	−10	7.25	*c*	1.80	6.14	4.00	4.48	3.84		7.8	7.8		5	1.8	5.5
$R_1 = R_2 = H$, $R_3 = CH_3$ (**12**)	SO_2	−10	1.05	−4.80	7.61	6.19	4.82	5.43	4.00			7.3	1.5	4.5		6.6

[a] Prepared from 4 + CH_3OSO_2F. [b] Prepared from **7** + TFA. [c] Averaged with solvent signal. [d] Averaged coupling constants for **5** and **5′**.

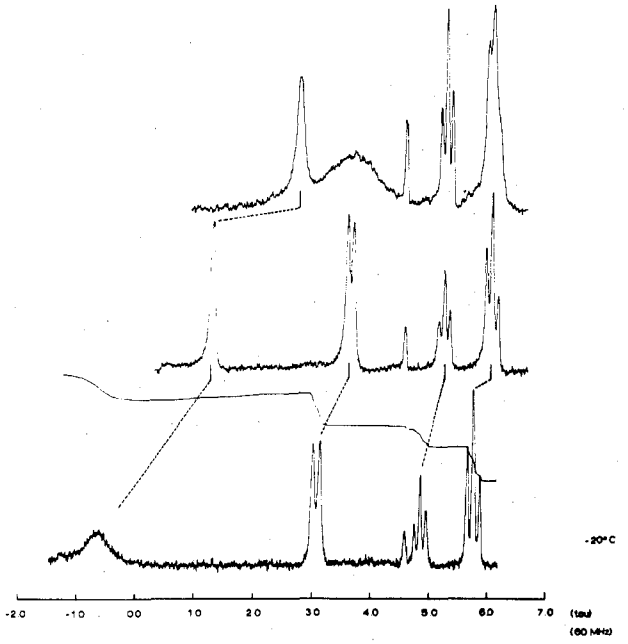


Figure 4. ^{1}H NMR (60 MHz) spectra of **4** and **5** in methylene-d_2 chloride: top, no TFA added; middle, trace of TFA added; bottom, 1 equiv of TFA added. The peak at τ 4.7 is due to solvent.

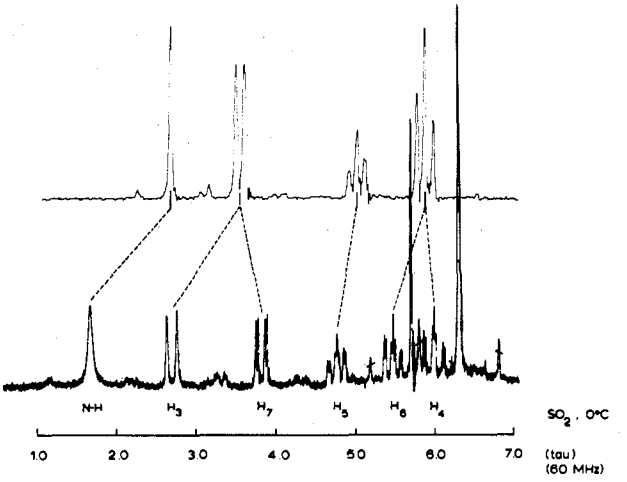


Figure 5. ^{1}H NMR (60 MHz) spectrum of ion **6** in liquid sulfur dioxide: top, complex **4** in SO_2; bottom, 1 equiv of methyl fluorosulfonate added.

for **4** in methylene-d_2 chloride. Protonation at the intrinsically *less* basic site to give imminium ions also occurs for pyrazoles[22] and for 2,3-dihydro-1,4-diazepines[23] to give symmetrical ions.

Confirmation of the fluxional nature and structure of the η^4 imminium ion complex **5** derives from its ^{13}C NMR spectrum in 80% aqueous TFA. At 0°C three sets of ring carbons are visible at 116.5 ($C_3 + C_7$), 94.7 (C_5), and 64.7 ($C_4 + C_6$) ppm with relative areas of 2:1:2 indicating the presence of a time-averaged symmetry plane. All carbonyl carbons are equivalent, giving a single peak at 213.4 ppm and indicating that the basal–apical carbonyl-exchange process[24] is fast at this temperature.

Methylation of **4** also appears to occur predominantly at the imine nitrogen to give ion **6**. Thus Figure 5 shows the result of adding 1 equiv of methyl fluorosulfonate to a solution of **4** in sulfur dioxide. Reaction proceeds slowly and, unlike protonation, distinct signals can be observed for both free base and cationic product. In this case, however, fluxionality is not expected since the intermolecular prototropic pathway is blocked by the presence of the N–CH_3 function. The ^{1}H NMR spectrum shows five distinct resonances for H_3, H_4, H_5, H_6, and H_7 (Table I) which persist to +30°C with only small changes in chemical shift. Thus there is also no evidence for the valence isomerization pathway, **6** ⇄ **6′**. The N_1–H signal for **6** is shifted significantly to higher fields compared to the fluxional η^4 ion **5** and more closely approximates the chemical shift of an amine as would be expected for the proposed static ion. Complete assignments are given in Table I.

The above results and considerations lead to the prediction that protonation of the *N*-methyl derivative **7** would give an imminium ion isomeric with **6**. Contrary to this expectation, we observed that protonation of **7** by use of excess TFA in SO_2 or with neat 95% aqueous TFA resulted in the formation of ion **6**. Addition of aliquots of TFA to an SO_2 solution of **7** at −20°C gave a marked decrease in the shift of H_7, while the shift of H_3 actually increased. The chemical shifts of H_4 and H_6 also approached each other. Continued addition of TFA again separated signals for $H_3 + H_7$ and $H_4 + H_6$ (Figure 6). After ca. 9 equiv of TFA had been added, no further changes in chemical shifts were apparent. Raising the temperature also tended to move together resonances due to H_3 and H_7. The temperature effects were completely reversible.

In the presence of excess acid or in neat 95% aqueous TFA at low temperature (−70°C), a limiting spectrum was obtained (Figure 7). It is important to note that while the N–H signal observed at τ 2.90 shows coupling to H_7 (J = 4.5Hz), no coupling to the *N*-methyl protons is evident. Thus protonation has occurred at the imine nitrogen with rearrangement and migration of the tricarbonyliron moiety. The limiting spectrum corresponds to **6**. The spectrum of **6** obtained as above from **7** is not identical with that for the same ion formed by methylation of **4** (Figure 5). The small differences in chemical shift and the lack of observable coupling with N–H can be

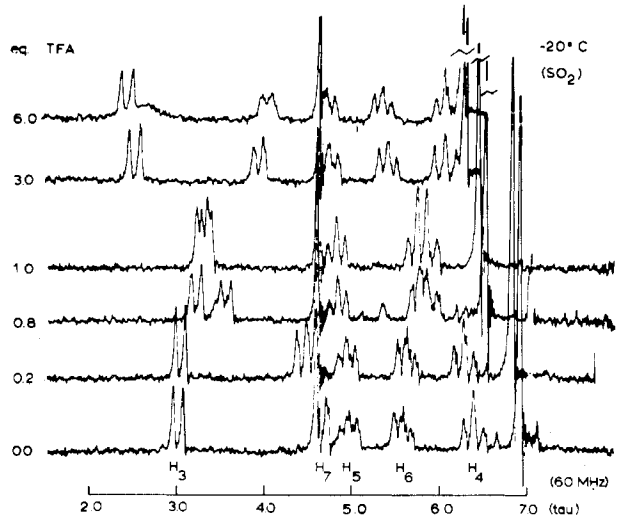


Figure 6. ^{1}H NMR (60 MHz) spectra of **7** in liquid sulfur dioxide showing the effect of added TFA.

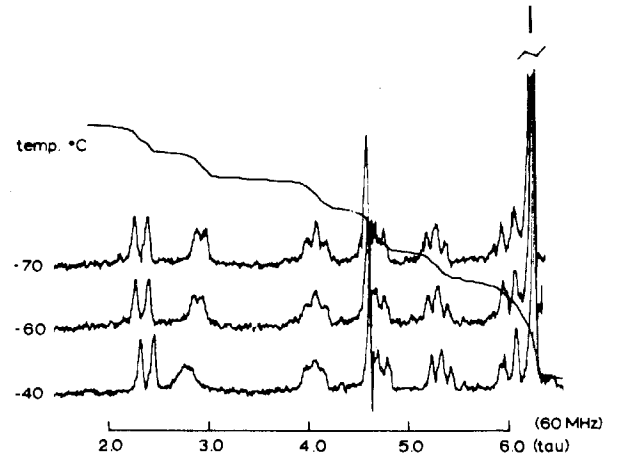
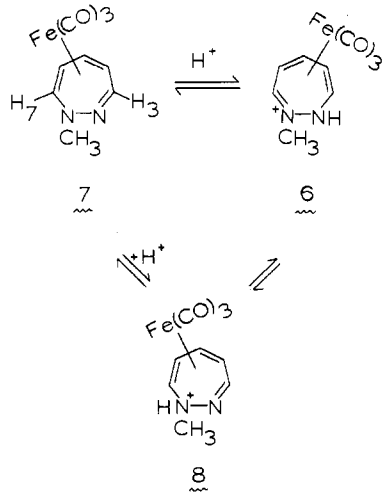
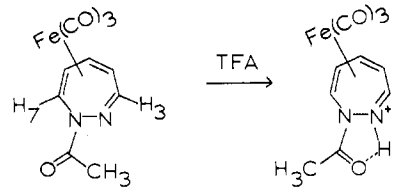


Figure 7. Temperature-dependent spectra of ion **6** prepared from **7** and TFA in liquid sulfur dioxide.

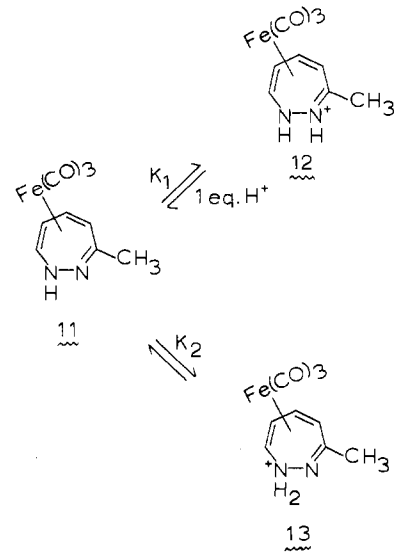
attributed to changes in solvation and to the presence of free base which catalyzes exchange in the sample of Figure 5. We cannot completely exclude the presence of an N_1-protonated species **8** which can lead to **6** via an intramolecular proton transfer. It is nevertheless clear that **8** cannot be the thermodynamic product of protonation of **7** since no N–H to N–CH_3 proton coupling is observed even at very low temperatures.



Conversion of **7** to **6** causes H_3 + H_7 and H_4 + H_6 to exchange *similar* but *not equivalent* environments. Hence average signals are never observed for either pair of protons as observed for the fluxional ion **5**. The temperature and acid dependence of the chemical shifts of H_3 + H_7 and H_4 + H_6 are likely the result of varying equilibrium concentrations of **7**, **6**, and possibly **8**. Solvation effects may also play a role. Protonation of tricarbonyl(4–7-η-1-acetyl-1(1*H*),2-diazepine)iron (**9**) with TFA also occurs at N_2 to give a static η^4 imminium ion (Table I). It is interesting to note that, in comparison to the free base,[2] H_3 is strongly deshielded ($\Delta\tau$ = −1.3 ppm) whereas H_7 actually moves upfield ($\Delta\tau$ = +0.32 ppm). This is undoubtedly due to the hydrogen bonding which conformationally locks the carbonyl group as in **10**, preventing long-range deshielding of H_7.[2,16]



Protonation of tricarbonyl(4–7-η-3-methyl-1(1*H*),2-diazepine)iron (**11**) which itself is incapable of achieving a time-averaged symmetry plane cannot lead to a fluxional ion. Figure 8 shows the result of adding 1 equiv of TFA to an SO_2 solution of **11**. Four nonequivalent ring protons with an essentially identical coupling pattern remain. At low temperatures (<−60°C) two N–H environments are observed at τ −4.8 and +1.1 ppm corresponding to the imminium and the amine site, respectively. As the temperature is increased, broadening due to site exchange commences but the four C–H resonances are unchanged. Finally at temperatures above +10°C a single average signal appears at τ −1.85 ppm. N–H site exchange must then occur via a small equilibrium concentration of ion **13** which is not observable in the ^{1}H NMR spectrum ($K_1 \gg K_2$). Figure 8 shows that broadening of the more acidic and more labile N_2 imminium proton resonance of **12** is more appreciable than that of the N_1 resonance.[25]



Ions **5**,[26] **12**, and **6** may be isolated as the corresponding trifluoroacetate (**5**, **12**) or fluorosulfonate (**6**) salts as described in the Experimental Section. A computer drawing of the structure of **5** is shown in Figure 9.

Protonation to give the imminium ions **5** and **12** is completely reversible and **4** and **11** may be recovered quantitatively

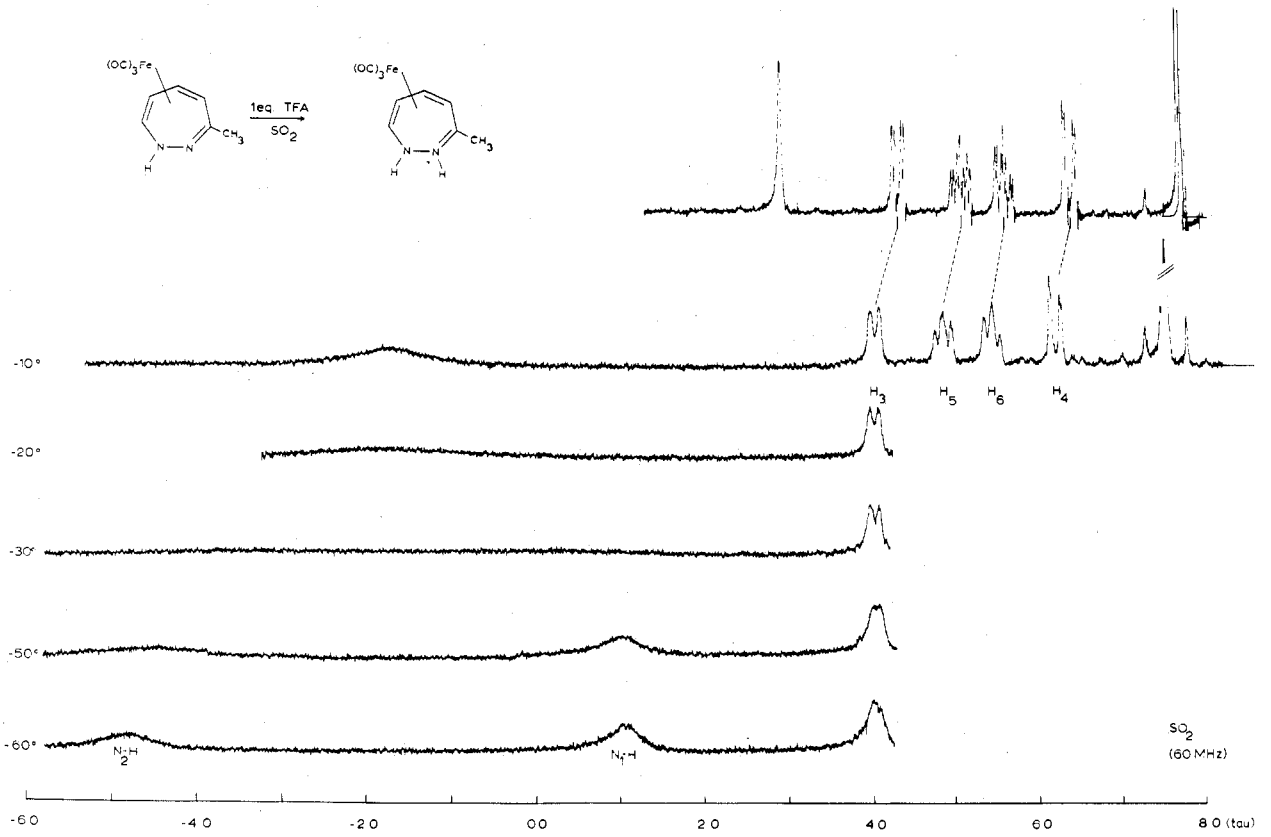
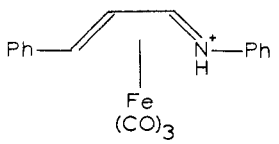


Figure 8. Top: ^{1}H NMR spectrum (60 MHz) of **11** in liquid sulfur dioxide. The remaining traces show the temperature dependence of ion **12** prepared by addition of 1 equiv of TFA.

by treatment of the ions with aqueous sodium bicarbonate. Proton abstraction from **6** prepared by either methylation of **4** or protonation of **7** occurs with rearrangement and gives low yields of the *N*-methyl complex **7**.

Conclusion

The concentration-dependent ir spectra and solvent-dependent ^{1}H NMR spectra of **4** indicate that the prototropy involved in the fluxional process **4** ⇄ **4'** is *intermolecular*. Facile proton transfer requires associated species, and when solution disrupts solute aggregation (e.g., in methanol), the fluxional process is inhibited. Solvents which are themselves less effective acceptors or donors will allow association thus facilitating intermolecular proton transfer and increasing fluxional rates. Unlike the related azepine complexes **3** which exhibit typical enamine reactivity with electrophilic reagents[27] or tropone,[13] cycloheptatriene,[8,28] and 1–4-η-cyclooctatetraene complexes[29] which give η^5-dienyl products via proton addition to complexed or uncomplexed double bonds, **4** prefers to protonate at the imine nitrogen. A related acyclic imminium ion **14** has recently been prepared by protonation of the parent Schiff base complex.[30]



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For the protonated diazepine complexes the greater thermodynamic stability of the imminium ion compared to the ammonium ion product (e.g., **12** vs. **13** or **6** vs. **8**) may well be a reflection of electron release to C3 *via* a transition metal β effect.[31] This effect is manifest in contributing structure **15** which shows a net increased transfer of electron density from the metal in a fashion resembling that proposed for carbonium ions bearing an α-ferrocenyl-,[32] α-cymantrenyl-,[33] α-benchrotrenyl-,[34] and α-tricarbonyl(cyclobutadiene)iron[35] and an α-tricarbonyl(1–4-η-butadiene)iron[36,37] substituent.

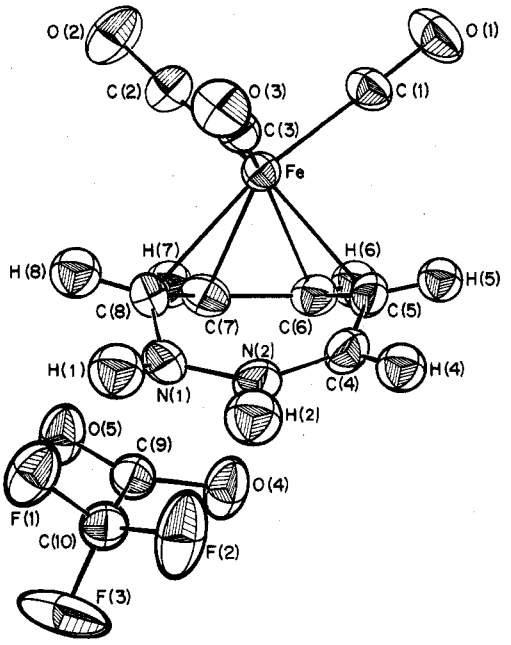
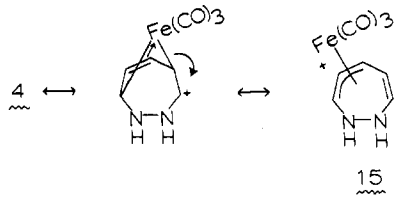


Figure 9. X-ray crystal structure of ion 5-OCOCF$_3$.

Experimental Section

Tricarbonyl(4–7-η-1-acetyl-1(1*H*),2-diazepine)iron (**9**) and tricarbonyl(4–7-η-1-acetyl-3-methyl-1(1*H*),2-diazepine)iron were prepared as previously described.[2] All preparations were carried out under an atmosphere of nitrogen using the general techniques described by Shriver.[38] ^{1}H NMR samples were prepared in serum-stoppered



NMR tubes which were flushed with nitrogen. Infrared spectra were measured on a Perkin-Elmer Model 180 instrument. ^{1}H NMR spectra were obtained with Varian HA-100 (100 MHz) or Perkin-Elmer R-12 (60 MHz) instruments equipped with variable-temperature probes. Carbon-13 NMR spectra were measured at 25.2 MHz using a Bruker WH-90 instrument.

Preparation of Compounds. Tricarbonyl(4–7-η-1(1*H*),2-diazepine)iron (4). To a stirred solution of sodium ethoxide prepared from sodium (0.14 g) and 20 ml of dry (distilled from $Mg(OEt)_2$) ethanol was added 1.64 g (0.59 mmol) of tricarbonyl(4–7-η-1-acetyl-1(1*H*),2-diazepine)iron (**9**). The resulting red solution was stirred at room temperature under a nitrogen atmosphere for 1.5 h and was then quenched with water (400 ml). The aqueous solution was extracted with five 50-ml portions of ether and the combined yellow organic layers were dried over anhydrous potassium carbonate. Removal of solvent gave the complex (1.34 g, 96%) as lemon yellow plates which can be recrystallized from pentane. Sublimation at 70° (10^{-4} mm) gave the analytically pure product, mp 118–119°. Ir (cm^{-1}): in Nujol mull, 2038 (s), 1950 (s), 1897 (s) (ν(C=O)); in C_6H_{12}, 2052 (s), 1990 (s), 1976 (s) (ν(C=O)). Mass spectrum: *m/e* 234 (molecular ion), 206, 178, 123, 94, 56. Exact mass measurements on the *m/e* 94 fragment indicated a composition $C_5N_2H_6$ (calcd, 94.0531; found, 94.0534). Anal. Calcd for $C_8H_6N_2O_3Fe$: C, 41.06; H, 2.58; N, 11.97. Found: C, 41.25; H, 2.64; N, 12.08.

Tricarbonyl(4–7-η-1-methyl-1(1*H*),2-diazepine)iron (7). To a solution of **4** (100 mg) and methyl bromide (10 g) in methanol (10 ml) was added sodium bicarbonate (50 mg). The reaction mixture was sealed in vacuo in a Carius tube and held at room temperature for 3 days. After briefly warming to 75°C for 0.5 h the tube was cooled to −78°C and opened. Removal of solvent and excess methyl bromide left a brown residue which was taken up in ether and washed with a solution of 10% aqueous sodium bicarbonate followed by several portions of distilled water. The ether extract was dried (potassium carbonate) and evaporated to dryness to give 69 mg (65%) of an orange oil which was recrystallized from pentane at −78°C. The yellow-orange product had mp 49–50°C (nitrogen-filled capillary). Ir (cm^{-1}): in C_6H_{12}, 2045 (s), 1975 (s), 1950 (s) (ν(C=O)). Mass spectrum: *m/e* 248 (molecular ion), 220, 192, 164, 149, 137, 135, 108, 97. ^{1}H NMR (SO_2, −10°C): τ 3.05 (2 H, d, J_{34} = 6.3 Hz, H_7), 4.64 (1 H, dd, J_{34} = 6.5 Hz, H_3), 5.03 (1 H, m, J_{45} = 6.9 Hz, H_5), 5.64 (1 H, m, J_{67} = 4.6 Hz, H_6), 6.37 (1 H, m, J_{46} = 1.9 Hz, H_4), 6.91 (3 H, s, CH_3). Anal. Calcd for $C_9H_8N_2O_3Fe$: C, 43.55; H, 3.23; N, 11.29. Found: C, 43.55; H, 3.23; N, 11.42.

Tricarbonyl(4–7-η-3-methyl-1(1*H*),2-diazepine)iron (11). Following the procedures described above, tricarbonyl(4–7-η-1-acetyl-3-methyl-1(1*H*),2-diazepine)iron (0.2 g) was allowed to react with sodium ethoxide prepared from 0.016 g of Na and 5 ml of dry ethanol. The crude brown product was chromatographed through a short alumina column eluting with ether. Removal of solvent gave 0.1 g (62%) of **11** as orange plates, mp 93–94°. Ir (cm^{-1}): in C_6H_{12}, 3410 (N—H), 2042 (s), 1975 (s), 1950 (s) (ν(C=O)). Mass spectrum: *m/e* 248 (molecular ion), 220, 192, 164, 137, 123, 108, 97, 93. ^{1}H NMR ($CDCl_3$): τ 3.80 (1 H, s, br, N_1–H), 4.25 (1 H, dd, J_{67} = 6.1 Hz, H_7), 5.33 (1 H, m, J_{56} = 4.5 Hz, H_5), 6.00 (1 H, m, J_{46} = 1.8 Hz, H_6), 6.40 (1 H, dd, J_{45} = 7.0 Hz, H_4). Anal. Calcd for $C_9H_8N_2O_3Fe$: C, 43.55; H, 3.23; N, 11.29. Found: C, 43.57; H, 3.12; N, 11.15.

Reactions with TFA. Isolation of 5 and 12. Equivalent amounts of trifluoroacetic acid were added via a syringe to concentrated methylene chloride solutions of **4** or **11** at room temperature. Cooling to −20°C overnight gave well-formed yellow-orange crystals of **5** (mp 99–100°) and **12** (mp 91–92°), respectively. The crystals were washed with anhydrous ether and dried on a vacuum line. Yields were in the range 50–60% although additional material could be recovered by adding ether to the solutions. Ir (cm^{-1}) for **5**: in Nujol mull, 2060 (s), 1985 (s) (ν(C=O)). Anal. Calcd for $C_{10}H_7O_5F_3N_2Fe$: C, 34.48; H, 2.07. Found: C, 34.46; H, 2.01. Ir (cm^{-1}) for **12**: in Nujol mull, 2065 (s), 1980 (s) (ν(C=O)). Anal. Calcd for $C_{11}H_9O_5F_3N_2Fe$: C, 36.46; H, 2.48. Found: C, 36.26; H, 2.41.

Attempts to apply the above procedure to isolate **6** from **7** were unsuccessful.

Reaction with Methyl Fluorosulfonate. Isolation of 6. Following the procedure described above, **4** was treated with an equimolar amount of methyl fluorosulfonate. Addition of ether gave a yellow powder (mp 105° dec) which, unlike **5** or **11**, was air sensitive. Ir (cm^{-1}): in Nujol mull, 2071 (s), 1975 (s) (ν(C=O)). Anal. Calcd for $C_9H_{11}N_2FO_7SFe{\cdot}H_2O$: C, 29.50; H, 3.00. Found: C, 29.07; H, 2.62.

Hydrolysis of 6. A sample of ion **6** (prepared from **4** (60 mg) and TFA (20.7 ml)) was dissolved in water to give a clear orange solution. Addition of sodium bicarbonate (200 mg) followed by extraction with several portions of ether gave a yellow organic extract which was shown to be **7** by comparison of infrared spectra and TLC behavior. The aqueous layer remained yellow, and when sodium hydroxide was added, extensive decomposition occurred. The total recovery of **7** was ca. 10–20%. Similar results were obtained with samples of **6** prepared by protonation of **7**. Addition of sodium carbonate to the yellow aqueous layer did not increase the recovery of **7**.

Hydrolysis of 5 and 12. Following the above procedure, quantitative yields of **4** and **11** could be obtained from aqueous solutions of **5** and **12**, respectively.

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Registry No. **4**, 51187-44-1; **5**-$OCOCF_3$, 57535-35-0; **6**, 57535-39-4; **7**, 57535-36-1; **9**, 34822-83-8; **10**, 57535-37-2; **11**, 51187-46-3; **12**, 57535-38-3; tricarbonyl(4–7-η-1-acetyl-3-methyl-1(1*H*),2-diazepine)iron, 51187-47-4.

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The Ferric Tris(dithiocarbamate) Spin Equilibrium Revisited. Variable-Temperature (4.2–296 K) Magnetic Susceptibility, (30–300 K) Infrared, and (4.2–85 K) Electron Paramagnetic Resonance Data

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Variable-temperature magnetic susceptibility (4.2–296 K), infrared (30–300 K), and electron paramagnetic resonance (4.2–85 K) data are reported for one high-spin and nine $^6A_1$–$^2T_2$ spin-equilibrium ferric dithiocarbamates and for two low-spin ruthenium dithiocarbamates. The susceptibility data for the spin-equilibrium systems are least-squares fit by diagonalizing the $^6A_1$ and $^2T_2$ matrices including spin–orbit, zero-field, and Zeeman interactions as a function of magnetic field. As has been indicated previously, it is shown that a good fit of the susceptibility data requires an additional parameter that multiplies at high temperatures the contribution of the $^6A_1$ state beyond that expected. In the past this parameter has been taken as the vibrational partition ratio between the $^6A_1$ and $^2T_2$ states or as a temperature-dependent energy difference between the same two states. Variable-temperature ir data for the spin-equilibrium ferric complexes generally show a $^6A_1$ iron–sulfur band system at $\sim$360 cm^{-1} which loses intensity to a multiplet of $^2T_2$ iron–sulfur bands in the range of $\sim$300–350 cm^{-1}. These ir observations tend to indicate that the vibrational partition factor derived from the susceptibility fitting is *not* correct. Close inspection of the ir data also shows that the energy difference between $^6A_1$ and $^2T_2$ barycenters is also probably *not* temperature dependent. It is suggested that both the $^2T_2$ and the $^6A_1$ ferric states are very vibronic and that this could explain the observed shifts. Infrared data are also reported for certain manganese(III), cobalt(III), and chromium(III) tris(dithiocarbamates). EPR data for the spin-equilibrium ferric systems are seen to serve two purposes. On the one hand, the presence of distinct high-spin and low-spin signals set an upper limit on the high- to low-spin flipping rate of $\sim 10^{10}$ sec^{-1}. Second, at temperatures approaching 4.2 K, signals are seen for the lowest Kramers doublet from the $^2T_2$ state and the magnitudes of $g_\parallel$ and $g_\perp$ again point to a vibronic system.

Introduction

As early as 1931 Cambi and coworkers[3] prepared iron(III) *N,N*-dialkyldithiocarbamates, the first compounds reported to exhibit a spin equilibrium. Since this initial work, the many reviews[4–8] are testimony to the considerable work on such spin-equilibria systems. The ferric tris(dithiocarbamates) [Fe(dtc)$_3$] are one of the most thoroughly studied of these. A considerable number of physical techniques (generally only to liquid nitrogen temperatures) have been employed.[4] From the many studies various interesting facts have surfaced. For instance, in a series of 20 Fe(dtc)$_3$ compounds with a variety of nitrogen substituents, all but four compounds have effective magnetic moments in solution (chloroform and benzene) which are similar to those that they have in the solid state.[9] Deviations of approximately $\pm$1.0 BM between the solid- and solution-state values are seen for the other four Fe(dtc)$_3$ species. With regard to such specific interactions, it is important to note that an x-ray crystal structure has been reported[10] for the dichloromethane solvate of tris(4-morpholinecarbodithioato-*S,S'*)iron(III). Also another very recent paper[11] has discussed the effects of environment, solution vs. solid, on the $^5T_{2g}$–$^1A_{1g}$ equilibrium for a series of Fe(II) complexes with hexadentate ligands.

Nevertheless, even with all of the work on the Fe(dtc)$_3$ systems there still remain some interesting and important questions—questions that apply to many spin-equilibria systems. It has been reported[12] that a theoretical fitting of magnetic susceptibility data down to 90 K for a series of intermediate-spin Fe(dtc)$_3$ complexes required a vibrational partition parameter to account for differences in FeS_6 vibrational frequencies of the $^6A_{1g}$ and $^2T_{2g}$ states. As an aside, it is to be noted that a mathematically equivalent approach is found in assuming that the energy separation between the barycenters of the $^6A_{1g}$ and $^2T_{2g}$ states is temperature dependent. This later approach has been used for $^5T_{2g}$–$^1A_{1g}$ Fe(II) systems where certain complexes show "abrupt" transitions in their μ_{eff} vs. temperature curves.[13] A very recent paper by Sorai and Seki[14] has presented heat capacity data for Fe(phen)$_2X_2$, X$^-$ = NCS$^-$ and NCSe$^-$, to show that the coupling between the electronic state and the phonon system plays a prominent role in the cooperative (abrupt) spin transitions observed for these compounds. In our work we have collected magnetic susceptibility data from 296 to 4.2 K for an extended series of Fe(dtc)$_3$ complexes and we have collected variable-temperature infrared data. These two types of data will be analyzed to investigate the need and validity of in-