forecasts for the terminal rings of many extended polyacenes can be obtained by comparing the last three rings of the hydrocarbon to anthracene or phenanthrene. Thus triphenylene, a very angular hydrocarbon, should be more favorable than phenanthrene toward $Cr(CO)_3$ derivatives, but the reverse for $Fe(CO)_3$ derivatives. As another example, both 1,2-benzopyrene and 4,5-benzopyrene should give $Cr(CO)_3$ derivatives more satisfactorily than anthracene; the existence of a $Cr(CO)_3$ derivative of benzopyrene (which isomer was unspecified) has been reported, but no details are available.[6] For a final contrast with $Fe(CO)_3$ derivatives we note that biphenylene should give a $Cr(CO)_3$ derivative without difficulty; the localization energy of a benzenoid ring is only 8.51β. For hydrocarbons where the benzenoid ring is only linked to the remaining unsaturated system at one carbon the localization energy is usually less than 8.5β; $Cr(CO)_3$ derivatives of many such hydrocarbons are known, for example, biphenyl,[47] 1,4-biphenylbutadiene,[5] and stilbene.[50] Insofar as a completely localized model proves acceptable, further predictions for $Cr(CO)_3$ derivatives can be easily deduced from the available molecular orbital data.[24]

The present methods could obviously be applied to other metal carbonyl derivatives, such as those with cobalt tricarbonyl bonded to an allyl group. There is, however, little information on allyl units in aromatic hydrocarbons, though the recently reported[51] π-benzylcyclopentadienylmolybdenum dicarbonyl has the metal interacting with the exocyclic allyl unit of the benzyl moiety, as is forecast by a partial localization energy approach. For completeness we should mention that the ability of hydrocarbons to form complexes with silver cations has been discussed in terms of bond orders[52] and delocalization from the hydrocarbon to the cation;[53] both approaches are intimately related to localization energies.[10d,11,12]

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Iron(II) Chelates of N,N′-Disubstituted Aminotroponeimines

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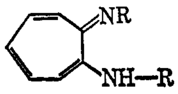
Abstract: Fe(II) chelates of representative aminotroponeimines have been synthesized and characterized. These paramagnetic chelates show large contact shifts in the nmr, and both solution and solid-state magnetic susceptibility studies show the presence of four unpaired electrons. Marked differences in reactivity of the chelates toward various complexing agents were found, and these are attributed to steric effects arising from shielding of the tetrahedral iron atom by substituents attached to nitrogen.

The synthesis and properties of N,N′-disubstituted aminotroponeimines (I) and of their nickel chelates have been reported.[1] Aminotroponeimines (ATI) are regarded as nonclassical aromatic systems on the basis of chemical and physical studies. Their paramagnetic nickel chelates are of special interest since large proton shifts have been observed in nuclear magnetic resonance studies. Through these studies information has been obtained on the manner in which an unpaired electron is delocalized into π systems.[2]



I

This paper describes the preparation and properties of paramagnetic iron(II) chelates of I, where R is methyl, ethyl, *t*-butyl, phenyl, and *p*-tolyl. Methods analogous to those used for the preparation of nickel(II) chelates gave iron(III) chelates in certain instances but failed to give the corresponding iron(II) derivatives. However, two syntheses were uncovered that with one exception yielded the desired iron(II) products. These procedures are (1) reaction of aminotroponeimines with iron pentacarbonyl in an open vessel and (2) reaction of N-lithioaminotroponeimines with anhydrous ferrous chloride. Of the two methods, the latter is preferred.

These procedures appear general, except for the

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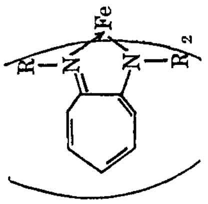
Table I. Fe(II) Chelates of Aminotroponeimines



R	Fe, % Calcd	Fe, % Found	N, % Calcd	N, % Found	C, % Calcd	C, % Found	H, % Calcd	H, % Found	Mp,[a] °C	Nmr bands, cps (at 60 Mc/sec) from TMS: ATI ring α	β	γ	N-Substd aliphatic CH$_2$	CH$_3$	N-Substd aromatic o-	m-	p-	p-CH$_3$	Magnetic susceptibility, BM[b]
CH$_3$	16.0	16.1	16.0	15.5	61.7	61.9	6.3	6.4	287 dec	+2773	−6005	+5883		−7520					4.8
C$_2$H$_5$	13.7	13.4	13.7	13.5	65.0	64.7	7.4	7.2	143–144	+3104	−7173	+6550	−5770	+3840					4.8
C$_6$H$_5$	9.3	8.8	9.3	9.1	76.3	75.6	5.1	5.2	238–239	+2430	−6800	+5780			+5690	−106	+2862		4.75
p-CH$_3$C$_6$H$_4$	8.5		8.5	8.5	77.1	76.7	5.9	5.9	302–304	+2580	−6930	+5865			+5656	−101		−1720	
t-C$_4$H$_9$	10.8	10.8	10.8	11.0	69.5	69.7	9.0	9.0	321	+3630	−6675	+6080		−385					5.3

[a] Determined in sealed tube. [b] Magnetic susceptibility data were obtained in benzene solution by the nmr method: D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

Fe(II) chelate of N,N′-dimethylaminotroponeimine. In this case, the product of both reactions is the Fe(III) chelate [(Me$_2$ATI)$_3$Fe]. In order to prepare the Fe(II) chelate it is necessary to trap this highly reactive product as a complex with either carbon monoxide or pyridine. Maximum yields are obtained if both carbon monoxide and pyridine are present during the synthesis, in which case the Fe(II) product is obtained as the monopyridine complex (Me$_2$ATI)$_2$Fe(py). Removal of pyridine under high vacuum at 150° yields pure (Me$_2$ATI)$_2$Fe^{II}.

The iron(II) chelates of aminotroponeimines are deep green-black, crystalline compounds with high solubility in aromatic hydrocarbons and carbon disulfide and with modest solubility in tetrahydrofuran, ether, and hot cyclohexane. Magnetic susceptibility studies on both solid and solution states show that the products are in the high-spin form with four unpaired electrons, and a tetrahedral configuration is presumed.

With Ni(II) chelates of aminotroponeimines there is an equilibrium in the solution state between the diamagnetic, square-planar structure and the paramagnetic, tetrahedral structure. At room temperature, the diamagnetic form predominates in the Ni chelate of Me$_2$ATI, while the paramagnetic form predominates in the Et$_2$ATI chelate. As a consequence, vast differences are seen for the contact shifts of the ring protons of the two species (~93 ppm for α, ~52 ppm for β, and ~133 ppm for γ). However, in the nmr spectra of Fe(II) chelates of aminotroponeimines, the contact shifts of the individual ring protons are essentially the same regardless of substitution on nitrogen, indicating that the Fe(II) chelates all have the same geometry (Table I).

In the nmr, the resonance positions are spread out over a field of 235 ppm (125 ppm to low field and 110 ppm to high field from tetramethylsilane). The resonance lines are much broader (30–500 cps) than those of the corresponding nickel chelates, and spin–spin coupling cannot be detected because of their breadth. Details are given in Table I; see Figure 1 for the spectrum of the Fe(II) chelate of Et$_2$ATI.

Reversible Dicarbonyl Complexes

Except for (t-Bu$_2$ATI)$_2$Fe^{II}, solutions of the chelates rapidly absorb carbon monoxide at ordinary temperatures to give diamagnetic dicarbonyl complexes in which the iron atom is isoelectronic with krypton. The complexed carbon monoxide is tightly bound at room temperature; no loss of CO occurs *at room temperature* on exposure of solutions of the complex or of the crystalline solid to high vacuum. On heating solutions of the complex, however, decarbonylation with generation of the original paramagnetic Fe(II) chelate occurs at temperatures above 70°. At 80° the half-life of (Et$_2$ATI)$_2$Fe(CO)$_2$ is about 15 min.

In the nmr (60 Mc/sec), (Me$_2$ATI)$_2$Fe(CO)$_2$ has two resonances of equal intensity separated by 24 cps, attributable to the methyl group. For (Et$_2$ATI)$_2$Fe(CO)$_2$, the resonances ascribable to the methyl group appear as two overlapping triplets giving rise to a symmetrical quintuplet pattern, and no single quartet assignable to the CH$_2$ group is found (Figure 2). Instead, a complex pattern that could result from two overlapping quartets is observed in the region where

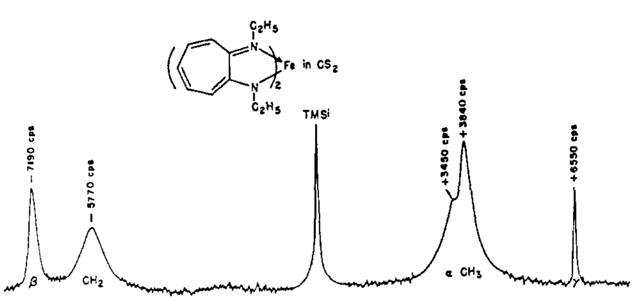


Figure 1. Nmr spectrum (60 Mc/sec) of the Fe(II) chelate of Et_2ATI in CS_2.

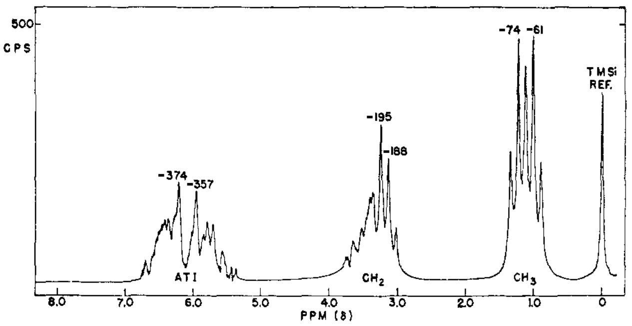


Figure 2. Nmr spectrum (60 Mc/sec) of $(Et_2ATI)_2Fe(CO)_2$ in CS_2.

the methylene protons of diamagnetic $(Et_2ATI)_2Zn$ are found. These nmr studies suggest that the carbonyl substituents occupy *cis* positions in the octahedral configuration (Figure 3) in which the singly starred R groups are in identical chemical environments and thus should be magnetically equivalent. The doubly starred R groups are also equivalent but are not identical with the singly starred groups. If the dicarbonyl complexes had the symmetrical *trans* configuration, single resonances would be expected for the protons of the methyl and ethyl groups.

Infrared spectra of the dicarbonyl complexes show two absorption bands at 5.05 and 5.15 mμ in the region attributable to the metal carbonyl function. These data support the unsymmetrical *cis* assignment since the *trans* configuration would be expected to show only a single absorption band in this region.

Variations in Complexing Ability of $(ATI)_2Fe$ Chelates

Marked differences in complexing ability of (N,N′-disubstituted $ATI)_2Fe^{II}$ chelates have been found for various donor systems. These differences are attributed to variations in the ability of alkyl groups attached to nitrogen to shield the iron atom in its tetrahedral configuration from attack by donor species. For example, it was found that $(Me_2ATI)_2Fe^{II}$ formed complexes with carbon monoxide, oxygen, nitric oxide (epr evidence), pyridine, and 2,5-dimethyl-2,5-hexane diisocyanide. In addition, evidence was obtained through nmr studies for formation of complexes with piperidine, pyridine N-oxide, triphenylphosphine oxide, 2,5-dimethylisoxazole, and hexafluoro-2-butyne.

In the case of the more crowded $(Et_2ATI)_2Fe^{II}$ and $(Ar_2ATI)_2Fe^{II}$, however, only small linear molecules such as carbon monoxide, oxygen,[3] and nitric oxide, as well as the diisocyanide containing the linear N≡C function, complexed with the chelates. Finally, the highly crowded $(t\text{-}Bu_2ATI)_2Fe^{II}$ failed to react even with oxygen, carbon monoxide, or nitric oxide. Studies of molecular models indicate that in this case the iron atom is completely shielded from approaching reagents.

Furthermore, differences were observed for decarbonylation of Me_2- and $(Et_2ATI)_2Fe(CO)_2$ compounds. Thus, the decarbonylation of the diethyl compound appears to be primarily dependent upon temperature and independent of solvent (including pyridine), whereas the dimethyl compound is stable in solution at room temperature but undergoes ready decarbonylation on addition of pyridine.

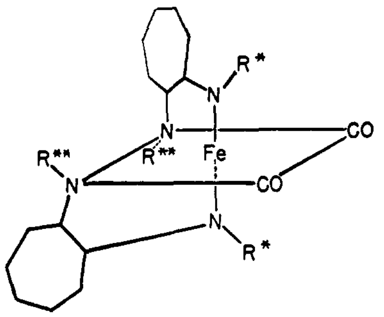


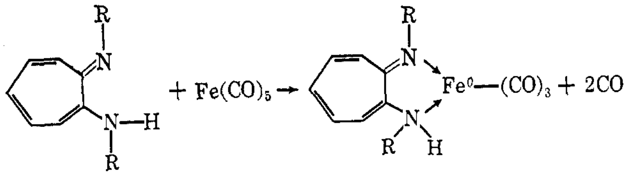
Figure 3.

Nmr studies have shown that addition of Me_2ATI to a hexadeuteriobenzene solution of the paramagnetic $(Me_2ATI)_2Fe^{II}$ at −20° gives a diamagnetic species in which the proton apparently is shared equally among the three ATI ligands or is attached to the iron atom. On warming to room temperature, a paramagnetic species is formed that has been identified as $(Me_2ATI)_3Fe^{III}$. Polarographic studies have indicated that $(Me_2ATI)_3Fe^{III}$ is reduced in tetrahydrofuran by a one-electron-transfer reaction.

On the other hand, no reaction is observed between $(Et_2ATI)_2Fe^{II}$ and Et_2ATI. Greater shielding of the iron atom by ethyl groups presumably accounts for the differences observed. Furthermore, efforts to prepare the tris chelate $(Et_2ATI)_3Fe^{III}$ have been unsuccessful.

Mechanism of Reaction of Iron Pentacarbonyl with Aminotroponeimine

It is proposed that the first step in the reaction of $Fe(CO)_5$ with ATI involves replacement of two carbonyls by ATI to give a zerovalent Fe complex.



Since the reaction proceeds to formation of the Fe(II) chelate [the Fe(III) chelate in the case of Me_2ATI], two electrons must eventually be lost by each iron atom, and each of the two ATI units must lose the proton attached to nitrogen. It is proposed that in the second step of the reaction the hydrogen on nitrogen might

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[3] The complexes of $(Et_2ATI)_2Fe^{II}$ with oxygen will be discussed in a separate paper. In the case of $(Me_2ATI)_2Fe^{II}$, the only soluble product obtained from the reaction with oxygen was $(Me_2ATI)_3Fe^{III}$.

Table II. Concentration Dependence of Proton Shifts of $Fe(Me_2ATI)_2(C_5H_5N)$ in C_6H_6

Concn[a] of $Fe(Me_2ATI)_2$-(C_5H_5N) in benzene, %	Proton shifts, cps[b]						
	ATI protons				C_5H_5N protons		
	CH_3	α	β	γ	α	β	γ
5	−5790	+2720	−5280	+5720	−2500	−440	−426[c]
10	−5400	+2700	−5180	+5700	−3150	−450	
15	−5050	+2560	−5120	+5560	−3600	−580	
20	−4680	+2480	−5000	+5480	Very broad	−620	
$Fe(Me_2ATI)_2$ in C_6H_6	−7500	+2770	−6000	+5885			
$Fe(Me_2ATI)_2$ in C_5H_5N	−3200	+1540	−4090	+4470	−520	−435	−460

[a] Concentrations are only approximate. [b] Determined at 60 Mc/sec using a Varian Associates HR60 spectrophotometer. [c] The γ band is not normally seen as it is under the C_6H_6 band. This value was obtained in a C_6D_6 solution.

be lost as a hydrogen atom or it might be transferred as a proton to either the Fe atom or a carbonyl group. Evidence for formation of an unstable Fe–H species has been found in infrared studies, which show a sharp absorption band at 4.2 mμ. In the remaining steps, it is presumed that another molecule of ATI becomes attached to the Fe atom, and, again, carbon monoxide and hydrogen are eliminated. Only 1 to 3% of the hydrogen is found in the form of hydrogen gas; the bulk is presumably consumed through reaction with ATI and/or solvent.

If the reaction with Et_2ATI is carried out under autogenous pressure in heptane at 115°, an equilibrium pressure, corresponding to only a fraction of what would be obtained by liberation of the theoretical amount of carbon monoxide, is quickly reached, and $(Et_2ATI)_2Fe(CO)_2$ is obtained in 8% yield. In an analogous reaction with Me_2ATI $(Me_2ATI)_3Fe^{III}$ is obtained in a similar yield. In both cases unreacted ATI was recovered to the extent of 80–90%.

If the pressure vessel used in the Et_2ATI reaction is cooled to room temperature and carbon monoxide vented, the same equilibrium pressure is reached on heating again to 115°. If this cycle is repeated until no further carbon monoxide is liberated, $(Et_2ATI)_2$-$Fe(CO)_2$ is obtained in 60–70% yield. This result suggests that at least the first step of the proposed mechanism is reversible.

Concentration Dependence of Proton Resonances of $(Me_2ATI)_2Fe(py)$

The position of proton resonances of solutions of the paramagnetic, pentacoordinated iron compound, $(Me_2ATI)_2Fe(py)$, shows strong concentration dependence (Table II). With increasing dilution of a solution of the complex in benzene, the proton resonances approach positions (*e.g.*, −7500 cps for protons of CH_3) found for those of $(Me_2ATI)_2Fe^{II}$ in benzene. With increasing concentration, the proton resonances approach positions found for those determined in pyridine solution for $(Me_2ATI)_2Fe^{II}$ (*e.g.*, −3200 cps for protons of CH_3). These results suggest that the complex is labile in solution and that the rate of exchange is rapid on the nmr time scale so that the position of the resonance line is an averaged value and is dependent upon the relative numbers of associated and unassociated species.[4]

$$(Me_2ATI)_2Fe(py) \rightleftharpoons (Me_2ATI)_2Fe + py$$

Proton resonances for diamagnetic pyridine are absent in benzene solutions of $(Me_2ATI)_2Fe(py)$, but three extra lines showing contact shifts are present indicating that spin is transmitted into the complexed pyridine molecule. The positions of these lines are also concentration dependent and approach the positions found in pyridine (diamagnetic) with increasing dilution or on addition of free pyridine.[4] These resonances are all shifted toward low field, and the magnitude of the shift drops off sharply with distance from the nitrogen atom (2 > 3 > 4) which would be expected if spin is transmitted into the complexed pyridine through a σ rather than a π bond.

Other Complexes

Although triphenylphosphine does not form a complex with $(Me_2ATI)_2Fe^{II}$, the less sterically hindered triphenylphosphine oxide does. Like the pyridine complex, this product is paramagnetic and partially dissociated in solution. In contrast to these labile complexes, $(Me_2ATI)_2Fe^{II}$ forms a diamagnetic dicarbonyl complex and a paramagnetic monopyridine oxide complex that do not dissociate in noncomplexing solvents such as benzene and tetrahydrofuran.

Experimental Section

In the preparation and isolation of the iron chelates, all operations were carried out under nitrogen, and sodium-dried solvents were used. Most of the chelates must also be protected from air in the crystalline state.

Nmr data were determined using Varian Associates A-60 and HR-60 spectrophotometers for the diamagnetic and paramagnetic compounds, respectively, at 60 Mc/sec with tetramethylsilane as an internal reference. Physical properties and analyses of the chelates are given in Table I.

Preparation of Fe(II) Chelates by Reaction of Ferrous Chloride with Lithium Derivative of an Aminotroponeimine. A solution of 10.6 g (0.06 mole) of N,N′-diethylaminotroponeimine (Et_2ATI) in 60 ml of tetrahydrofuran was stirred at 0° while 38 ml of 1.6 *N* *n*-butyllithium (0.06 mole) in hexane was added dropwise. Anhydrous ferrous chloride[5] (4.3 g, 0.033 mole) was added, and the reaction mixture was stirred at room temperature for 3 hr. Solvent was removed from the reaction mixture under reduced pressure, and the residue was extracted with 250 ml of refluxing hexane. The solid obtained on cooling the hexane extract to 0° was recrystallized from cyclohexane to give 8.6 g (70% yield) of greenish black crystals of the Fe(II) chelate of Et_2ATI, mp 143–144°.

Fe(II) chelates of the N,N′-diarylaminotroponeimines were obtained in a similar manner. However, the Fe(III) chelate was obtained with N,N′-dimethylaminotroponeimine. A solution of 9.45 g (0.064 mole) of Me_2ATI in 60 ml of THF was stirred at 0° while 40 ml of 1.6 *N* *n*-butyllithium in hexane was added dropwise. Anhydrous ferrous chloride (4.6 g, 0.036 mole) was added, and the reaction mixture was stirred at room temperature for 3 hr and then

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[4] J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).

[5] P. Kovacic and N. O. Brace, *J. Am. Chem. Soc.*, **76**, 5491 (1954).

filtered. No chelate was extracted from this solid with boiling hexane or cyclohexane. The residue was then extracted with 140 ml of benzene in a Soxhlet apparatus. Black crystals (6.5 g, 61% yield), mp 287–288°, of $(Me_2ATI)_3Fe^{III}$ were obtained on filtering the benzene extract. The magnetic susceptibility determined in chloroform by the nmr method is 2.0 BM.

Anal. Calcd for $C_{27}H_{33}N_6Fe$: N, 16.9; C, 65.3; H, 6.7; Fe, 11.2. Found: N, 17.0; C, 65.5; H, 6.8; Fe, 10.7.

The nmr spectrum in CS_2 has resonances at −1560 (β), −922 (CH_3), +2471 (α), and +3372 cps (γ). In a polarographic study in THF containing 0.1 *m* $LiClO_4$, a well-defined reduction wave is found at $E_{1/2}$ of −1.17 v *vs.* the saturated calomel electrode. A plot of *E vs.* log $i/(i_d - i)$ has a slope of 0.056; theory for a reversible one-electron reduction is 0.059.

Preparation of Fe(II) Chelates by Reaction of $Fe(CO)_5$ with Aminotroponeimines. A solution of 9.5 g (0.054 mole) of Et_2ATI and 15 g (0.077 mole) of iron pentacarbonyl in 50 ml of diglyme was stirred and heated under reflux at 120–125° for 2.5 hr. A total of about 0.12 mole of gas was evolved during the period, and analysis showed it to be mainly carbon monoxide containing some $Fe(CO)_5$ and hydrogen. The $CO{:}H_2$ ratio was 100:1. The reaction mixture was concentrated to one-half its original volume by distillation under reduced pressure. The solid separating on cooling the concentrated solution to 0° was recrystallized from cyclohexane to give 6.2 g (57% yield) of black needles of $(Et_2ATI)_2Fe^{II}$.

Fe(II) chelates of the N,N′-diarylaminotroponeimines and of N,N′-di-*t*-butylaminotroponeimine were prepared in similar yields by an analogous procedure except that reaction temperatures of 135° for 2 hr and of 140° for 3 hr, respectively, were required. The reaction of iron pentacarbonyl with N,N′-dimethylaminotroponeimine is complete in 2 hr at a temperature of only 95–100° but, as discussed above, the product of the reaction is the Fe(III) chelate.

Monopyridine Complex of the Fe(II) Chelate of Me_2ATI. A solution of 9.2 g (0.062 mole) of Me_2ATI in 60 ml of THF was stirred at 0° while 39 ml of 1.6 *N n*-butyllithium in hexane was added dropwise. This reaction mixture was added dropwise at room temperature to a stirred solution of 6.4 g (0.031 mole) of anhydrous ferrous chloride in 30 ml of pyridine and 120 ml of tetrahydrofuran under an atmosphere of carbon monoxide. There was an absorption of 650 ml of carbon monoxide during the 20-min addition period. The reaction mixture was stirred until the absorption of carbon monoxide was complete. This required 30 min, and an additional 630 ml of gas was absorbed. The 1280-ml total is 85% of theory for formation of the dicarbonyl complex $(Me_2ATI)_2Fe(CO)_2$. The solvent was removed from the reaction mixture under reduced pressure at room temperature. The residue was extracted with refluxing cyclohexane. The solid obtaned on diluting the extract with pentane was recrystallized from cyclohexane to give 7.5 g (57% yield) of black crystals of $(Me_2ATI)_2Fe(py)$, mp 156°.

Anal. Calcd for $C_{23}H_{27}N_5Fe$: C, 64.4; H, 6.3; N, 16.3; Fe, 13.0. Found: C, 63.7; H, 6.4; N, 16.0; Fe, 13.0.

Solid magnetic susceptibility measurements showed a magnetic moment of 4.98 BM (four unpaired electrons). Proton nmr data are given in Table II.

***cis*-Dicarbonyl Complexes of Fe(II) Chelates.** A solution of 4.1 g (10 mmoles) of $(Et_2ATI)_2Fe$ in 130 ml of diethyl ether was stirred at 0° under carbon monoxide at atmospheric pressure. In 10 min, a total of 450 ml (80% of theory) of gas was absorbed, and the solution changed in color from black to blood-red. The red powder (3.6 g, 78% yield) obtained on filtering was recrystallized by dissolving it at room temperature in a benzene–pentane mixture and cooling to −10° to give black crystals, melting in a sealed tube at 109° dec.

Anal. Calcd for $C_{24}H_{30}N_4O_2Fe$: C, 62.4; H, 6.5; N, 12.1; Fe, 12.0. Found: C, 61.8; H, 6.7; N, 12.4; Fe, 11.9.

The *cis*-dicarbonyl complex of the Fe(II) chelate of Me_2ATI, melting in a sealed tube at 133° dec, was also prepared by the above procedure.

Anal. Calcd for $C_{20}H_{22}N_4O_2Fe$: C, 59.3; H, 5.5; N, 13.8; Fe, 13.7. Found: C, 59.4; H, 5.6; N, 14.0; Fe, 13.7.

Absorption bands in the infrared attributable to a metal–carbonyl function are present at 5.05 and 5.15 mμ. The nmr spectra in the −330- to −410-cps region of carbon disulfide solutions of each of the dicarbonyl complexes have complex patterns similar to those for the ring protons of diamagnetic ATI chelates. In addition, $(Me_2ATI)_2Fe(CO)_2$ shows resonances of equal intensity at −186 and −162 cps that are assigned to the protons of the CH_3 groups attached to nitrogen. $(Et_2ATI)_2Fe(CO)_2$ has resonance lines in the form of a quintet that result from two overlapping triplets centered at −61 and −74 cps that are assigned to the CH_3 protons of the ethyl group attached to nitrogen. The more complex pattern attributed to two overlapping quartets centered at −191 and −212 cps is assigned to the CH_2 protons of the ethyl group.

2,5-Dimethyl-2,5-hexane Diisocyanide Adduct of the Fe(II) Chelate of Me_2ATI. To a solution of 0.86 g (2 mmoles) of $(Me_2ATI)_2Fe(py)$ in 10 ml of benzene and 5 ml of methylcyclohexane was added 0.33 g (2 mmoles) of 2,5-dimethyl-2,5-hexane diisocyanide. The reaction mixture turned the same deep, blood-red color encountered on forming dicarbonyl complexes of Fe(II) chelates. The reaction mixture was stirred at room temperature for 1 hr, cooled to 0°, and filtered. The red solid was recrystallized to give 0.4 g of diamagnetic black crystals. In CS_2, the nmr spectrum shows a resonance pattern from −324 to −368 cps that is characteristic of the ring proton resonances of diamagnetic ATI chelates. There are two resonances of equal intensities at −172 and −155 cps that are assigned to the protons of the methyl groups attached to nitrogen. This compound would be expected to have the same *cis* configuration as pictured in Figure 3 for the dicarbonyl complex, which also shows two methyl resonances. There is a complex resonance pattern centered at −79 cps that is assigned to the CH_2 and CH_3 protons of the complexed 2,5-dimethyl-2,5-hexane diisocyanide. Integration of the nmr spectrum supports formulation as a 1:1 complex.

Di-*t*-butylaminotroponeimine. A solution of 214 g (3 moles) of *t*-butylamine in 750 ml of methanol was stirred at 5–8°, and 50 g (0.3 mole) of 5,5,6,6-tetrafluoro-1,3-cycloheptadiene[6] was added dropwise over a 45-min period. The reaction mixture was stirred at this temperature for an additional 5 hr and then under reflux for 2 hr. Most of the solvent and excess amine were removed by distillation on a steam bath. The residue was poured onto cracked ice. An aqueous solution of 67.2 g (1.2 moles) of potassium hydroxide was added, and the mixture was steam distilled to remove volatile products. The residual, yellow solid was separated and extracted with hot methanol. The crude product obtained on cooling the extract was recrystallized from methanol to give 36 g (54% yield) of yellow crystals, mp 79.5–80°. In $CDCl_3$ the methyl resonance in the nmr spectrum appears as a single line at −85 cps.

Anal. Calcd for $C_{15}H_{24}N_2$: C, 77.5; H, 10.4; N, 12.1. Found: C, 77.2; H, 10.4; N, 12.1.

2,5-Dimethyl-2,5-hexane Diisocyanide.[7] 2,5-Dimethyl-2,5-hexanediamine (200 g, 1.52 moles) in 800 g (13.3 moles) of methyl formate was heated in a 1-l. pressure vessel at 100° for 8 hr. After removal of solvent, 286 g of crude diformamide was obtained by distillation at 176–178° (0.25 mm). The product solidified on standing and was recrystallized from ethyl acetate to give 266 g (90% yield) of N,N′-(1,1,4,4-tetramethyltetramethylene)bisformamide, mp 106–107.5°.

To a slurry of 40 g (0.20 mole) of (1,1,4,4-tetramethyltetramethylene)bisformamide in 160 ml of pyridine at room temperature was added portionwise during 15 min 35.3 g (0.40 mole) of benzenesulfonyl chloride. The mixture was stirred for 1 hr and then poured into 1 l. of water. The solid that separated was recrystallized from hexane to give 4.0 g of white crystals of 2,5-dimethyl-2,5-hexane diisocyanide, mp 124–125°.

Anal. Calcd for $C_{10}H_{16}N_2$: C, 73.12; H, 9.82; N, 17.06. Found: C, 73.28; H, 9.90; N, 17.27.

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(7) Prepared by Dr. W. R. Hasek.