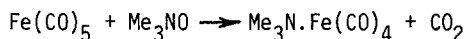


Amminotetracarbonyl Iron (0) Complexes

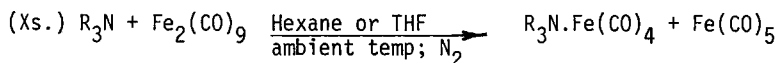
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Summary: Aliphatic amino complexes of the type $R_3N.Fe(CO)_4$ were prepared. Their spectral properties, stability and reactivity were investigated.

Stable and isolable amminotetracarbonyl iron (0) complexes are rare compounds. Few have been detected in solution^{1,2}. Aromatic amines complexes viz. pyridine^{1,3} picoline¹, pyrazine³, quinoline¹ and lutidine¹ were prepared and are fairly stable in the solid state. The absence of aliphatic trialkylamminotetracarbonyl iron (0) complexes from the literature is striking and is most probably associated with the disproportionation reaction of iron (0) in presence of amines⁴. An aliphatic amine complex, $Me_3N.Fe(CO)_4$, was reported by us⁵ in connection with our work on the amine oxide reaction^{6,7}, and later by Hogeveen⁸. In both cases^{5,8} the complex was obtained via the following reaction:



In the present report we describe the synthesis, stability and reactions of new aliphatic trialkylamminotetracarbonyl iron (0) complexes. In variance with the above reaction, the following direct reaction between aliphatic tertiary amines (R_3N) and $Fe_2(CO)_9$ was used and gave fair to good yields of the desired complexes (Table I).

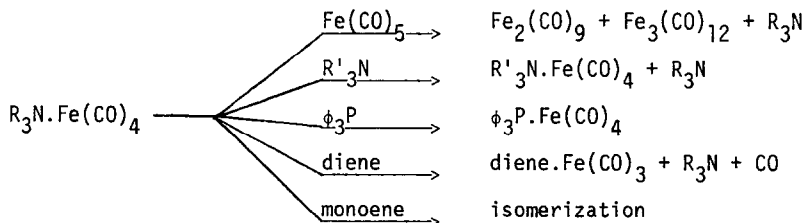


The progress of the reaction was monitored by ir (CO stretching region). Prolonged reaction time led to gradual decomposition of the complex. The first two complexes are sublimable. Hexane or benzene-hexane mixtures were used for crystallization.

N,N-dimethylaniline failed to react (ir). We failed in isolating a bidentate chelate complex with N,N,N,N-tetramethyl-1,2-diaminoethane. Instead, an ill defined, most probably mono-ligand complex, was formed.

The structures of the solid complexes follow from ir, nmr, mass spectra and analytical data. For the three liquid complexes ir data provide convincing structural proof.

Our preliminary studies of these complexes (Table I) revealed the following reactions manifold:



Central to the chemical reactivity of these complexes is most probably the initial reversible dissociation reaction:

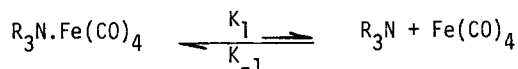


Table I. Properties of Amino Tetracarbonyl Iron (0) Complexes

Compounds	Yield (%)	dec. p. (°C)	mass spec. (m/e)	$\nu_{C \equiv O}^a$ (cm ⁻¹)	nmr (C ₆ D ₆ : δ , ppm)
Me ₃ N.Fe(CO) ₄	34	51	227,199,171 143,115	1900,1935 1966,2050	1.90(s)
Et ₃ N.Fe(CO) ₄	27	57	269,241,213 185,157	1900,1930 1960,2045	0.65(9H,t);2.00 (6H,q)
n-Pr ₃ N.Fe(CO) ₄		liq		1940,1968 2045	
n-Bu ₃ N.Fe(CO) ₄		liq		1937,1963 2047	
(ϕ CH ₂) ₂ MeN.Fe(CO) ₄		liq		1934,1962 2045	
DABN ^b .Fe(CO) ₄	76	98	280,252,224 196,168	1926,1967 2050	1.92(6H,AA');2.32 (6H,BB')
DABN[Fe(CO) ₄] ₂ ^b	60	95-7		1932,1964 2042	1.90(s)
HMTA.Fe(CO) ₄ ^d	82	123	308,280,252 224,196	1933,1966 2045	3.64(s,6H); 4.23(s,6H)
HMTA[Fe(CO) ₄] ₂ ^d	60	99	c	1938,1967 2042	2.90(s,2H);3.57 (s,8H);4.15(s,2H)
Quinuclidine.	44	122	279,251,223 195,167	1930,1962 2055	

^a Where four bands were recorded the low frequency one is of very low intensity.

^b DABN=1,4-Diazabicyclo[2.2.2]nonane

^c Satisfactory elemental analysis was obtained.

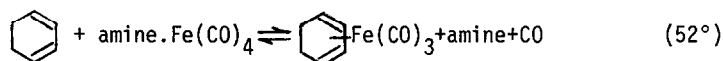
^d HMTA=Hexamethylenetetramine.

NMR spectra of the complexes in solution containing the corresponding free amine are of the superimposed rather than exchanging type. This must indicate that K_1 is small (K_{-1} must be large) relative to the nmr time scale. The above results are in apparent contradiction with singlet recorded for all the benzyl protons of $(\phi\text{CH}_2)_2\text{MeN.Fe(CO)}_4$ at -80° .

All complexes in Table I and also Pyr.Fe(CO)_4 decompose in hydrocarbon solution at room temperature under nitrogen. Such solution exhibit intensity attenuation of the ir CO stretching bands (complex) with concomitant appearance of new bands associated with Fe(CO)_5 and formation of insoluble amorphous solids. Transitory formation of $\text{Fe}_3(\text{CO})_{12}$ was noted. The insoluble solids are polynuclear charged species (ir, solubility properties). They must result from the known disproportionation reaction of iron⁴. Such decomposition was totally quenched in the presence of free amine. The decomposition of the various complexes at room temperature, follows first order kinetics with observed $t_{1/2}$ values in the range of 0.5-6h (hexane). The following relative order of kinetic stability was found with the complexes of the type amine. Fe(CO)_4 . Amine:HMTA>Quinuclidine \approx Pyr>DABN>Me₃N>Et₃N. Qualitatively the stability order can be rationalized in terms of combination of steric effects, $\text{p}K_a$ of the amines and the number of nitrogen atoms per molecule available for bonding.

The amine-phosphine exchange was performed with $\text{Me}_3\text{N.Fe(CO)}_4$ at 60° in pet ether-benzene mixture. The reaction is complete after 0.5h with quantitative yield.

The amine-diene exchange reaction was studied with 1,3-cyclohexadiene in hydrocarbon solution at 52° . The reaction is reversible:



It could be initiated from either side of the equilibrium equation, and could conceivably be used as a simple non-oxidative method for disengagement of organic ligands from their iron carbonyl complexes. Reliable K_{eq} values were difficult to obtain due to concomitant decomposition of the amino complexes.

Trialkylamminotetracarbonyl iron (0) complexes isomerize olefins catalytically to a thermodynamic mixture of double bond isomers (GC analysis). The reaction was followed by observing the rate of disappearance of 1-heptene (GC) in presence of 10mol percent of the complexes. The data presented in Table II in two solvents.

Table II. Fractional Life Times of 1-Heptene at 68° (C,1.0M in 1-heptene;0.1M in complex)

Cpd.:	$\text{Fe}_2(\text{CO})_9$	$\text{Et}_3\text{N.Fe(CO)}_4$	$\text{Me}_3\text{N.Fe(CO)}_4$	DABN.Fe(CO)_4^*	Pyr.Fe(CO)_4	Fe(CO)_5
t_n (min): in Hexane	43 _{0.5}	84 _{0.5}	166 _{0.5}	195 _{0.5}	80 _{0.04}	1400 _{0.002}
t_n (min): in Benzene	57 _{0.5}	100 _{0.005}			200 _{0.03}	

* DABN \equiv 1,4-Diazabicyclo[2.2.2]nonane

None of the rates (hexane) exceeds that of $\text{Fe}_2(\text{CO})_9$ but all are impressively larger than the one with $\text{Fe}(\text{CO})_5$. With the amino complexes the relative rates isomerization of 1-heptene follow the relative order of kinetic stability, previously established. Striking is the change to benzene solvent which hardly affects the rate with $\text{Fe}_2(\text{CO})_9$, but drastically attenuate the rates of isomerization with the amino complexes. These and other related aspects of this class of compounds are currently being investigated.

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