Organonitrogen Derivatives of Metal Carbonyls. IV. The Reaction between σ-Methyl-π-cyclopentadienyliron Dicarbonyl and Trifluoroacetonitrile[1,2]

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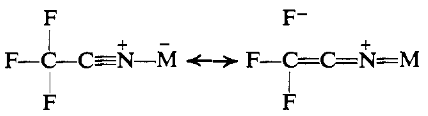
Abstract: The reaction of $CH_3Fe(CO)_2C_5H_5$ with trifluoroacetonitrile under pressure at 90° gives the black volatile complex $CF_3C(NH)Fe(CO)(NCCF_3)(C_5H_5)$, containing the novel trifluoroacetonitrile and trifluoroacetimino ligands. The infrared, nmr, and mass spectra of this new complex are discussed. Upon ultraviolet irradiation of this complex with the tricovalent phosphorus derivatives PR_3 ($R = C_6H_5$ or OC_6H_5) in hexane solution, the carbonyl group is replaced to yield the substitution products $CF_3C(NH)Fe(PR_3)(NCCF_3)(C_5H_5)$ ($R = C_6H_5$ or OC_6H_5).

The primary factor responsible for the unique and extensive chemistry of the metal carbonyls is the strong π-acceptor ability of the CO ligand. Recently, Kruck[5] has developed a similar but not identical chemistry of isoleptic[6] metal trifluorophosphine derivatives likewise arising from the strong π-acceptor strength of PF_3. In this latter case the accepting power of the tricovalent phosphorus atom is enhanced by the electronegative fluorine substituents. In a search for additional ligands with abnormally strong π-acceptor strengths trifluoroacetonitrile was investigated for the following reasons: (a) retrodative π bonding in trifluoroacetonitrile complexes can be enhanced by the contribution of no-bond resonance structures such as Ib; (b) trifluoroacetonitrile is a commercially available gas, bp −62°, which can react with appropriate metal derivatives under pressure.

An exploratory study of the reactions of trifluoroacetonitrile with a variety of transition metal carbonyl and cyclopentadienyl derivatives suggests that a wide variety of novel substances can be prepared. In most cases the formulas of these compounds remain obscure even when analytical and mass spectral data become available. However, in the one case described in this paper, the unusual black compound, $CF_3C(NH)Fe(CO)(NCCF_3)(C_5H_5)$, has been clearly identified as the major product obtained from the reaction between $CH_3Fe(CO)_2C_5H_5$ and trifluoroacetonitrile under pressure.



$$F_3C{-}C{\equiv}\overset{+}{N}{-}\overset{-}{M} \longleftrightarrow F^-\;F_2C{=}C{=}\overset{+}{N}{=}M$$

Ia Ib

Experimental Section

Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Infrared spectra were taken of KBr pellets and recorded on a Perkin-Elmer Model 621 spectrometer. The proton nmr spectra reported in Table I were taken of acetone solutions and recorded on a Varian HA-100 spectrometer. The ^{19}F nmr spectrum was obtained by Professor Charles Moreland of the North Carolina State University at Raleigh, N. C., for a dichloromethane solution and recorded on a Varian HA-100 spectrometer operating at 94.1 Mc. The mass spectrum (Table II) was taken on the standard Associated Electrical Industries Ltd. MS-9 mass spectrometer located at the Mellon Institute in Pittsburgh, Pa.

Table I. Proton Nmr Spectra of $CF_3C(NH)Fe(L)(NCCF_3)(C_5H_5)$ Derivatives[a]

L	τ(NH)[b]	$\tau(C_6H_5)$	$\tau(C_5H_5)$[d]
CO	−1.3 (~30)	. . .	5.00 s
$(C_6H_5O)_3P$	−0.1 (~8)	2.6–2.9[c]	5.60 d (1.8)
$(C_6H_5)_3P$	−0.2 (~15)	2.61	5.53 d (1.8)

[a] These spectra were taken of acetone solutions on a Varian HA-100 spectrometer. [b] The NH resonances were very broad. The approximate width at half-height in cps is given in parentheses. [c] An unsymmetrical set of five major resonances was observed. [d] s = singlet, d = doublet. The splitting of the doublets in cps is given in parentheses.

Trifluoroacetonitrile was purchased in cylinders from Peninsular Chem Research, Inc., Gainesville, Fla. Quantities were measured by distilling from the cylinder into a graduated glass reaction vessel cooled to −196° and connected to a vacuum system of conventional design. The pressure reactions were carried out in 30-ml stainless-steel cylinders rated at 120 atm working pressure, manufactured by Hoke, Inc., Tenakill, N. J. Ultraviolet irradiations were carried out with an Englehard-Hanovia lamp protected by a Pyrex sleeve and immersed in the reaction mixture.

Reaction between Trifluoroacetonitrile and $CH_3Fe(CO)_2C_5H_5$. The 30-ml stainless-steel reaction vessel was charged with 3.0 g (15.6 mmoles) of $CH_3Fe(CO)_2C_5H_5$[7] and evacuated, and ~5 ml (~7.5 g, ~90 mmoles) of trifluoroacetonitrile was distilled in. The reaction vessel was heated in an oven at 90° for 16 hr. After cooling to room temperature the vessel was opened and the contents were rinsed out with several small portions of dichloromethane. The dichloromethane solutions were evaporated at ~25° (40 mm). The residue was dissolved in about 50 ml of diethyl ether and chromatographed on a 2.5 × 40 cm alumina column. A black band of $CF_3C(NH)Fe(CO)(NCCF_3)(C_5H_5)$ was observed. This band was eluted with diethyl ether and the solvent removed from the filtered eluate at ~25° (40 mm). The black residue from the black band was sublimed at 65–90° (0.03 mm) to give up to 1.62 g (30% yield) of black crystalline $CF_3C(NH)Fe(CO)(NCCF_3)(C_5H_5)$, mp 149–151°.

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(1) For part III of this series, see R. B. King and M. B. Bisnette, *Inorg. Chem.*, **5**, 306 (1966).

(2) Portions of this work were presented at the 19th Southeastern Regional Meeting of the American Chemical Society, Atlanta, Ga., Nov 1967.

(3) Fellow of the Alfred P. Sloan Foundation, 1967–1969.

(4) Postdoctoral Research Associate supported during the period Nov 1966 to May 1967, by the Grant AF-AFOSR-1211-67 from the Air Force of Scientific Research.

(5) T. Kruck, *Angew. Chem. Intern. Ed. Engl.*, **6**, 53 (1967).

(6) The term "isoleptic" is a convenient, recently introduced term to designate complexes with all ligands identical: J. Becconsall, B. E. Job, and S. O'Brien, *J. Chem. Soc., A*, 423 (1967).

(7) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956); R. B. King, *Organometal. Syn.*, **1**, 151 (1965).

Table II. Mass Spectrum of $CF_3C(NH)Fe(CO)(NCCF_3)(C_5H_5)$

m/e	Ion	Rel abundance
340	$CF_3C(NH)Fe(CO)(NCCF_3)(C_5H_5)^+$	29
312	$CF_3C(NH)Fe(NCCF_3)C_5H_5)^+$	51
293	$CF_3C(NH)Fe(NCCF_2)(C_5H_5)^+$	10
275		2.5
256		4.6
255		3.6
218	$CF_3C(NH_2)FeC_5H_5^+$	9.6
217	$CF_3C(NH)FeC_5H_5^+$	20
200		2.9
199		2.5
198		6.4
197		5.0
186	$(C_5H_5)_2Fe^+$	86
167	$C_5H_5FeF(CNH)^+$	29
148	$C_5H_5FeCNH^+$	14
140	$C_5H_5FeF^+$	52
121	$C_5H_5Fe^+$	100
104		8.6
103		10
102		5.7
96	CF_3CNH^+	20
95	CF_3CN^+, $C_3H_3Fe^+$	11
94	$C_3H_2Fe^+$	7.5
93	C_3HFe^+	6.1
81	C_2HFe^+	5.7
77	$C_6H_5^+$	6.1
76	$C_6H_4^+$, $HFeF^+$	8.9
75	FeF^+	9.6
69	CF_3^+	45
66	$C_5H_6^+$	20
65	$C_5H_5^+$	20
63	$C_5H_3^+$	5.3
56	Fe^+	42
51	HCF_2^+	4.6
50	CF_2^+	7.1
40	$C_3H_4^+$	6.1
39	C_3H_3	24

Metastable transitions

m/e	Process	Neutral fragment lost
286.2 (s)	340 (−28) → 312	CO
128.6 (m)	217 (−50) → 167	CF_2
117.2 (w)	167 (−27) → 140	HCN
78.7 (m)	186 (−65) → 121	C_5H_5
64.2 (w)	66 (−1) → 65	H
25.8 (vw)	121 (−65) → 56	C_5H_5

Anal. Calcd for $C_{10}H_6F_6FeN_2O$: C, 35.3; H, 1.8; N, 8.2; F, 33.5; Fe, 16.5. Found: C, 35.6; H, 1.8; N, 8.3; F, 33.6; Fe, 16.3.

In some experiments a by-product was the acetyl derivative[8] $CH_3COFe(CO)_2C_5H_5$, undoubtedly formed by carbonylation of some of the $CH_3Fe(CO)_2C_5H_5$ with carbon monoxide arising as a decomposition product.

The infrared spectrum showed the following: ν(NH) band at 3340 (w, br) cm^{-1}; ν(CH) band at 3130 (m) cm^{-1}; ν(CO) band at 1995 (s) cm^{-1}; ν(CN) band at 1552 (w) cm^{-1}; ν(CF) bands at 1283 (s), 1252 (s), 1184 (s), 1159 (s), 1145 (s), 1120 (s), and 1105 (s) cm^{-1}; other bands at 1427 (m), 1388 (m), 1058 (w), 1013 (w), 976 (m), 928 (vw), 847 (w), 836 (w), 821 (w), 737 (w), 734 (w), 709 (w), and 679 (w) cm^{-1}. The ^{19}F nmr spectrum had two sharp singlet resonances of equal relative intensities at 67.5 and 70.5 ppm upfield from $CFCl_3$ in dichloromethane solution.

Preparation of $CF_3C(NH)Fe[P(OC_6H_5)_3](NCCF_3)(C_5H_5)$. A mixture of 0.2 g (0.6 mmole) of $CF_3C(NH)Fe(CO)(NCCF_3)(C_5H_5)$, 0.2 g (0.65 mmole) of triphenyl phosphite, and 250 ml of hexane was exposed to ultraviolet irradiation for 12 hr. The solvent was removed from the filtered solution. A concentrated solution of the residue in dichloromethane was chromatographed on a 2 × 40 cm alumina column. The chromatogram was developed with 200 ml of hexane, and then the emerald green band of the product was eluted with dichloromethane. The solvent was removed from the eluate, and the resulting crystals were recrystallized once from a mixture of dichloromethane and hexane to give 0.10 g (29% yield) of green-black crystalline $CF_3C(NH)Fe[P(OC_6H_5)_3](NCCF_3)(C_5H_5)$, mp 133–134°.

Anal. Calcd for $C_{27}H_{16}F_6FeN_2O_3P$: C, 52.1; H, 3.4; N, 4.5; P, 5.0; F, 18.3. Found: C, 52.1; H, 3.4; N, 4.3; P, 5.0; F, 18.5.

The infrared spectrum had a ν(NH) band at 3340 (w) cm^{-1}; ν(CH) band too weak to be observed unequivocally; no ν(CO) bands; ν(CN) band at 1491 (m) cm^{-1}; other bands including ν(CF)[9] bands at 1596 (w), 1592 (w), 1427 (w), 1412 (w), 1398 (vw), 1363 (w), 1351 (vw), 1345 (vw), 1261 (m), 1250 (m), 1218 (m), 1192 (m), 1160 (m), 1151 (w), 1141 (vw), 1102 (m), 1069 (vw), 1021 (w), 978 (w), 912 (m), 907 (m,sh), 899 (m), 879 (m), 850 (vw), 835 (w), 822 (w), 769 (m), 752 (m), 728 (w), 714 (vw), 703 (vw), 683 (w), 668 (w), 613 (w), 594 (w), 587 (w), 560 (vw), and 509 (vw) cm^{-1}.

Preparation of $CF_3C(NH)Fe[P(C_6H_5)_3](NCCF_3)(C_5H_5)$. A mixture of 0.2 g (0.6 mmole) of $CF_3C(NH)Fe(CO)(NCCF_3)(C_5H_5)$, 0.17 g (0.65 mmole) of triphenylphosphine, and 250 ml of hexane was converted to 0.09 g (27% yield) of the olive green triphenylphosphine derivative $CF_3C(NH)Fe[P(C_6H_5)_3](NCCF_3)(C_5H_5)$, mp ~173° dec, by a procedure completely analogous to that used for the triphenyl phosphite derivative described above.

Anal. Calcd for $C_{27}H_{16}F_6FeN_2P$: C, 56.4; H, 3.7; N, 4.9; P, 5.4; F, 19.8. Found: C, 56.8; H, 3.7; N, 4.6; P, 4.9; F, 20.8.

The infrared spectrum had a ν(NH) band at 3315 (w) cm^{-1}; ν(CH) bands at 3071 (vw) and 3045 (vvw) cm^{-1}; no ν(CO) bands; ν(CN) band at 1479 (w) cm^{-1}; other bands including ν(CF)[9] bands at 1431 (m), 1420 (vw), 1400 (vw), 1325 (m), 1318 (m), 1255 (m), 1235 (m), 1185 (m), 1153 (m), 1123 (m), 1112 (m), 1097 (m), 1085 (m), 991 (vw), 969 (m), 843 (w), 835 (w), 815 (w), 764 (vw), 742 (w), 734 (w), 727 (w), 715 (vw), and 700 (w) cm^{-1}.

Discussion

Analytical data on the black compound obtained from CF_3CN and $CH_3Fe(CO)_2C_5H_5$ are consistent with the approximate composition $C_5H_5Fe(CO)(CF_3CN)_2$. The mass spectrum establishes the presence of the "extra" hydrogen atom indicating the general stoichiometry $C_5H_5Fe(CO)(CF_3CN)_2H$. The two singlets of equal relative intensity in the ^{19}F nmr spectrum indicate the two CF_3 groups and hence the two CF_3CN residues to be nonequivalent. Furthermore, the unsplit nature of the two ^{19}F resonances suggests that the "extra" hydrogen atom is too remote from either CF_3 group to couple with it. The singlet resonance at τ 5.0 in the ^{1}H nmr spectrum indicates that the π-cyclopentadienyl ring is intact and has not been converted into a substituted π-cyclopentadiene ligand. A second very broad resonance was observed at the very low chemical shift value of τ −1.3 corresponding to the single "extra" hydrogen atom. The breadth of this resonance suggests that this "extra" proton is bonded to nitrogen, an atom with a quadrupole moment. The sharp π-C_5H_5 and CF_3 peaks and normal chemical shifts in both the ^{1}H and ^{19}F nmr spectra of this compound indicate its diamagnetism suggestive of a rare gas electronic configuration. The infrared spectrum exhibits bands in the expected regions and of the expected relative intensities for a nitrogen–hydrogen stretching mode, a carbon–hydrogen stretching mode, a carbon–oxygen stretching mode of a single metal carbonyl group, a carbon–nitrogen double bond stretching mode, and several carbon–fluorine stretching modes.

All of these considerations lead us to propose the formulation $CF_3C(NH)Fe(CO)(NCCF_3)(C_5H_5)$ (II, L = CO) for this new black iron complex. In this proposed

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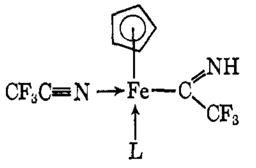
(8) R. B. King, *J. Am. Chem. Soc.*, **85**, 1918 (1963).

(9) The presence of both ν(CF) bands and bands from the benzene rings of the R_3P ligands in similar regions made assignment of the ν(CF) frequencies uncertain.

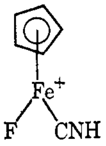
structure the iron atom is surrounded by the following four different ligands: (1) C_5H_5, a normal type of π-cyclopentadienyl ligand; (2) CO, a metal carbonyl group; (3) CF_3CN, a trifluoroacetonitrile ligand coordinated through the nitrogen atom; and (4) $CF_3C(NH)$–, a trifluoroacetimino group completely analogous to a trifluoroacetyl group (CF_3CO) except for the presence of an imino (NH) group in place of the isoelectronic oxo (O) group.

This unusual structure for $CF_3C(NH)Fe(CO)(NCCF_3)(C_5H_5)$ makes the fragmentation pattern of the mass spectrum (Table II) of particular interest. The parent ion (*m/e* 340) first loses its carbonyl ligand[10] giving the ion $CF_3C(NH)Fe(NCCF_3)(C_5H_5)^+$ (*m/e* 312). This ion may either lose a fluorine fragment (mass 19) or a trifluoroacetonitrile ligand (mass 95); in the latter case the ion $CF_3C(NH)FeC_5H_5^+$ (*m/e* 217) is formed.

The next fragmentation step of the $CF_3C(NH)FeC_5H_5^+$ (*m/e* 217) ion is particularly unusual. A neutral CF_2 fragment is lost forming the ion $C_5H_5FeF(CNH)^+$ (*m/e* 167). This process is supported by the observation of a metastable ion at *m/e* 128.6 ($167^2/217 = 128.6$). A reasonable structure for the ion $C_5H_5FeF(CNH)^+$ (*m/e* 167) is III in which the central iron atom is surrounded by a π-cyclopentadienyl group, a fluorine atom, and a hydrogen isocyanide ligand.[11] The loss of CF_2 from $CF_3C(NH)FeC_5H_5^+$ (*m/e* 217) must involve a fluorine shift from carbon to iron as indicated in IV. A similar process, but involving rupture of different bonds, has been postulated[12] for the elimination of ketene from the ion $CH_3OCOCH_2FeC_5H_5^+$ (*m/e* 194) in the mass spectrum of $CH_3OCOCH_2Fe(CO)_2C_5H_5$.



II



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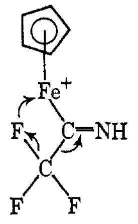

IV

The structure III with a hydrogen isocyanide ligand[13] for the ion $C_5H_5FeF(CNH)^+$ (*m/e* 167) is further suggested by its loss of HCN to give the $C_5H_5FeF^+$ (*m/e* 140) ion. This process is supported by a metastable ion at *m/e* 117.2 ($140^2/167 = 117.4$). Other features of the mass spectrum of $CF_3C(NH)Fe(CO)(NCCF_3)(C_5H_5)$ have been noted in other fluorocarbon[14] or π-cyclopentadienyl[12] derivatives of iron and will not be discussed further here.

The iron compound $CF_3C(NH)Fe(CO)(NCCF_3)(C_5H_5)$ is a black solid volatile at 70° (0.1 mm). In the solid state it is stable in air for at least a few days. It dissolves in polar organic solvents such as dichloromethane, diethyl ether, or tetrahydrofuran to form black-green solutions. These solutions oxidize in air over a period of hours depositing brown iron oxides.

The unusual nature of the iron complex $CF_3C(NH)Fe(CO)(NCCF_3)(C_5H_5)$ (II, L = CO) prompted a study of its reactions. Treatment of this complex with excess bromine cleaved the π-cyclopentadienyl ring giving a 35% yield of a single isomer of 1,2,3,4,5-pentabromocyclopentane, mp 103–104° (lit.[15] mp 103–104°), nmr τ 2.88 (singlet). Ultraviolet irradiation of $CF_3C(NH)Fe(CO)(NCCF_3)(C_5H_5)$ with the ligands PR_3 (R = C_6H_5 or OC_6H_5) in hexane solution removed the single carbonyl group giving the green-black substitution products $CF_3C(NH)Fe(PR_3)(NCCF_3)(C_5H_5)$ (II, L = PR_3; R = C_6H_5 or OC_6H_5). As expected, the infrared spectrum of these substitution products still exhibited the ν(NH) frequency, but no longer exhibited the ν(CO) frequency. The π-C_5H_5 protons appeared 0.5–0.6 ppm to higher field in the nmr spectra of the substitution products II (L = PR_3) than in the nmr spectrum of the parent carbonyl II (L = CO). This is the effect expected by substitution of the more weakly π-accepting PR_3 ligands for the CO ligand, a very strong π-acceptor. Also the π-C_5H_5 nmr resonance in the compounds $CF_3C(NH)Fe(PR_3)(NCCF_3)(C_5H_5)$ (II, L = PR_3) was a doublet owing to coupling with the phosphorus atom.

The compound $CF_3C(NH)Fe(CO)(NCCF_3)(C_5H_5)$ is the first metal complex containing the trifluoroacetonitrile ligand. In an attempt to assess the relative π-acceptor strength of the trifluoroacetonitrile ligand, the ν(CO) frequency in $CF_3C(NH)Fe(CO)(NCCF_3)(C_5H_5)$ was compared with those of other compounds of the type $C_5H_5Fe(CO)XL$ (Table III). The dependence of the ν(CO) frequencies on the π-acceptor strengths of the other ligands attached to the same metal atom is now a well-established phenomenon.[16] As the π-acceptor strengths of the other ligands increase, the electron density on the metal atom available for retrodative π bonding with the carbonyl ligand(s) decreases. This lowers the metal–carbon bond order, thereby increasing the carbon–oxygen bond order and thus the frequency. For this reason the higher the ν(CO) frequency of a metal carbonyl ligand, the higher the π-acceptor strengths of the other ligands attached to the metal atom.

Table III indicates that the ν(CO) frequency of $CF_3C(NH)Fe(CO)(NCCF_3)(C_5H_5)$ is higher than that of other $C_5H_5Fe(CO)XL$ compounds, where X and L represent various combinations of tertiary phosphine, sulfide, and σ-bonded alkyl and acyl ligands. However, this indicates that only the *combination* of the trifluoroacetimino ($CF_3C(NH)$) and trifluoroacetonitrile (CF_3CN) ligands has a relatively high π-acceptor strength. Nevertheless, the trifluoroacetimino ligand would be expected to be a relatively poor π acceptor since possible resonance forms of the trifluoroacetimino-metal bond (V) with carbon-metal double bonds have relatively unfavorable features such as a

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[10] The stepwise loss of carbonyl groups is a well-established phenomenon in the mass spectra of metal carbonyl derivatives. For a detailed study of the stepwise loss of carbonyl groups in the mass spectrum of tetracarbonylnickel, see S. M. Schildrout, G. A. Pressley, Jr., and F. E. Stafford, *J. Am. Chem. Soc.*, **89**, 1617 (1967).

[11] For a report on metal complexes of hydrogen isocyanide, see R. B. King, *Inorg. Chem.*, 6, 25 (1967).

[12] R. B. King, *J. Am. Chem. Soc.*, 90, 1417 (1968).

[13] The alternative possibility of a hydrogen cyanide (HCN) rather than a hydrogen isocyanide (HNC) ligand in this ion cannot be rigorously excluded. However, the bonding of the $CF_3C(NH)$ ligand to the iron atom with an iron–carbon bond makes a hydrogen isocyanide ligand which would form an iron–carbon bond more likely than a hydrogen cyanide ligand which would form an iron–nitrogen bond.

[14] R. B. King, submitted for publication.

[15] A. N. Nesmeyanov, E. G. Perevalova, and V. A. Nesmeyanova, *Dokl. Akad. Nauk SSSR*, **100**, 1099 (1955).

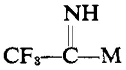
[16] F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, 84, 4432 (1962); C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963); F. A. Cotton, *ibid.*, **3**, 702 (1964).

Table III. Some ν(CO) Frequencies of $C_5H_5Fe(CO)XL$ (cm^{-1})

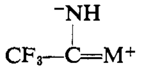
Compound]	ν(CO)	Medium	Ref
$CF_3C(NH)Fe(CO)(NCCF_3)(C_5H_5)$	1996	CCl_4	*a*
$CF_3C(NH)Fe(CO)(NCCF_3)(C_5H_5)$	1995	KBr	*a*
$C_5H_5FeCOS_2CSR$ ($R = CH_3, C_2H_5, C_6H_5$)	1965 ± 1	CCl_4	*b*
$C_5H_5Fe(CO)[P(C_6H_5)_3]X$ (X = Cl, Br, I)	1950 ± 15	$CHCl_3$ or Nujol	*c*
$C_5H_5Fe(CO)(\pi\text{-}C_3H_5)$	1950	CS_2	*d*
$C_5H_5Fe(CO)[P(OC_6H_5)_3]C_6F_5$	1940	Vaseline	*e*
$C_5H_5Fe(CO)[P(OC_6H_5)_3]C_6H_5$	1935	Vaseline	*e*
$CH_3SCH_2CH_2COFe(CO)C_5H_5$	1935	Halocarbon	*f*
$C_5H_5Fe(CO)[P(C_6H_5)_3]COCH_3)$	1920	$CHCl_3$	*c*
$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$	1905	$CHCl_3$	*c*
$(CH_3)_2\underbrace{NCH_2CH_2CO}Fe(CO)_5H_5$	1890	KBr	*g*

[a] This work. [b] R. Bruce and G. R. Knox, *J. Organometal. Chem.* (Amsterdam), **6,** 67 (1966). [c] P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, **5,** 1177 (1966). [d] M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963). [e] A. Nesmeyanov, Yu. A. Chapovsky, and Yu. A. Ustynyuk, *J. Organometal. Chem.* (Amsterdam), **9,** 345 (1967). [f] R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4,** 486 (1965). [g] R. B. King and M. B. Bisnette, *ibid.*, **5,** 293 (1966).

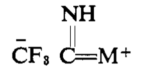
negatively charged two-coordinate nitrogen atom (Vb) or no bond between the two carbon atoms (Vc). Thus the high π-acceptor strength of the trifluoroacetimino–trifluoroacetonitrile combination must come from the trifluoroacetonitrile ligand rather than the trifluoroacetimino ligand. Further verification of the high π-acceptor strength of the trifluoroacetonitrile ligand will have to await the synthesis of trifluoroacetonitrile complexes with more conventional other ligands.


$CF_3\text{—}\overset{\overset{\displaystyle NH}{\|}}{C}\text{—}M$

Va


$CF_3\text{—}\overset{\overset{\displaystyle ^{-}NH}{|}}{C}{=}M^+$

Vb


$\bar{C}F_3\ \overset{\overset{\displaystyle NH}{\|}}{C}{=}M^+$

Vc

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The Influence of Solvent on Ion Association. Proton Nuclear Magnetic Resonance of Trioctylmethylammonium Hexacyanoferrate(III)

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Abstract: The proton magnetic resonance spectra of trioctylmethylammonium hexacyanoferrate(III) and -cobaltate(III) were obtained in 17 different solvents. The dipolar shift of the N-methyl and N-methylene protons of the ammonium ion were determined for 0.1 *M* solutions, and the N-methyl shift was found to vary linearly with the dielectric constant of the solvent, ϵ, when ϵ ranges from 2.76 to 47.6. An explanation for this linear relationship is given. The shifts were measured at various concentrations in propylene carbonate, CD_3SOCD_3, $CDCl_3$, CH_3NO_2, and CD_3COCD_3. The temperature variation of the shifts in CD_3SOCD_3 and $CDCl_3$ was determined.

According to the coordination model for nonaqueous solvent behavior, donor strength and solvating ability are two of the essential properties needed for the understanding of these systems. Since these properties cannot be directly measured toward most solutes, one must attempt to estimate them indirectly by procedures which have been described.[2] A qualitative ordering of the solvents as a function of these properties results. The greater the number and types of systems employed to deduce solvating and donor orders, the more complete the understanding and the more sure one is of the ordering. In this connection it was of interest to examine the ion-pairing interaction in $[(C_8H_{17})_3NCH_3]_3Fe(CN)_6$ as a function of solvent by taking advantage of the pseudocontact shift of the proton nmr. The better solvating solvents will lead to decreased ion pairing and smaller pseudocontact shifts. If such an approach were to prove successful, it would result in a much more convenient procedure for estimating solvating ability of solvents than that offered from the evaluation of association constants.

Several recent articles on ion association, or ion pairing, have dealt with the study of the association of paramagnetic anions with quaternary ammonium cations[3-6] by measuring the nuclear magnetic resonance (nmr) isotropic shifts of the cation protons. The dipolar shift of a given *i*th proton, $\Delta\nu_{pi}$, is the difference between the measured frequency, ν_{pi}, of the proton in a paramagnetic environment minus the frequency, ν_{Di}, of the proton under diamagnetic conditions. When there is rapid exchange between

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