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REACTIONS OF CO-ORDINATED LIGANDS—II

PREPARATION OF A NEW CLASS OF IRON ISONITRILE COMPLEXES, $(RCH_2NC)_5Fe^{II}CNX$

W. Z. Heldt
E. I. du Pont de Nemours and Company, Inc.
Explosives Department, Experimental Station Laboratory
Wilmington, Delaware

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Abstract—A convenient method for the preparation of a new class of iron isonitrile complexes, $(RCH_2NC)_5Fe^{II}CNX$(I), from alkali ferrocyanides and alkyl halides activated in the α-position by a carbon–carbon double bond is described. The structure proof for $(C_6H_5CH_2NC)_5FeCNBr$ is given by its conversions to $(C_6H_5CH_2NC)_4Fe(CN)_2$ and $(C_6H_5CH_2NC)_6FeBr_2$; hydrolysis to benzylamine; reduction to benzylamine and N-methylbenzylamine, and oxidation to benzoic acid. The preparation of $(RCH_2NC)_4Fe(CN)_2$(II) and $(RCH_2NC)_6FeBr_2$(III) complexes from (I) or directly from alkali ferrocyanides is given. The probable reaction mechanism of this reaction is the displacement of halide from the alkyl halide by the ferrocyanide anion or the partially alkylated ferrocyanide anion. Both the ionization of the alkyl halide and the nucleophilicity of the anion appear to influence the rate of the reaction.

In a previous communication(1) we have described attempts to displace the isonitrile group in an iron isonitrile complex by hydrogen cyanide. The decomposition of the iron isocyanide–cyanide complex was a complex reaction which appeared to be catalysed by impurities deposited on the walls of the reaction vessel. Since iron isonitriles are reported to be stable compounds,(2) it is the purpose of this paper to develop a reliable synthesis of iron isonitrile complexes for the study of their reactions. This paper describes the synthesis of the heretofore unknown class of iron isonitrile complexes, $(RCH_2NC)_5Fe^{II}CNX$ and their conversion to $(RCH_2NC)_4Fe^{II}(CN)_2$ and $(RCH_2NC)_6Fe^{II}Br_2$.

EXPERIMENTAL

Preparation of $(C_6H_5CH_2NC)_5FeCNBr\cdot H_2O$ (*Procedure A*)

Potassium ferrocyanide trihydrate (General Chemical Division, Allied Chemical and Dye Corp., New York, N.Y.) was dried at 150°C/24 mm Hg for 4 hr. (Found: (Karl Fischer) 0·27% H_2O. Calc. for the monohydrate = 4·66).

Potassium ferrocyanide, 61·5 g (= 0·166 mole) and benzyl bromide, 171 g (= 1·0 mole) were stirred and heated on a steambath for 55 hr in a three neck flask closed by a calcium chloride drying tube. The brown, viscous reaction mixture was washed with 2 l. of petroleum ether, and the petroleum ether-insoluble brown oil was extracted with 2 × 500 ml of boiling chloroform; the last chloroform extracts were only slightly yellow. The chloroform-insoluble material, 144 g, was neglected. The chloroform extracts were evaporated to dryness under vacuum, without heating. The brown residue was dissolved in 150 ml of boiling methyl ethyl ketone; upon cooling yellow crystals of $[(C_6H_5CH_2NC)_5FeCN]Br\cdot H_2O$ crystallized out. (In several cases when the reaction time was

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(1) W. Z. Heldt, *J. Org. Chem.* In press.

(2) L. Malatesta, *Progress in Inorganic Chemistry* (Edited by F. A. Cotton) Vol. 1, p. 320. Interscience, New York (1959).

extended beyond 55 hr, the brown oil could not be crystallized from methyl ethyl ketone. It was then pressed on porous plate and allowed to dry overnight. The brown semisolid then always crystallized from methyl ethyl ketone). After 5–10 recrystallizations from methyl ethyl ketone and drying at 0·1 mm/25°C, m.p. 101–104°C, 109 g of slightly yellowish long needles were obtained. (Found: C, 64·36, 63·76; H, 4·98, 4·79; N, 10·63, 10·88, 10·80; Fe, 7·30, 7·39; Br, 10·50, 9·65. Calc. for $(C_6H_5CH_2NC)_5FeCNBr{\cdot}H_2O$: C, 64·33; H, 4·87; N, 10·98; Fe, 7·30; Br, 10·44%).

The infra-red spectrum of this compound is recorded in Fig. 1b; prolonged (71·2 hr) drying at 0·1 mm/25°C, removed the water of crystallization in the above complex and the melting point increased to 111–112°C. (Found: C, 65·78; H, 5·15; N, 11·27; Fe, 7·83; Br, 9·66, 11·35. Calc. for $(C_6H_5CH_2NC)_5FeCNBr$: C, 65·87; H, 4·72; N, 11·24; Fe, 7·47; Br, 10·69%).

Distillation of the pet. ether extracts at 10 mm Hg yielded 13 g of benzylbromide and 1·5 g of an amide, b.p. 140–163°C/10 mm, probably N-benzyl formamide.

Molecular weight determinations of the anhydrous compound (mol. wt. = 747) in nitrobenzene (20 g) by the freezing point method indicate dissociation into two ions:

mg of (I)	94	161	308	495	525
mol. wt.	380	350	371	565	500

Cryoscopic molecular weight determinations in diphenyl amine or bromoform indicated a mol. wt. of 642 ± 12, or 729 ± 9 respectively; as expected, this was a much lower dissociation than in nitrobenzene.

Conductivity determinations in purified nitrobenzene, using a dip-type cell and bright Pt electrodes,(3) gave the following results:

TABLE A.—CONDUCTIVITY DETERMINATIONS IN NITROBENZENE AT 25°C

Concentration		Specific conductance in nitrobenzene (Ω^{-1})
$[(C_6H_5CH_2NC)_5FeCN]Br$	5×10^{-5} molar	$1{\cdot}48 \times 10^{-6}$
$[(C_6H_5CH_2NC)_5FeCN]Br$	5×10^{-4} molar	$1{\cdot}44 \times 10^{-5}$
$[(C_6H_5CH_2NC)_5FeCN]Br$	1×10^{-3} molar	$2{\cdot}58 \times 10^{-5}$
$(CH_3CH_2)_4NCl$	5×10^{-5} molar	$1{\cdot}74 \times 10^{-6}$
$(CH_3CH_2)_4NCl$	1×10^{-3} molar	$3{\cdot}6 \times 10^{-5}$

These data are in agreement with specific conductance in nitrobenzene as reported for other univalent: univalent ions.(3,4) Therefore, the complex must be a 1 : 1 electrolyte in nitrobenzene.

No decomposition of the complex took place over a period of three years when it was exposed to sunlight and "atmospheric conditions" in the laboratory. A single crystal of the complex was also stable during extensive exposure to X-rays.(5)

Preparation of $(C_6H_5CH_2NC)_5FeCNBr$ *and* $(C_6H_5CH_2NC)_4Fe(CN)_2$ (*Procedure B*)

To 184 g (= 0·5 moles) of $K_4Fe(CN)_6$ were added 342 g (2·0 moles) of benzyl bromide and the heterogeneous reaction mixture was stirred on a steambath for 47 hr in a vessel closed by a calcium chloride drying tube. The reaction mixture was then treated with 500 ml of petroleum ether to remove the non-reacted benzyl bromide and the petroleum ether extracts were neglected. The petroleum ether insoluble material was extracted with 3 × 500 ml of boiling chloroform. The chloroform extracts were then evaporated to near dryness, yielding a yellow solid FI 152 g m.p. 165–200°C, and a viscous brown oil as the filtrate (FII). The crystalline material (FI) was boiled with 500 ml of methyl ethyl ketone and was filtered hot. The material, soluble in hot methyl ethyl ketone, crystallized upon evaporation of the solvent to about 100 ml, yielding 60 g of yellow crystals. After drying at 25°C/1·0

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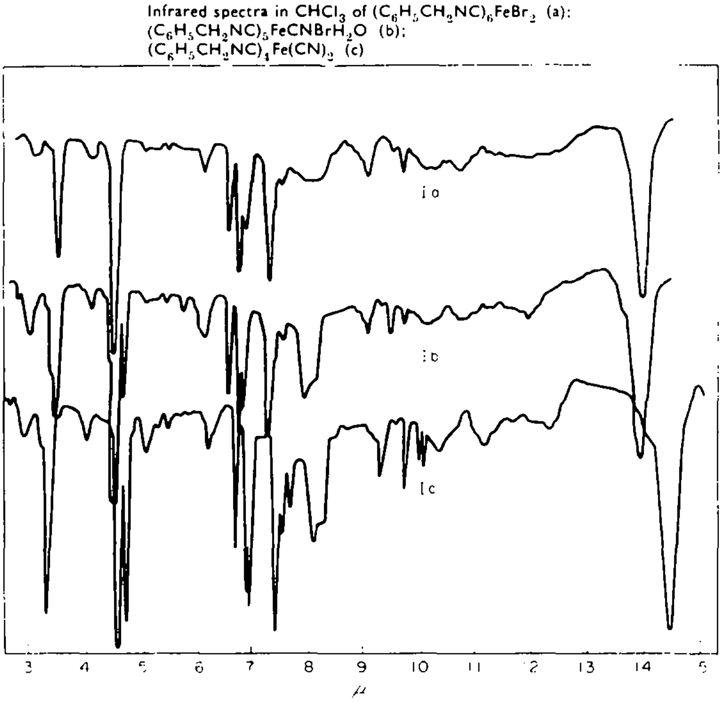
(3) R. S. NYHOLM and A. KABESH, *J. Chem. Soc.* 38 (1951).
(4) C. R. WISCHONKE and C. A. KRAUS, *J. Amer. Chem. Soc.* **69**, 2472 (1947).
(5) A. G. SCOTT. Private communication (1958).

mm Hg for several hours, the substance melted at 100–102°C. (Found: C, 63·73; H, 4·99; N, 10·90; Fe, 7·46. Calc. for $(C_6H_5CH_2NC)_5FeCNBr{\cdot}H_2O$: C, 64·33; H, 4·87; N, 10·98; Fe, 7·30%).

The infra-red spectrum of this material was identical with the infra-red spectrum with the previously prepared $(C_6H_5CH_2NC)_5FeCNBr{\cdot}H_2O$.

The methyl ethyl ketone insoluble fraction, 95 g, was recrystallized twice from chloroform and carbon tetrachloride; after drying at 25°C/1·0 mm Hg for 3 hr, it melted at 229·5–230·0°C. (Found C, 70·88, 70·64; H, 4·93, 5·14; N, 13·69, 13·70; Fe, 9·82, 9·60; Br, 0%; mol. wt., 520, 530 (cryoscopic). Calc. for $(C_6H_5CH_2NC)_4Fe(CN)_2$: C, 70·96; H, 4·90; N, 14·60; Fe, 9·71%; mol. wt., 576).



Infrared spectra in $CHCl_3$ of $(C_6H_5CH_2NC)_6FeBr_2$ (a); $(C_6H_5CH_2NC)_5FeCNBrH_2O$ (b); $(C_6H_5CH_2NC)_4Fe(CN)_2$ (c)

FIG. 1.

The infra-red spectrum of this compound is recorded in Fig. 1c; the filtrates FII were evaporated to dryness and were crystallized partially from ethylene glycol dimethyl ether. The crystalline material, 61 g, was recrystallized from chloroform and carbon tetrachloride. After several recrystallizations from methyl ethyl ketone, the material had a m.p. 100–102°C. This material did not depress the melting point of $(C_6H_5CH_2NC)_5FeCNBr{\cdot}H_2O$ upon admixture, and the infra-red spectra of both samples were superimposable.

Preparation of $(p\text{-}ClC_6H_4CH_2NC)_5FeCNBr$ *(Procedure C)*

p-Chlorobenzyl bromide was prepared by the bromination of *p*-chlorotoluene at 160°C according to the procedure of SHOESMITH(6) in 70 per cent conversion, b.p. 91–129°C/10 mm. This material yielded the pure *p*-chlorobenzyl bromide after recrystallization from petroleum ether, m.p. 43–45°C. *p*-Chlorobenzyl bromide, 51·2 g (0·25 mole) and 18·3 g (0·05 mole) of $K_4Fe(CN)_6$ were heated on a steambath for 60 hr. The brown reaction mixture was then extracted with 3 × 100 ml of petroleum ether and the petroleum ether-insoluble brown oil was extracted with 3 × 150 ml of boiling chloroform, the last extracts being only slightly yellow. The chloroform insoluble material, 23 g, was neglected. The chloroform extracts were evaporated to dryness to yield 19 g of brown oil, which failed to crystallize. The chloroform extract residues were dissolved then in the least amount of chloroform and were chromatographed on 200 g of alumina.

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(6) J. B. SHOESMITH and R. H. SLATER, *J. Chem. Soc.* 219 (1926).

TABLE 1.—REACTION OF $K_4Fe(CN)_6$

Alkylhalide (moles)	$K_4Fe(CN)_6$ (moles)	Solvent	Time (hrs)	Temp. (°C)	Isonitrile complex isolated Formula	Conv. crude (g)	M.P.(1)
$C_6H_5CH_2Br$ (2·0)	(·334)	none	(a) 48 (b) 120	100 25	$(C_6H_5CH_2NC)_5FeCNBr$	35	110–112
					$(C_6H_5CH_2NC)_6FeBr_2 \cdot H_2O$	30	119–121·2
$C_6H_5CH_2Br$ (2·0)	(0·5)	none	47	100	$(C_6H_5CH_2NC)_4Fe(CN)_2$	95	229·5–230
					$(C_6H_5CH_2NC)_5FeCNBr \cdot H_2O$	121	100–102
$oCH_3C_6H_4CH_2Br$ (0·5)	(0·1)	none	45	100	$(oCH_3C_6H_4CH_2NC)_4Fe(CN)_2 \cdot H_2O$	33	247–249·5
					$(oCH_3C_6H_4CH_2NC)_5FeCNBr$	37	143·4–145·6
$mCH_3C_6H_4CH_2Br$ (0·5)	(0·1)	none	45	100	$(mCH_3C_6H_4CH_2NC)_5FeCNBr \cdot H_2O$	39	oil
$pCH_3C_6H_4CH_2Br$ (0·5)	(0·1)	none	45	100	$(pCH_3C_6H_4CH_2NC)_5FeCNBr \cdot H_2O$	72	147·8–149·8
$pClC_6H_4CH_2Br$(2) M.P. 43–45°C (0·25)	(0·05)	none	60	100	$(pClC_6H_4CH_2NC)_5FeCNBr$	12·4	160·2–162·6
$pCH_3CO_2C_6H_4CH_2Br$(3) M.P. 44–48°C (0·25)	(0·05)	none	48	100	$(pCH_3CO_2C_6H_4CH_2NC)_5FeCNBr \cdot H_2O$	2·95	185–186·2
(C_6H_5) CHBr(4) M.P. 28°C (0·5)	(0·1)	none	10	100	$[(C_6H_5)_2CHNC]_4Fe(CN)_2$	102·0	242–244
					$[(C_6H_5)_2CHNC]_4FeCNBr$	8·5	122–123·5
$(C_6H_3)_3CBr$ (0·05)	(0·01)	$CHCl_3$ 100 ml	18	reflux	$[(C_6H_5)_3CNC]_5FeCNBr$	6·07	298–300
$CH_2=CHCH_2Br$ (1·0)	(0·17)	none	48	reflux	$(CH_2=CHCH_2NC)_5FeCNBr \cdot H_2O$	85·0	56–58
3-Thenyl Br(5) (0·5)	(0·1)	$CH_3COCH_2CH_3$	48	reflux	$(C_4H_3SCH_2NC)_5FeBr_2 \cdot H_2O$ (?)	48·1	oil

(1) Uncorrected. (2) SHOESMITH and SLATER, *J. Chem. Soc.* 219 (1926). (3) FUSAN and COOKE, *J. Amer. Chem. Soc.* 62, 1180 (1940) (4) FRIEDEL, *Bull. Soc. Chim., (France)* series 2, 33, 337 (1880). (5) CAMPAIGNE, *J. Amer. Chem. Soc.* 70, 1555 (1949). (6) Methyl ethyl ketone insoluble, recrystallized from $CHCl_3$–CCl_3. (7) I 6 × 50 ml, 9·65 g; II 6 × 50 ml, 11·69 g; III 4 × 50 ml, 6·26 g; IV 6 × 50 ml, 6·26 g; I and II were rechromatographed but failed to crystallize; after drying at 25°C/0·1 mm Hg submitted to analysis; recrystallized from methyl ethyl ketone. (9) I 10 × 50 24·46 g; II 4 × 50, 0·426 g; III 3 × 50, 0·103 g; IV 3 × 50, 0·347 g; V 4 × 50, 2·95 g. Fraction V was recrystallized several times from methyl ethyl ketone and was dried at 35°C/0·1 mm Hg. (10) Crystallized from chloroform-acetone and dried at 56°C/0·1 mm Hg. (11) Reduce filtrates of (1) to dryness and crystallize residue from $CHCl_3$–CCl_3 by slowly allowing the solvent to evaporate. Recrystallized from $CHCl_3$–CCl_3 and dried at 56°C/0·1 mm

Alumina was prepared by suspending 1 kg (F = 20 mesh alumina; Aluminum Company of America) in 2 l. of water and then adding to this suspension 50 per cent sulphuric acid until the pH of the supernatant liquor stayed at pH = 6·70–7·00 after two hours of rapid stirring. The alumina was then filtered off and was dried at 120–150°C/24 mm in a vacuum oven for 12–14 hr. The dried alumina (10–15 times the weight of the material to be chromatographed) was placed in chloroform. The column was washed with (I) 5 × 50 ml of chloroform, (II) 2 × 50 ml of 50 per cent chloroform acetone, (III) 4 × 50 ml of acetone, (IV) 6 × 50 ml 50 per cent acetone-methanol and 7 × 50 ml of methanol. (All solvents used in this chromatography were "analytical grade".) From fraction I there crystallized 4·45 g of starting material, and FIII yielded on slow evaporation of the solvent and addition of ethyl methyl ketone 12·4 g (27 per cent conversion) of an isonitrile complex. After three recrystallizations from methyl ethyl ketone and drying at 25°C/0·1 mm, the compound melted at 160·2–162·6°C. (Found C. 53·48; H, 3·50; N, 10·34; Fe, 6·65; Cl, 18·84. Calc. for $(p\text{-}ClC_6H_4CH_2NC)_5FeCNBr$: C, 53·54; H, 3·29; N, 9·14; Fe, 6·07; Cl, 19·17%).
Infra-red spectrum ($CHCl_3$): 3·42 (*m*), 4·55 (*vs*), 4·72 (*m*), 6·25 (*w*), 6·68 (*s*), 6·95 (*m*), 7·10 (*m*), 7·45 (*m*) 8·80 (broad), 9·85 (*m*), 13·80 (broad) (μ).

The compounds described in Table 1 were synthesized by either of these three procedures. Details are given in the footnotes to Table 1.

WITH ALKYL BROMIDES

Procedure (see expt.)	Specific magnetic susceptibility × 10⁵	Carbon		Hydrogen		Nitrogen		Iron		Bromide		Sulphur or chlorine	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
B	−0·48	65·87	65·74	4·72	5·08	11·24	11·28	7·47	7·41	10·69	11·35		
B$^{(5)}$		61·55	61·81	4·74	4·84	8·98	9·09	5·96	6·64	17·07	17·23		
B	0·39	70·96	70·88 70·64	4·90	4·93 5·14	14·60	13·69 13·70	9·71	9·82 9·60				
B		64·33	63·73	4·87	4·99	10·98	10·00	7·30	7·46				
B$^{(6)}$		70·15	69·33 69·36	5·89	6·11 6·12	12·91	12·37 12·42	8·54	8·40 8·56				
B		67·62	67·18 67·12	5·55	5·65 5·85	10·28	11·67	6·83	7·07	9·77	8·44 8·67		
C$^{(7)}$		66·11	66·02	5·67	5·92	10·06	9·44	6·68	6·09	9·56	10·14 10·15		
A$^{(8)}$	0·32	66·11	66·78	5·67	5·67	10·06	10·26	6·68	6·98	9·56	9·29		
C		53·54	53·48	3·29	3·50	9·14	10·34	6·07	6·65	8·64	6·95	Cl 19·17	18·84
C$^{(9)}$		58·01	57·29	4·48	4·72	7·95	8·22	5·28	5·28	7·56	7·95		
B$^{(10)}$		79·08	78·63 78·69	5·04	5·27 5·21	9·54	8·90 9·42	6·34	6·66				
B$^{(11)}$		73·24	74·29	4·74	4·95	7·49	7·22	5·96	6·23	8·55	8·49		
C$^{(12)}$		80·41	80·90	5·01	5·25	6·57	6·71	3·70	3·89	5·29	4·08		
A$^{(13)}$		50·72	50·35	5·07	5·46	16·91	16·23	11·23	10·58	16·07	15·85		
C$^{(14)}$		42·40	42·14	3·20	3·23	8·24	8·36 8·20	6·57	6·94			S 18·87	17·19

Hg. (12) I 6 × 50, 7·894 g; II 6 × 50, 3·33 g; III 4 × 50, 0·022 g; IV 2 × 50, 0·005 g; V 4 × 50, 1·415 g. Fraction II was recrystallized about 5 times from $CHCl_3$-CCl_3 and was dried at 56°C/0·1 mm Hg. (13) Evaporate $CHCl_3$ extract to dryness; crystallized from acetone at 0°C after about 2–4 months. (14) I 20 × 50, 1·2 g; II 20 × 50, 0·979 g; III 20 × 50, 7·03 g; IV 40 × 50, 28·5 g; V 40 × 50, 28·5 g. Fractions III–V contained the isonitrile complex; the chromatography was repeated, whereby the purest isonitrile fraction was isolated in IV but which failed to crystallize. This material was dried for analysis 25°C/0·1 mm. IR (CHCl) 3·38 (s), 350 (m), 4·56 (vs), 4·72 (m), 5·60 (w), 5·80 (vw), 6·72 (w), 6·95 (w), 7·08 (w), 7·24 (m), 7·42 (m), 7·55 (m), 8·72 (m), 9·05 (s), 9·70 (m), 11·68 (m), 12·05 (m).

Permanganate oxidation of $(C_6H_5CH_2NC)_5FeCNBr\cdot H_2O$

To a solution of 24·0 g (0·6 mole) of sodium hydroxide in 300 ml of water were added 15·8 g (0·1 mole) of potassium permanganate. The solution was cooled to room temperature. 7·3 g (- 0.0095 mole) of $[(C_6H_5CH_2NC)_5FeCN]Br\cdot H_2O$ were added and the reaction mixture was heated to 100°C for 15 min. The heating mantle was then removed and when the reaction mixture reached 60 C, methyl alcohol was added until the excess permanganate decolorized. The reaction mixture was filtered from the MnO_2 and the filtrate was cooled to 10°C and acidified with 50 ml of concentrated HCl. After the filtrate had stood for one hour on ice the benzoic acid was filtered off. The benzoic acid filtrate was reduced to one-fourth of its volume; upon cooling a little more benzoic acid crystallized out. The total amounts of benzoic acid isolated, after drying at 25 C/1·0 mm Hg were 5·0 g (0·041 mole) or 86 per cent conversion. The benzoic acid was identified by mixed melting point of an authentic sample and by its infra-red spectrum.

Catalytic hydrogenation of $[(C_6H_5CH_2NC)_5FeCN]Br\cdot H_2O$

To a solution of 54 g (– 0·07 mole) of $(C_6H_5CH_2NC)_5FeCNBr\cdot H_2O$ in 200 ml of methanol in a stainless steel pressure tube were added two teaspoons of Raney-Nickel catalyst and the reaction mixture was kept at 130 C and 195–210 atm pressure of hydrogen for 15 hr. The total hydrogen absorbed was about 83 atm. To ensure complete hydrogenation two more teaspoons of Raney-Nickel were added and the reaction mixture was kept at 130°C and 480–500 atm pressure for 4·5 hr. The pressure drop was only about 20 atm. The reaction mixture was filtered from the Raney-Nickel catalyst and the catalyst was washed with 5 × 20 ml of methanol. The filtrates were reduced to about 50 ml under vacuum at 20 mm/35°C, whereby a solid residue remained (F A). The liquid portion of the filtrate was distilled through a short distillation column (ca. 10 plates) and all material boiling below 65°C/760 mm was neglected. The higher boiling residue was designated (F B). Fraction A was washed with 3 × 100 ml of ether, then was treated with 2 × 200 ml of boiling chloroform. The chloroform extracts were allowed to come to room temperature, whereby 523 mg of a blue precipitate separated out, which evolved $HCN(H_4Fe(CN)_6$ or polymerization products?) The organic extracts of Fraction A were combined with Fraction B. The chloroform-insoluble portion of Fraction A, 6 g, m.p. 208–215°C, formed a precipitate with silver nitrate, i.e., it was apparently an amine hydrobromide.

When one gramme of this bromide was made alkaline with 30 ml of 20% NaOH and reacted with 1·6 g of *p*-toluenesulphonyl chloride, a tosylate formed. After two recrystallizations from 95 per cent ethyl alcohol and drying, the product melted at 113·5–114·5°C. (Found: C, 64·80; H, 5·95; N, 5·30. Calc. for $C_6H_5CH_2NHSO_2C_6H_4$*p*-CH_3: C, 64·34; H, 5·79; N, 5·36%)

A mixed melting point with an authentic sample did not give a melting point depression.

Fraction B was washed 6 × 100 ml with 2N HCl. The organic layer was dried with $MgSO_4$ and was distilled first at 760 mm and subsequently under reduced pressure.

DISTILLATION

Fraction	Boiling point (°C)	Pressure (mm)	Wt distilled (mg)
I	45–69	20	74
II	113–119	20	390
III	121	20	120
			Total 584 mg

The infrared spectra of FII and FIII were identical, indicating the presence of an amide (2·95 μ, 5·95–6·01 μ), presumably N-benzyl formamide.

The HCl extracts were made alkaline; the alkaline solution was extracted with 3 × 300 ml of ether, the ether layers were dried with $MgSO_4$ and distilled through a fractionating column, first under 760 mm and subsequently under reduced pressure.

DISTILLATION

Fraction	b.p. (°C)	Pressure (mm)	Wt. (g) distilled	Analysis (%)	
				Found	Calculated
1	36–61	760	11·8	Note: Contains no amine No ppt. with HCl–ether.	
2	61–183	760	6·9	Note: Yields 7·1 g of amine hydrochloride.	
3	83–88	20	8·0		
4	88–173	20	4·2		
5	173–170	20	4·5	C, 84·00; H, 8·26; N, 7·00	$(C_6H_5CH_2)_2NH$ C, 85·23; H, 7·66; N, 7·10
6	165–175	7	1·5		
7	Residue		2·2	*Note*: No amine, no tosylate, no picrate.	
			Total 27·3		

Fraction 3 was an amine, from this amine only one base-insoluble tosylate could be prepared, m.p. 94·0–94·7 C, which was identical with N-methyl-N-benzyl *p*-toluenesulphonamide. No traces of α-phenyl ethyl amine were detected in Fractions 2, 3, and 4 when these were analysed by vapour phase chromatography.

Hydrolysis of $(C_6H_5CH_2NC)_5FeCNBr{\cdot}H_2O$ *with* 20 *per cent sulphuric acid in acetic acid*

To a solution of 52·4 g (0·5 mole) concentrated sulphuric acid in 160 ml of water was added a solution of 54 g (0·07 mole) of $(C_6H_5CH_2NC)_5FeCNBr{\cdot}H_2O$ dissolved in 100 ml of glacial acetic acid and the heterogeneous solution was refluxed for 49 hr. The mixture became homogeneous after about one day. The reaction mixture was then cooled to room temperature and was poured into a slurry of 70 g (0·524 mole) of barium oxide in 100 ml of water. The barium sulphate, which precipitated out, was filtered through a fine fritted funnel. The filtrate was then freeze-dried, the distillate of water and glacial acetic acid being neglected. There remained a residue, which was extracted with 200 ml of acetone and subsequently with 200 ml of absolute ethyl alcohol in a soxhlet extractor. Each extraction was run for three days (Extract A). To ensure the removal of any entrapped organic material in the $BaSO_4$ precipitate, the $BaSO_4$ was extracted with 2 500 ml acetone and then with 1 500 ml absolute ethanol in a soxhlet, each extraction running for three days: finally the $BaSO_4$ was steam distilled, the distillate being extracted with 3 150 ml of ether. All organic extracts were combined with Extract A and were reduced under 5 mm/25 C vacuum to a semi-solid mass (benzylamine boils at about 5 mm/50 C therefore, little or no benzylamine was lost). The semi-solid brown residue was dissolved in 400 ml of chloroform and the chloroform layer was extracted with 3 10 ml of 4 N hydrochloric acid. The chloroform layer was then washed with water, dried with $MgSO_4$ and was chromatographed on 500 g of alumina. The column was washed with (I) 800 ml of chloroform, (II) 100 ml 50 per cent chloroform-acetone, (III) 200 ml acetone, (IV) 100 ml 50 per cent acetone-methanol (V) 1200 ml of methanol. Fractions I VI yielded upon evaporation of the solvent 28·33 g (54 per cent) of starting material. Evaporation of FV yielded 8·79 g of a yellow oil which failed to crystallize. Infra-red ($CHCl_3$): 3·00(*s*), 3·40(*s*), 4·52(*vs*), 5·85(*s*), 6·25(*w*), 6·38(*s*), 6·68(*s*), 6·88(*s*), 6·95(*s*), 7·42(*s*), 8·10(*broad*), 8·50(*w*), 9·28(*s*), 9·73(*s*), 11·00(*w*), 14·42(*s*). No traces of an organic acid were detected. The hydrochloric acid extracts were made strongly basic and were extracted with 3 200 ml of ether. After being dried with $MgSO_4$, the ether extracts were distilled first at 760 mm and then at reduced pressure.

DISTILLATION

Fraction	b.p. (C)	Pressure (mm)	Wt. distilled (g)	Remarks
a	96–97	38	0·55	Infra-red indicates an amine with traces of an amide. Redistillation (spinning band column, ca. 50 plates)
b	97–106	38	1·735	
c	106–128	38	1·88	
d	128–141	38	0·25	
e	141	38	0·30	
1	35–98	38	0·20	
2	98–101	38	6·90	
3	101–138	38	4·90	
4	132–135	38	1·40	
5	Residue		1·20	

Fraction 2 yielded only one *p*-toluenesulphonamide, m.p. 114·5–114·9 C.

(Found: C, 63·87; H, 5·92; N, 5·35; S, 12·07. Calc. for $C_6H_5CH_2NHSO_2C_6H_4(p\text{-}CH_3)$: C, 64·34; H, 5·79; N, 5·36; S, 12·27%). The admixture of this sample did not depress the m.p. of an authentic sample of N-benzyl-*p*-toluene sulphonamide. Fractions 3a and 3b consisted only of benzylamine, which was identified as the *p*-toluene sulphonamide. The infra-red spectra of Fractions 3c and3d

TABLE 2.—SYNTHESIS OF VARIOUS

$(C_6H_5CH_2NC)_5FeCNBr{\cdot}H_2O$ (mole)	MeX (mole)	Procedure	CH_3OH (ml)	H_2O (ml)	Time (hrs)	Temp. (°C)	M.P.
(0·005)	NaCl (0·05)	E(1)	(100)	(50)	1	25	106–108·5
(0·005)	KI (0·05)	E(2)	(100)	—	1	25	119·2–119·6
(0·009)	KSCN (0·1)	E(2)	(10)	(25)	1	25	110–111·2
(0·009)	$LiClO_4$ (0·1)	E(3)	(50)	(100)	1	25	139–140
(0·009)	$C_6H_5CO_2K$ (0·05)	E(4)	(60)	(25)	1	25	114·5–117
(0·009)	CF_3CO_2Ag (0·01)	D	(40)	(50)	1	25	113–115
(0·005)	Ag_2SO_4 (0·0025)	D(5)	(50)	(150)	5	100	122–124
(0·05)	H_2SO_4 80%, 104 ml	F	—		4	100	156·8–157·8

(1) Column was eluted with I 4 × 50 methyl ethyl ketone, 0·148 g; II 4 × 50 ml 50% methyl ethyl ketone-methanol, 3·01 g; III 4 × 50 ml methanol, 0·083 g, III was recrystallized several timed for methyl ethyl ketone and was dried at 25°C/0·1 mm Hg.

(2) Organic filtrates reduced to dryness and recrystallized from methyl ethyl ketone and dried at 25°C/0·1 mm Hg for analysis.

were identical with N-benzyl formamide; Fractions 3c and 3d were hydrolysed with 90% $H_2SO_4$for 2 hr on a steambath yielding only benzylamines, identified as the *p*-toluene sulphonamides.

Anion exchanges in $(C_6H_5CH_2NC)_5FeCNBr$ (*Procedure D, Table* 2)

$[(C_6H_5CH_2NC)_5FeCN]NO_3{\cdot}H_2O$ was prepared by the addition of a solution of 7·86 g (– 0·01 mole) of $[(C_6H_5CH_2NC)_5FeCN]Br{\cdot}H_2O$ dissolved in 40 ml of absolute ethyl alcohol to 1·69 g (= 0·01 mole) of silver nitrate dissolved in 10 ml of distilled water. The silver bromide was filtered off and the filtrate was evaporated to dryness under vacuum. The solid residue was dissolved in acetone and CCl_4 was added until the solution became just cloudy. The solution was cooled on dry-ice and was then allowed to stand at room temperature for several days. Two types of rosettes crystallized out, which were separated mechanically: (a) m.p. 85–87°C, (b) m.p. 105–107°C. Fraction (a), 665 mg, was then chromatographed on alumina and eluted in the manner described in Procedure C above. The column was washed with 14 × 50 ml of $CHCl_3$. Fractions 12–14 were recrystallized from $CHCl_3$–CCl_4 and subsequently from methyl ethyl ketone: m.p. 85·5–87·5°C after drying at 0·4 mm/25°C. (Found: C, 66·28, 66·72; H, 4·95, 4·43; N, 12·79; Fe, 7·90. Calc. for $[(C_6H_5CH_2NC)_5$-$FeCN]NO_3{\cdot}H_2O$: C, 65·89; H, 4·99; N, 13·12; Fe, 7·47%).

Fraction (b), 1·5 g, was dissolved in methyl ethyl ketone and was filtered through alumina suspended in methyl ethyl ketone. The main fraction crystallized from methyl ethyl ketone melted at 106–108°C after drying at 0·4 mm/25°C. Found: C, 67·38, 66·75; H, 4.95, 5·05; N, 13·31, 13·35; Fe, 7·70. Calc. for $[(C_6H_5CH_2NC)_5FeCN]NO_3$: C, 67·50; H, 4·83; N, 13·44; Fe, 7·66%.

Infra-red ($CHCl_3$): 2·98(*w*), 3·37(*m*), 4·62(*vs*), 4·78(*m*), 6·22(*w*), 6·68(*m*), 6·87(*s*), 6·95(*s*), 7·42(*vs*), 8·12(*w*), 9·28(*w*), 9·72(*w*), 9·98(*w*), 12·06(*w*), 14·40(*vs*), 15·15(*s*), (*μ*).

Procedure E

A compound assumed to be $[(C_6H_5CH_2NC)_5FeCN]SCN$ was prepared by the addition of a solution of 7·1 g (= 0·009 mole) of $[(C_6H_5CH_2NC)FeCN]Br{\cdot}H_2O$ in 10 ml of methanol to a solution

$(C_6H_5CH_2NC)_5FeCNx\cdot XH_2O$ COMPLEXES

Isonitrile complex isolated	Carbon		Hydrogen		Nitrogen		Iron		Miscellaneous	
	calcd.	found	calcd.	found	calcd.	found	calcd.	found	calcd.	found
$(L_5FeCN)Cl\cdot 2H_2O$ (?)	66·62	65·24	5·32	4·77	11·37	11·21	7·55	7·57	Cl 4·80	6·39
$(L_5FeCN)I\cdot H_2O$ (?)	60·58	60·65	4·59	4·44	10·34	8·91	6·87	6·87	I 15·62	18·22
$(L_5FeCN)SCN$	69·51	68·91	4·86	4·97	13·51	13·40	7·70	8·07	S 4·42	4·52
$(L_5FeCN)ClO_4$	64·19	64·32	4·60	4·46	10·96	10·81	7·28	7·48	Cl 4·62	4·26
$(L_5FeCN)OH\cdot 5H_2O$	63·56	63·71	5·98	5·15	10·85	11·09	7·21	7·39	Br 0	0
$(L_5FeCN)CO_2CF_3$	66·16	66·49	4·51	5·09	10·75	10·79	7·15	7·63		
$(L_5FeCN)_2SO_4\cdot 2H_2O$	64·28	63·83	4·90	4·99	11·36	11·60	9·06	8·86	S 2·60	2·77
$(L_5FeCN)HSO_4\cdot H_2O$	62·99	63·26	4·88	4·82	10·74	10·61	7·14	7·57	S 4·10	3·90

(3) I 4 × 50 ml chloroform, 6·049 g; II 4 × 50 ml 50% chloroformacetone, 0·580 g; III 4 × 50 ml acetone, 0·874 g; IV 4 × 50 ml 50% acetone-methanol, 0·250 g; V 2 × 50 ml methanol, 0·05 g. I was crystallized several times from methyl ethyl ketone and was dried at 25°C/0·1 mm.

(4) Column eluted with 10 × 50 ml of 90% methyl ethyl ketone-methanol; F 3–4 were recrystallized from methyl ethyl ketone and were dried at 25°C/0·1 mm Hg.

(5) Recrystallized from methyl ethyl ketone and dried at 25°C/0·1 mm Hg.

of 10 g (0·1 mole) of KSCN in 25 ml of water. After 14 days at room tempreature (a slight pinkish colour developed after this time) the solution was evaporated to dryness under vacuum and the residue was extracted with chloroform (3 × 50 ml). The chloroform extracts were washed with water, dried with $MgSO_4$, evaporated to dryness and crystallized from cold methyl ethyl ketone. After several recrystallizations from methyl ethyl ketone, the product melted at 110–111·2°C after drying at 0·1 mm/25°C. (Found: C, 68·91, 68·70; H, 5·15, 4·97; N, 13·40, 12·65; S, 4·52; Fe, 8·07. Calc. for $[(C_6H_5CH_2NC)_5FeCN]SCN$: C, 69·51; H, 4·86; N, 13·51; S, 4·42; Fe, 7·70%.)

Infra-red ($CHCl_3$): 3·38(*s*), 4·62(*vs*), 4·72(*s*), 4·87(*s*), 6·24(*w*), 6·68(*s*), 6·87(*s*), 6·95(*s*), 7·42(*s*), 8·25 (*broad*), 9·30(*w*), 9·75(*w*), 14·40(*s*), 15·15(*m*), (μ).

Procedure F

To 105 ml of 81 per cent sulphuric acid solution cooled to 25°C were added 36 g (0·05 moles) of $(C_6H_5CH_2NC)_5FeCNBr\cdot H_2O$ and the reaction mixture was heated on the steambath for 4 hr. The reaction mixture was then cooled to room temperature and was poured onto 400 ml of water. Forty-two grammes of a yellow, water insoluble oil separated out, which solidified after two washings with about 100 ml fresh batches of water. After three recrystallizations from methyl ethyl ketone and drying at 56°C/0·1 mm Hg, the compound melted at 156·8–157·8°C. (Found: C, 63·26; H, 4·82; N, 9·93; Fe, 7·57; S, 3·90. Calc. for $(C_6H_5CH_2NC)_5FeCNHSO_4\cdot H_2O$: C, 62·99; H, 4·88; N, 10·74; Fe, 7·14; S, 4·10%).

Infra-red ($CHCl_3$): 2·95(*w*), 3·12(*m*), 3·40(*s*), 4·55(*vs*), 4·72(*s*), 6·25(*w*), 6·68(*s*), 6·89(*s*), 6·95(*s*), 7·10(*w*), 7·42(*s*), 8·30(*broad*), 9·50(*s*), 11·65(*broad*), 14·40(*s*), (μ).

Preparation of $(C_6H_5CH_2NC)_4Fe(CN)_2$ *from* $(C_6H_5CH_2NC)_5FeCNBr$

Forty-six grammes (0·06 moles) of $(C_6H_5CH_2NC)_5FeCNBr$ were placed into a small still equipped with a graduate cylinder as a receiver and the system was evacuated to 0·4 mm Hg. The reaction vessel was placed on a steambath and the progress of the reaction was followed by measuring the amount of benzyl bromide collected in the still.

DISTILLATION (100°C/0·4 mm Hg)

Time (min)	Wt. distilled (g)	Reaction (%)
0	0	0
93	0·34	3
140	1·02	10
228	2·37	23
408	4·94	48
618	5·31	51
1000	7·00	68

The yellow residue from the distillation was extracted with 3 × 150 ml of boiling methyl ethyl ketone and the solution was filtered hot. The methyl ethyl ketone insoluble material, 25 g, (70 per cent conversion melted at 245–249°C. After one recrystallization from $CHCl_3$–CCl_4, the material had a m.p. 228–230°C. The specimen did not depress the melting point of $(C_6H_5CH_2NC)_4Fe(CN)_2$ prepared above and their infra-red spectra (Fig. 1c) were identical.

Reaction of $(C_6H_5CH_2NC)_5FeCNBr$ *with an excess of benzyl bromide*

A mixture of 3·6 g (= 0·005 mole) of $(C_6H_5CH_2NC)_5FeCNBr$, m.p. 111–112°C, was heated with 10 g (= 0·06 mole) of benzyl bromide on a steambath for 12 hr. The brown reaction mixture was then washed with petroleum ether (2 × 50 ml) and ether (1 × 50 ml) in order to remove the excess benzyl bromide. The oily residue was taken up in boiling methyl ethyl ketone and was filtered from a trace of insoluble material (I). Upon cooling there crystallized in two crops 3·85 g of a solid (II) m.p. 120–125°C. Fraction I was recrystallized from chloroform yielding ~700 mg of yellowish crystals, m.p. 130–135°C. The second band present in the starting material at 4·72 μ almost disappeared in this complex, and the infra-red spectrum was almost identical with $(C_6H_5CH_2NC)_6FeBr_2$. Fraction II was chromatographed on 30 g of alumina suspended in chloroform. Elution of the column with chloroform and 50 per cent chloroform acetone yielded 1·8 g of starting material. Further elution of the column with 50 per cent acetone-methanol yielded 1·7 g of a material, m.p. 120–130. After several recrystallizations from methyl ethyl ketone, the material melted at 134·2–135·2°C, after drying at 25°C/0·1 mm Hg. (Found: C, 61·84; H, 4·75; Br, 17·40; Fe, 6·64; N, 9·09. Calc. for $(C_6H_5CH_2NC)_6FeBr_2$: C, 62·76; H, 4·61; N, 9·15; Fe, 6·08; Br, 17·40%).

The infra-red spectrum of this material was identical with $(C_6H_5CH_2NC)_6FeBr_2$. Although the melting point was different from the $(C_6H_5CH_2NC)_6FeBr_2$ prepared above, probably these two materials represent two dimorphic forms of the same compound.

Hydrogenation of $(C_6H_5CH_2NC)_6FeBr_2$ *with Raney-nickel*

$(C_6H_5CH_2NC)_6FeBr_2$, m.p. 119–121·2°C, 10 g (0·011 mole), prepared from benzyl bromide and potassium ferrocyanide, was dissolved in 70 ml of absolute methanol, and then one half teaspoon Raney-Nickel catalyst was added to this solution. The reaction mixture was pressurized in a stainless steel vessel with 600 atm H_2 and was heated for 6 hr at this pressure. A total of 35 atm H_2 was consumed after this time. The stainless steel vessel was washed thoroughly with methanol and the organic liquors were filtered from the catalyst and were evaporated to dryness under vacuum. In the residue there remained a compound, 3·8 g, which crystallized when washed with ether and after chromatography on alumina melted at 167·5–168°C. (Found: C, 47·75; H, 5·99; N, 7·00. Calc. for $C_6H_5CH_2NHCH_3{\cdot}HBr$: C, 47·54; H, 5.98; N, 6·93%).

The distillate and the ether wash of the residue were combined and were distilled at 15 mm Hg. Fractions a–c reacted with *p*-toluenesulphonyl chloride to yield only one *p*-toluenesulphonate, after several recrystallizations, m.p. 94·0–94·5°C. (Found: C, 65·00; H, 6·45; N, 4·99. Calc. for $C_{15}H_{17}NSO_2$: C, 65·42; H, 6·22; N. 5·09%).

The sample did not give any melting point depression with an authentic sample of N-benzyl N-methyl *p*-toluenesulphonamide. The total material accounting in this experiment was about 90 per cent.

DISTILLATION

Fraction	b.p. (°C)	Wt. distilled (g)	n_D^{29}
a	70–75	1·89	1·5180
b	75–90	1·29	1·5238
c	90–100	0·39	1·5272
		3·57	

Reaction of $(C_6H_5CH_2NC)_6FeBr_2$ *with* $LiClO_4$

To a solution of 3·0 g (= 0·0033 mole) of $(C_6H_5CH_2NC)_6FeBr_2$, m.p. 119–121·2°C, in 50 ml of absolute methanol were added 5·3 g (0·05 mole) of $LiClO_4$ and the reaction mixture was evaporated to dryness. The residue was extracted with $CHCl_3$ several times, was filtered and the filtrate was chromatographed on 100 g of alumina (see above) suspended in $CHCl_3$. The first three fractions, 150 ml, eluted with $CHCl_3$, 3·184 g, m.p. 160–165°C were recrystallized several times from methyl ethyl ketone. After drying at 25°C/0·1 mm Hg, the compound melted at 163·5–164°C. (Found: C, 60·57; H, 4·86; N, 8·14; Fe, 5·68; Cl, 7·06. Calc. for $(C_6H_5CH_2NC)_6Fe(ClO_4)_2$: C, 60·19; H, 4·42; N, 8·77; Fe, 5·83; Cl, 7·41%).

Infra-red ($CHCl_3$): 3·39(*m*), 4·52(*vs*), 6·25(*w*), 6·72(*m*), 6·92(*m*), 7·00(*m*), 7·45(*m*), 9·18(*vs*), 14·45(*vs*), (μ).

Reaction of benzyl isonitrile with $Fe(ClO_4)_2 \cdot 6H_2O$

Benzyl isonitrile was prepared according to the procedure of HOFMAN(7), from benzyl amine and chloroform, b.p. 122–125°C/50 mm, infra-red strong band at 4·55 μ.

To a solution of 3·6 g (= 0·01 mole) of $Fe(ClO_4)_2 \cdot 6H_2O$ in 50 ml of absolute methanol was added at room temperature with stirring a solution of 8·4 g (0·072 mole) of benzylisonitrile in 50 ml of methanol. Immediately the yellow reaction mixture turned red but no precipitate appeared. The solvent was reduced to about one quarter of its volume and was placed in the refrigerator. After about one week, yellow crystals separated out, 8·2 g or 90 per cent. After two recrystallizations from methyl ethyl ketone and drying at 25°C/0·1 mm, the compound melted at 163·2–165·3°C. (Found: C, 60·50; H, 4·72; N, 8·73; Fe, 6·19; Cl, 7·35. Calc. for $(C_6H_5CH_2NC)_6Fe(ClO_4)_2$: C, 60·19; H, 4·42; N, 8·77; Fe, 5·83; Cl, 7·40%).

This sample did not give a melting point depression with the diperchlorate prepared above.

Reaction of $K_3Fe(CN)_6$ *with trityl bromide*

To 3·38 g (0·01 mole) of $K_3Fe(CN)_6$ (dried at 150°C/0·1 mm) in 100 ml of dry chloroform were added 16·15 g (0·05 mole) of trityl bromide and the reaction mixture was refluxed for 66 hr. The reaction mixture was cooled and was filtered from the chloroform insoluble material. The residue was extracted with 100 ml of boiling chloroform, the organic extracts were combined and were placed on a column prepared from 250 g of alumina (see above) suspended in chloroform. The column was eluted with 4 × 100 ml of chloroform (I), 4 × 100 ml of 50 per cent chloroform–acetone (II), 5 × 100 ml acetone (III) and finally with 2 × 100 ml of 50 per cent acetone–methanol (IV). Only one fraction was isolated from (I) and (II), 18·4 g (wet) which crystallized from chloroform–carbon tetrachloride and dried at 25°C/0·1 mm Hg, m.p. 291–303°C. Two recrystallizations from methyl ethyl ketone and drying at 80°C/0·1 mm Hg yielded a compound with a m.p. 303–306·5°C. (Found: C, 76·10; H, 4·77; N, 6·90; Fe, 4·52; Br, 6·32. Calc. for $[(C_6H_5)_3CNC]_4Fe^{III}(CN)_2Br$: C, 77·84; H, 4·78; N, 6·64; Fe, 4·41; Br, 6·33%).

Specific magnetic susceptibility $\chi = (+)\ 1{\cdot}46 \times 10^{-6}$ c.g.s. at 26°C.

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(7) A. W. HOFMANN, *Ann.* **144**, 114 (1867).

RESULTS AND DISCUSSION

A. *Physical properties of* $(C_6H_5CH_2NC)_5FeCNBr$

When a mixture consisting of 1 mole of anhydrous potassium ferrocyanide and 5 mole of benzyl bromide is vigorously stirred on a steambath for 40–55 hr, a brown, semisolid product is formed (see Fig. 2 and Table 1). When the reaction mixture is processed, a greenish-white solid is obtained. This material is insoluble in benzene and water but dissolves readily in chloroform acetone and alcohol. Ultimate analysis of this material corresponds to the empirical formula $[(C_6H_5CH_2NC)_5Fe^{II}CN]Br$(I). Molecular weight determinations of the monohydrate of I (mol. wt. 765·5) by the single crystal X-ray diffraction method indicated a molecular weight of 775.(5) Molecular weight determinations and conductivity measurements in nitrobenzene indicated that I dissociates into two univalent ions in this solvent.

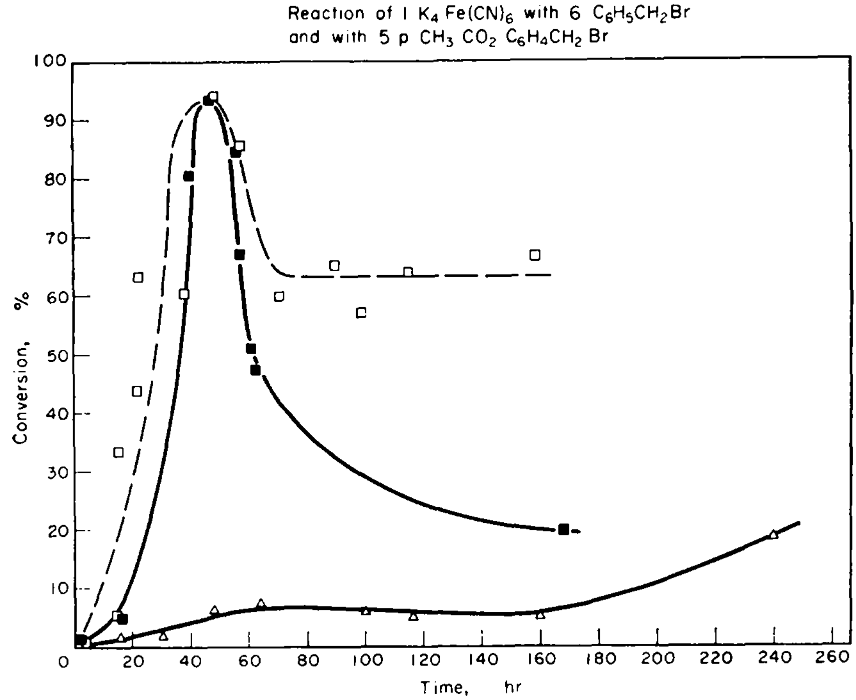

FIG. 2.

The infra-red spectrum of the hydrate of I (Fig. 1b) exhibits peaks at 3·00, 4·56 and 4·72 μ. These may be interpreted as OH stretching frequency (3·00 μ)(8), C≡N stretching frequency for either a nitrile or an isonitrile ligand(8,9) (4·56 μ) and a C≡N stretching frequency for an inorganic cyanide (4·72 μ)?

Complex I is diamagnetic; the specific magnetic susceptibility χ is (—) $0{\cdot}48 \times 10^{-6}$ c.g.s. at 26°C (see also Table 1).

B. *Structure proof for* $(C_6H_5CH_2NC)_5FeCNBr$

The structure proof for $(C_6H_5CH_2NC)_5FeCNBr$ is summarized in Fig. 3.

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(8) L. J. BELLAMY, *The Infra-red Spectra of Complex Molecules*. J. Wiley, New York (1958).

(9) I. UGI and R. MEYR, *Ber. Dtsch. Chem. Ges.* **93**, 239 (1960).

When I was dissolved in methanol and an excess of a foreign anion was added a metathetical reaction took place in which the bromide ion was exchanged with the foreign anion added.

$$[(C_6H_5CH_2NC)_5FeCN]Br \cdot H_2O + NaX \rightarrow [(C_6H_5CH_2NC)_5FeCN]X \cdot H_2O + NaBr$$
$$= Cl, I, SCN, ClO_4, OH, HSO_4X$$

The bromide ion must therefore serve as anion for the monopositive

$$[(C_6H_5CH_2NC)_5FeCN]^+$$

complex ion. The products of metathesis are crystalline materials, which may or may not contain water of hydration. The presence of water in the complexes was shown by ultimate analysis, infra-red spectra, nuclear magnetic resonance spectra and, in case of $X = NO_3$ and Br, by preparation of both the anhydrous and hydrated complexes. Potassium benzoate yielded the corresponding hydroxide ($X = OH$) as the only product of metathesis, instead of the expected benzoate ($X = C_6H_5CO_2$).

The relatively high water content of these compounds suggests a clathrate structure for these compositions. POWELL and BARTINDALE found earlier that a similar compound, $(CH_3NC)_6Fe^{II}Cl_2$, forms a clathrate complex with water.(10)

Alternative methods for replacement of the bromide were (a) addition of the silver salt of an anion or (b) heating I with slightly diluted strong acids, such as 80% H_2SO_4 at 100°C. The preparations of various $(C_6H_5CH_2NC)_5FeCNX \cdot xH_2O$ salts are summarized in Table 2 and the three methods employed are described in some detail in the Experimental Part.

Oxidation of I with alkaline permanganate yielded 4·3 moles of benzoic acid per mole of I. This evidence is in agreement with the formula assigned to I.

The cyano penta-benzylisonitrile iron (II) cation is extremely stable toward acids such as warm conc. H_2SO_4 and in 80% H_2SO_4 to about 120°C. At higher temperatures decomposition of the complex takes place. Partial hydrolysis of I (about 30 per cent) took place when I was refluxed with 20% H_2SO_4 in aqueous acetic acid for 49 hr. When the reaction mixture was processed 28·23 g of I were recovered, benzyl amine and N-benzyl formamide were identified in about 30 per cent conversion and a new isonitrile complex was formed in about 10–15 per cent conversions. This new isonitrile complex has only one cyanide band at 4·55 μ, the second cyanide peak present in the starting material at 4·72 μ and tentatively assigned to the inorganic cyanide group having disappeared.

A potentiometric titration of I in liquid ammonia with a standard solution of potassium in liquid ammonia, an experiment performed by WATT of the University of Texas,(11) clearly indicated only a one-electron reduction. This reduction could yield two distinctly different types of complexes (assuming no reduction of double bonds takes place):

$$[(C_6H_5CH_2NC)_5Fe^{II}CN]Br + K \rightarrow (C_6H_5CH_2NC)_5Fe^{I}CN + KBr$$

or

$$[(C_6H_5CH_2NC)_5Fe^{II}CN]Br + K \rightarrow (C_6H_5CH_2NC)_5Fe^{I}Br + KCN$$

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(10) H. M. POWELL and G. W. R. BARTINDALE, *J. Chem. Soc.* 799 (1945).

(11) G. W. WATT. Private communication (1957).

A larger scale reduction in dried liquid ammonia with potassium in a closed system yielded an oil, which after chromatography on alumina, yielded a reddish material which thus far could not be crystallized. Qualitative tests with $AgNO_3$ indicate that little or no bromine is present in this material.

Provided that no isomerization precedes the hydrogenation, the hydrogenation of benzyl isonitrile would yield the following compounds as main constituents:

$$C_6H_5CH_2NC + H_2 \xrightarrow{\text{catalyst}} C_6H_5CH_2NHCH_3 + C_6H_5CH_2NH_2$$

On the other hand, hydrogenation of the benzyl cyanide should yield β-phenylethylamine as the only product of hydrogenation.

Hydrogenation of I with Raney-Nickel catalyst at 200 atm and 130°C yields only products which are derived from benzyl isonitrile, i.e., benzylamine and N-methylbenzylamines and N,N-dibenzylamine. The materials were identified by ultimate analysis and preparation of their corresponding *p*-toluenesulphonamides. The total material accounting in this experiment was 76–80 per cent. This experiment indicates that the complex does not contain benzylcyanide as a ligand and that the isomerization of complexed benzylisocyanide to benzylcyanide does not take place below 130°C.

Dry distillation of I under reduced pressure yielded $(C_6H_5CH_2NC)_4Fe(CN)_2$ in nearly quantitative conversion. Tetrabenzyl isonitrile iron^{II} cyanide had two cyanide bands at 4·58 μ and 4·78 μ a slight shift of both bands toward higher wave length as compared to I. The higher wave length band assigned tentatively to the inorganic cyanide increased in intensity as compared to the same peak in I (Fig. 1c).

Alkylation of I with benzyl bromide yielded the expected $(C_6H_5CH_2NC)_6FeBr_2$. The structure of this compound has been proven by ultimate analysis; by reduction to the expected benzyl amine and N-methyl benzyl amine; by an independent synthesis (see Experimental Part), and by metathesis to hexabenzyl isocyano iron^{II} diperchlorate. The same compound was prepared independently by the addition of benzyl isonitrile to iron perchlorate hexahydrate according to the method of MALATESTA.(12) (See Fig. 3.) The second cyanide peak at 4·72 μ, characteristic of the inorganic cyanide in I, is no longer present in this compound (Fig. 1a), and the co-ordinated isonitrile stretching vibration is shifted to 4·50 μ.

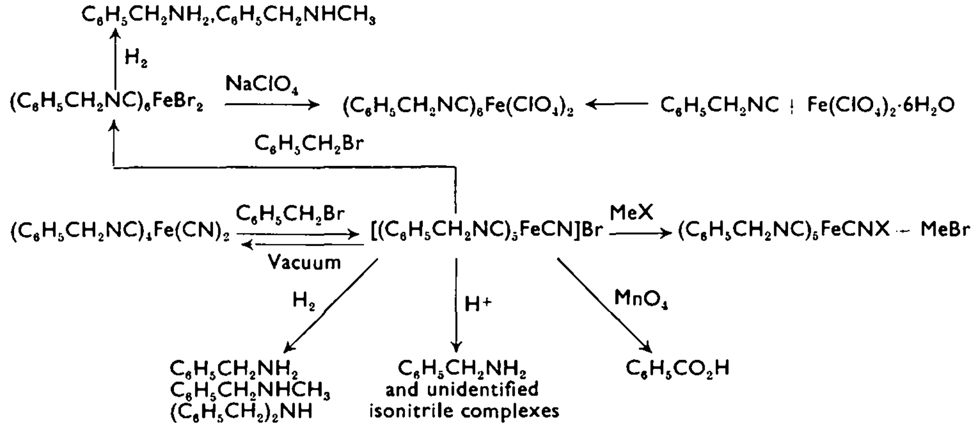

FIG. 3.—Structure proof for $(C_6H_5CH_2NC)_5Fe^{II}CNBr$

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(12) L. MALATESTA, A. SACCO and G. PADOA, *Ann. Chim.* (*Rome*) **43**, 622 (1953).

It is perhaps important to point out that most of the isonitrile complexes described in this paper could be isolated in forms having different melting points depending on the solvent used for recrystallization. $(C_6H_5CH_2NC)_6Fe^{II}Br_2$ for example showed polymorphism. When prepared directly from benzyl bromide and $K_4Fe(CN)_6$ and recrystallized from $CHCl_3$–CCl_4 the salt melted at 119–121·2°C. The same compound prepared from I and benzyl bromide and recrystallized from methyl ethyl ketone melted, on the other hand, at 134·2–135·2°C.

C. *Comments on the reaction mechanism*

The alkylation of $K_4Fe(CN)_6$ with alkyl halides is a heterogeneous reaction. All attempts to study this reaction under homogeneous conditions failed. Some of the variables investigated in this reaction are summarized in Table 3. The stirring rate, an important variable in a heterogeneous reaction, was not investigated but was kept constant at approximately 400 rev/min.

Benzyl bromide yields highest conversions to isonitrile complexes if Me in $Me_4Fe^{II}(CN)_6$ is potassium: K > Na ≈ $(CH_4)N$ > Li. No isonitrile complexes are formed with Ca, Ba and Pb^{II} ferrocyanides under similar conditions.

Solvents of high solvolytic power(13) (which favour ionization) have relatively little influence on this reaction (Table 3). Good conversions to I were obtained when the solvent was benzyl bromide, acetonitrile and methyl ethyl ketone, solvents of widely different solvolytic powers. The alkylation of $K_4Fe(CN)_6$ takes place also in nucleophilic solvents(14) such as dimethyl sulphoxide and alcohols (Table 3). The yields are rather poor since the solvent appears to compete with the ferrocyanide for the intermediate carbonium ion. Isonitrile complex formation took place fastest when the alkylating agent was benzyl bromide:

$$C_6H_5CH_2Br > C_6H_5CH_2OSO_2C_6H_4pCH_3 > C_6H_5CH_2Cl$$

Under corresponding conditions, benzyl chloride gave only very small conversions (1 per cent) to $(RCH_2NC)_5FeCNCl$. No isonitrile complexes were isolated in the reaction of benzyl iodide with $K_4Fe(CN)_6$, since under these conditions the rate of decomposition of benzyl iodide appears to be faster than the rate of isonitrile complex formation.

The alkylation of complex ferrocyanide with an alkylating agent may be summarized in the following equation:

$$K_4[Fe(CN)_6]^{4-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} K_3[(LNC)Fe(CN)_5]^3 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \cdots \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}}$$

$$(LNC)_4Fe(CN)_2 \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} [(LNC)_5FeCN]Br \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} [(LNC)_6Fe]Br_2$$

At the beginning of the reaction, the alkyl halide reacts with tetra-valent anion but in the last stage with a univalent cation. Furthermore, whereas at the beginning stages of the reaction the nucleophile is quite insoluble in the alkylhalide, toward the end of the reaction its solubility should be increased considerably. There is thus present a multiplicity of nucleophiles reacting with the alyklating agents.

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(13) E. M. Kosower, *J. Amer. Chem. Soc.* **80**, 3233 (1958).

(14) S. Winstein, E. Grunwald and H. W. Jones, *J. Amer. Chem. Soc.* 73, 2700 (1951).

TABLE 3. THE SYNTHESIS OF IRON ISONITRILE COMPLEXES: INFLUENCES OF REACTANTS AND REACTION CONDITIONS

Alkylating agent (mole)	Metalferro cyanide (mole)	Solvent (Ml)	Reaction conditions Time (hrs)	Temp. (°C)	Conversion to products % Total isonitrile complex	$(RCH_2NC)_5Fe(CN)Br$
$C_6H_5CH_2Br$ (05)	$[(CH_3)_4N]_4Fe(CN)_6$(1) (0·046)	none	48	100	36	
$C_6H_5CH_2Br$ (0.26)	$Li_4Fe(CN)_6$ (0·04)	none	48	100		10
$C_6H_5CH_2Br$ (0·6)	$Na_4Fe(CN)_6$ (0·3)	none	48	100		26
$C_6H_5CH_2Br$ (5·5)	$K_4Fe(CN)_6$ (1·0)	none	48	100	78	47
$C_6H_5CH_2Br$ (0·05)	$Ca_2Fe(CN)_6$ (0·05)	none	48	100	none	
$C_6H_5CH_2Br$ (0·26)	$Ba_2Fe(CN)_6$ (0·04)	none	48	100	none	
$C_6H_5CH_2Br$ (0·5)	$Pb_2Fe(CN)_6$ (0·1)	none	48	100	none	
$C_6H_5CH_2Cl$ (1·0)	$K_4Fe(CN)_6$ (0·7)	none	4	reflux		about 1
$C_6H_5CH_2Br$ (2·0)	$K_4Fe(CN)_6$ (0·3)	none	12	100	43	

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$C_6H_5CH_2I$ (0·20)	$K_4Fe(CN)_6$ (0·05)	none	12	100	none	
$C_6H_5CH_2OSO_2C_6H_4(pCH_3)^{(2)}$ (0·15)	$K_4Fe(CN)_6$ (0·03)	$CH_3COCH_2CH_3$ (200)	96	reflux		35
$C_6H_5CH_2Br$ (0·3)	$K_4Fe(CN)_6$ (0·047)	$CHCl_3$ (150)	48	reflux	none	
$C_6H_5CH_2Br$ (0·3)	$K_4Fe(CN)_6$ (0·047)	dioxane (150)	48	reflux	none	
$C_6H_5CH_2Br$ (2·0)	$K_4Fe(CN)_6$ (0·33)	CH_3CN (300)	66	reflux	43	
$C_6H_5CH_2Br$ (0·3)	$K_4Fe(CN)_6$ (0·047)	CH_3CH_2OH (150)	48	reflux	14	
$C_6H_5CH_2Br$ (0·3)	$K_4Fe(CN)_6$ (0 047)	CH_2OHCH_2OH (150)	48	100	23	
$C_6H_5CH_2Br$ (0·5)	$K_4Fe(CN)_6$ (0·09)	$(CH_3)_2NCHO$ (100)	48	100	46	
$C_6H_5CH_2Br$ (0·5)	$K_4Fe(CN)_6$ (0·1)	$(CH_3)_2SO$ (100)	48	100	6·5	
$C_6H_5CH_2Br$ (0·5)	$K_4Fe(CN)_6$ (0·09)	C_5H_5N (100)	48	80	none	
$C_6H_5CH_2Br$ (2·92)	$K_4Fe(CN)_6$ (0·33)	$CH_3COCH_2CH_3$ (500)	92	reflux	47	

(1) Prepared from $(CH_3)_4NOH$ and $H_4Fe(CN)_6$.

(2) Prepared according to the procedure of TIPSON, *J. Org. Chem.* **9**, 235 (1944).

A typical reaction-profile for an alkylation reaction is represented in Fig. 2, for the reaction of six moles of benzyl bromide with one mole of $K_4Fe(CN)_6$ at 100°C with no solvent employed. (Each reaction mixture was processed according to Procedure A (see Experimental Part) in order to determine the amount of I formed.) There is a distinct induction period of about 16 hr followed by a maximum conversion to I of 93 per cent, at 48 hr and a subsequent sharp decline of the conversion to I. The induction period is probably determined by the sum of the initial rate constants $(k_1/k_{-1} + k_2/k_{-2} + k_3/k_{-3})$. Following the induction period is the formation of $(RCH_2NC)_4Fe(CN)_2$ which in turn at 48 hr is completely converted to I. After this time, a decomposition of I to $(RCH_2NC)_6FeBr_2$ and unknown products (See Experimental) takes place. All of the substituted benzyl bromides investigated in any detail exhibited similar behavior. The induction periods for the following compounds were:

$$p\text{-}CH_3C_6H_4CH_2Br = 8 \text{ hr}; o\text{-}CH_3C_6H_4CH_2Br \cong 12 \text{ hr}$$

$$p\text{-}ClC_6H_4CH_2Br = 35 \text{ hr}; p\text{-}CH_3CO_6C_6H_4CH_2Br = 220 \text{ hr}$$

$$\text{and } p\text{-}NO_2C_6H_4CH_2Br = \gg 400 \text{ hr}$$

Isonitrile complexes, very probably the total of $(RCH_2NC)_4Fe(CN)_2$ and $(RCH_2NC)_5FeCNBr$, were formed in maximum conversions after the following times of reaction with the given halides:

$$p\text{-}CH_3C_6H_4CH_2Br \text{ and } o\text{-}CH_3C_6H_4CH_2Br = 25 \text{ hr}, \ p\text{-}ClC_6H_4CH_2Br = 63\text{–}80 \text{ hr}$$
$$\text{and} \quad p\text{-}CH_3CO_2C_6H_4CH_2Br \gg 240 \text{ hr}$$

The approximate rate of reaction of one mole of $(C_6H_5CH_2NC)_4Fe(CN)_2$ and one mole of I with two moles of benzyl bromide at 100°C in a sealed tube was studied briefly. These rates are not strictly comparable with the rates in the original heterogeneous reaction since the mixing due to shaking of the heterogeneous solution in the tube is not comparable to the stirring in the heterogeneous system in a reaction vessel. The benzyl bromide consumed was determined by an infra-red spectroscopic method. Fifty per cent of $(RCH_2NC)_4Fe(CN)_2$ was converted to I (i.e. k_5/k_{-5}) in 8–10 hr and 50 per cent of I was converted into $(RCH_2NC)_6FeBr_2$ (i.e. k_6/k_{-6}) in 35–40 hr. This experiment indicated that there are differences in the reactivity of the different nucleophiles present toward $C_6H_5CH_2Br$. It would be expected that if the reaction is at all ionic $(RCH_2NC)_4Fe(CN)_2$, a neutral species, should react faster with $C_6H_5CH_2Br$ than $[(RCH_2NC)_5FeCN]^{\oplus}Br^{\ominus}$, a positive cation. The experiment also showed that diffusion in these reactions is of lesser importance than is the nucleophilicity of the anions.

When the $C_6H_5CH_2Br/K_4Fe(CN)_6$ ratio was decreased from five to four, the formation of $(C_6H_5CH_2NC)_4Fe(CN)_2$ was favoured, but a considerable amount of I was nevertheless isolated (see Experimental and Table 1).

The qualitative rate of reaction of RCH_2Br with $K_4Fe(CN)_6$ under comparable conditions decreases in the following sequence:

$$(C_6H_5)_3CBr > (C_6H_5)_2CHBr > p\text{-}CH_3C_6H_4CH_2Br \cong o\text{-}CH_3C_6H_4CH_2Br >$$
$$C_6H_5CH_2Br \cong CH_2{=}CH{-}CH_2Br > p\text{-}ClC_6H_4CH_2Br >$$
$$p CH_3CO_2C_6H_4CH_2Br > p\text{-}NO_2C_6H_4CH_2Br \cong (CH_3)_3CBr$$

In the case of triphenyl bromoethane the reaction proceeded even in chloroform as the solvent, whereas no reaction of benzyl bromide with $K_4Fe(CN)_6$ was observed in this solvent. Only trace-quantities of an isonitrile complex were isolated in the reaction of tert-butyl bromide with $K_4Fe(CN)_6$. The above sequence coincides with the sequence for carbonium ion stability, the most stable carbonium ion being the triphenylmethyl carbonium ion.(15) The resonance stabilization of the carbonium ion facilities both the S_{N_1} and S_{N_2} mechanism of the reaction but particularly strongly the S_{N_1} mechanism. If in this series the rate-determining step is the ionization of the alkyl halide (S_{N_1}) then the reaction of triphenyl bromomethane with $K_4Fe(CN)_6$ should certainly be determined by the rate of triphenyl bromomethane ionization.

Attempts to form ferricyanide complexes by the reaction of benzyl bromide and $K_3Fe(CN)_6$ failed. This difference between the $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ anion seems to be due to the greater basicity or nucleophilicity of the latter anion.(16) The solubility of both salts in benzyl bromide is very small. If there is a difference the less charged ferricyanide complex would be expected to show a greater solubility and mobility.(17) Triphenyl bromomethane, on the other hand, reacted with $K_3Fe^{III}(CN)_6$ to yield the expected ferricyanide complex $[(C_6H_5)_3CNC]_4Fe^{III}(CN)_2Br$, although at a slower rate than with $K_4Fe(CN)_6$. It must therefore be inferred that the nucleophilic power of the anion is of some importance even in the reaction of triphenyl bromomethane, provided that the rate of diffusion of both anions is comparable. Therefore, triphenyl bromomethane and most certainly alkylating agents forming carbonium ions of lesser stability will react with the ferrocyanide complex by the S_{N_2} mechanism in nonpolar solvents.

In a series of para-substituted benzyl bromides the "initiation" period (see above) and maximum conversion to isonitrile complexes is related to the σ value of the para-substitutent. This effect is due to (a) the ionization of the alkyl halide and (b) to differences in the nucleophilicity of the cyanides in the partially substituted ferrocyanide complex, i.e. $K_3[RNCFe(CN)_5]$ etc. This last hypothesis requires that the effect of the para-substituent be transmitted through a ten atom chain ($N\check{C}FeCNCH_2C_6H_4pX$) containing a methylene group, and therefore this effect is probably mainly inductive in origin.(18)

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