549. *Some Ketenimine Complexes of Iron.*[1]

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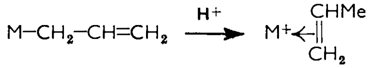
Cyanoalkyl complexes $C_5H_5Fe(CO)_2R$ (where R = $CH_2{\cdot}CN$, $CH_2{\cdot}CH_2{\cdot}CN$, and $CHMe{\cdot}CN$) have been prepared and characterised. The 1-cyanoalkyl complexes are readily and reversibly protonated by strong acids, forming cationic complexes, $[C_5H_5Fe(CO)_2RH]^+$. Crystalline salts containing these cations have been prepared and the infrared and nuclear magnetic resonance spectra of the protonated and the deuterated isomers have been studied. Structures containing a ketenimine–iron system are proposed for the cations.

Recently it has been shown that some transition metal–σ-allyl systems are readily protonated forming π-ethylenic cations:



$$M{-}CH_2{-}CH{=}CH_2 \xrightarrow{H^+} M^+\leftarrow\begin{matrix}CHMe\\ \| \\ CH_2\end{matrix}$$

where M = Fe,[2] Mn,[3] Mo,[4] or W.[3] This work is now extended to a study of the protonation of the related systems Fe–CHR·CN, where R = H or Me.

Reaction of the sodium salt[5] $Na^+[C_5H_5Fe(CO)_2]^-$ with the cyanoalkyl halides $Cl{\cdot}CH_2{\cdot}CN$ and $Br{\cdot}CH_2{\cdot}CH_2{\cdot}CN$ affords small yields of the cyanoalkyl complexes $C_5H_5Fe(CO)_2(CH_2{\cdot}CN)$, and $C_5H_5Fe(CO)_2(CH_2{\cdot}CH_2{\cdot}CN)$, respectively. The 1-cyanoethyl complex $C_5H_5Fe(CO)_2(CHMe{\cdot}CN)$ was prepared by the reaction of the hydride[6] $C_5H_5FeH(CO)_2$ with acrylonitrile:

$$C_5H_5FeH(CO)_2 + CH_2{=}CH{\cdot}CN \longrightarrow C_5H_5Fe(CO)_2(CHMe{\cdot}CN)$$

No 2-cyanoethyl complex was formed in this reaction and thus the course of the addition of the Fe–H system across a double bond adjacent to a group with a strong $-I$ effect indicates that the Fe–hydrogen is essentially hydridic in nature. The infrared and nuclear magnetic resonance spectra and the analytical data of the cyanoalkyl complexes, given in

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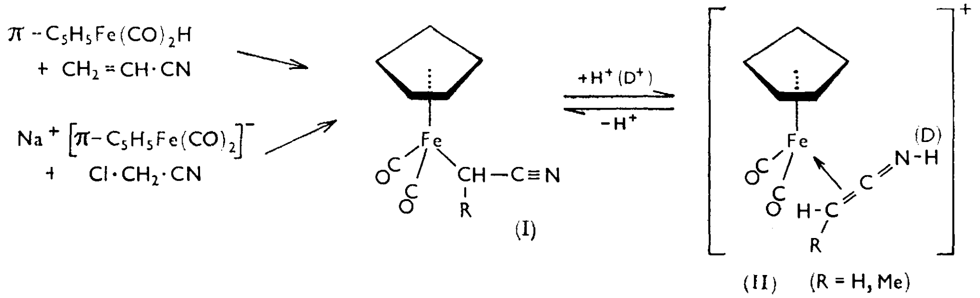
[1] Presented in part at the 7th Internat. Co-ordination Chemistry Conference, Stockholm, 1962.
[2] Green and Nagy, *Proc. Chem. Soc.*, 1961, 378; *J.*, 1962, 189.
[3] Green, Nagy, and Stears, unpublished work.
[4] Cousins and Green, *J.*, 1963, 889.
[5] Piper and Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.
[6] Green, Street, and Wilkinson, *Z. Naturforsch.*, 1959, **14**b, 738.

Tables 1, 2, and 3, are entirely consistent with the formulations given above (see also formulæ below) and this evidence is not further discussed.

Chemical Properties.—The cyanoalkyl complexes form orange-yellow crystals which are moderately stable to atmospheric oxidation and may be handled in air for short periods. They sublime readily *in vacuo*, and are moderately soluble in light petroleum and very soluble in ether, tetrahydrofuran, and chloroform. Ethereal solutions when kept in air are ~50% decomposed after four hours. Remarkably, the 1-cyanoalkyl complexes dissolve in water from which they may be re-extracted with ether. The aqueous solutions are stable under nitrogen but decompose rapidly when treated with base. These complexes are very soluble in mineral acids, giving deep orange-yellow solutions which are stable in air. Neutralisation of the acid solutions with calcium carbonate yields the original complexes which may then be extracted into ether; slight decomposition also occurs. The pH of a solution of the cyanomethyl complex in water showed that it is a weak base; its p*K* (13—14) is of the same order as that of water. The neutral and acidic aqueous solutions of the 1-cyanoalkyl complexes give precipitates with suitable large anions, indicating the presence of organometallic cations. The nature of the cations is discussed below. In general, the 2-cyanoalkyl complex is similar in properties to the 1-cyano-analogues; however, it does not dissolve in water or acids.

Protonation of the 1-*Cyanoalkyl Complexes.*—Treatment of these complexes (I; R = H or Me) with dry hydrogen chloride yields deep-yellow precipitates which are very soluble in water. The aqueous solutions are strongly acidic and give precipitates on treatment with solutions containing large anions. The hexachloroantimonates, hexachloroplatinates, and silicotungstates of the cations formed from the complexes (I; R = H or Me) were prepared in this way; the cations are designated (II; R = H or Me, respectively), the structure shown being only formal. The perchlorates, chlorides, and trifluoroacetates of the cations (II) have also been prepared. Unfortunately, except for the hexachloroantimonates, the salts crystallised with water of crystallisation; therefore most of the physical measurements were determined on the hexachloroantimonates. All the salts are moderately stable to oxidation and may be handled in air for short periods. The salts dissolve readily in liquid sulphur dioxide from which they may be recrystallised.



(I)

(II) (R = H, Me)

When heated in a vacuum at 100° the chloride of the cation (II; R = H) and the trifluoroacetate of the analogue (II; R = Me) slowly decompose, and the neutral complexes (I; R = H or Me respectively) sublime free. Conductivity measurements and analyses show that the hexachloroantimonates are 1 : 1 electrolytes and must be formulated as the salts $BH^+SbCl_6^-$ (BH^+ being the complex cation). Analyses of the other salts show that they may be similarly formulated, usually also containing one or two molecules of water of crystallisation. The deuterated salts $BD^+SbCl_6^-$ were prepared in order to assist in the interpretation of the spectra. Attempts to prepare an *N*-methyl derivative of the cation (III; R = H) by reaction with diazomethane were unsuccessful.

Spectral Studies.—The infrared spectra in the region 4000—700 cm.$^{-1}$ are given in Table 1, and the proton magnetic resonance spectra are given in Table 2. Both types of

TABLE 1.

Infrared spectra.[a]

R(CH$_2$·CN)	R(Me·CHCN)	R(CH$_2$·CH$_2$·CN)	[R(CH$_2$=C=NH)]$^+$ SbCl$_6$$^-$ [i]	[R(CH$_2$=C=ND)]$^+$ SbCl$_6$$^-$	[R(CHMe=C=NH)]$^+$ SbCl$_6$$^-$	[R(CHMe=C=ND)]$^+$ SbCl$_6$$^-$
3100w [b]	3110w [b]	3090w [b]	3380m		3350m	
2950w	2960m	2905s	3254m [f]		3240m [f]	
2915w [c]	2925m [c]	2820w [c]	3204m		3190m	
	2870m		3110m [b]	3104m [b]	3100m [b]	3106m [b]
			2988w	2984w	2995w	2998w
2204s [d]	2210s [d]	2220m [d]	2944w [g]	2934w [g]	2940w [g]	2950w [g]
2041vs } [e]	2028vs } [e]	2022vs } [e]	2061vs }	2540m		2515m
1988vs	1974vs	1963vs	2021vs	2500w [h]		2480w [h]
1433m	1456m	1550(sh)	1989m	2400m		2380m
1423m	1435m	1521s	1663s [k]	2062vs } [e]	2069vs } [e]	2070vs }
1360w	1422m	1435s	1556s [m]	2017vs	2024vs	2028vs
1060w	1380m	1424m	1486s [k]	1987m	1996m	2016m
1015m [j]	1362w	1362w	1435m	1580m	1657s [k]	1565 m [m]
1000m [j]	1103w	1315w	1422m	1554s [m]	1565s [m]	1535m
940w	1075m	1289w	1383m	1435m	1474m [k]	1458m
843s [j]	1018m [j]	1237m	1365w	1422w	1457m	1440m
	1000m [j]	1156w	1281w	1403w	1450m	1427m
	960w	1017m	1193s	1385m	1435m	1390m [l]
	935w	1001s [j]	1176w	1363w [l]	1422m	1278w
	840s [j]	935w	1118w	1270m	1384m	1243w
		840s	1065w	1193m	1363w	1145m [l]
			1015m	1175m	1285w	1125w
			1000m [j]	1145m [l]	1247w	1095w
			927w	1077m	1192s	1062m
			902w	1014m [j]	1080m	1028m
			865m	1000m [j]	1065m	1017m [j]
			835w	895w	1017m [j]	1000m [j]
			785s	865s [j]	1000m [j]	970m
			743w	835m	972m	880w
				723s	883m	860s [j]
					862s [j]	795m
					790s	765m

[a] R = C$_5$H$_5$Fe(CO)$_2$–; for conditions of measurement see the Experimental section. [b] C–H stretch of π-C$_5$H$_5$. [c] C–H stretch of alkanes. [d] CN stretch. [e] C≡O stretch. [f] N–H stretches and also an overtone or combination band. [g] C–H stretch of alkenes. [h] N–D stretches and also an overtone or combination band. [i] For solution spectrum in liquid sulphur dioxide bands at 3376m, 3202m, 2995w, 2950w, and C≡O stretches at 2028vs and 2065vs; the third, lower band assigned to a C≡O stretch in the mull spectra is absent from the solution spectra and is therefore presumably due to lattice effects. [j] π-C$_5$H$_5$ frequencies. [k] N–H bend. [l] N–D bend. [m] C=N stretch.

TABLE 2.

Proton magnetic resonance data.

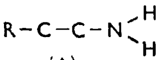
Compound and conditions of measurement §	Band posn. $\tau = 10$ *	Rel. intensity †	Multiplicity ‡	Sepn. between components (c./sec.)	Assignment
R(CH$_2$·CN) in CCl$_4$	5·10	5	1	--	C$_5$H$_5$
	9·10	2	1	—	–CH$_2$–
R(CHMe·CN) in CCl$_4$	5·10	5	1	—	C$_5$H$_5$
	7·76	1	4	app. *J* (H, Me) 6·8	tert. CH
	8·67	3	2	app. *J* (Me, H) 6·8	–CH$_3$
R(CH$_2$·CH$_2$·CN) in CCl$_4$	5·20	5	1	—	C$_5$H$_5$
	8·13	4	Complex band (14)		–CH$_2$·CH$_2$
[R(CH$_2$=C=NH)]$^+$	4·60	5	1	—	C$_5$H$_5$
SbCl$_6$$^-$ in liquid SO$_2$	4·93	2	1	—	=CH$_2$
	6·25	1	1	Broad	=N–H
	7·30		1	Broad	
[R(CH$_2$=C=ND)]$^+$	4·63	5	1	—	C$_5$H$_5$
SbCl$_6$$^-$ in liquid SO$_2$	4·96	2	1	—	=CH$_2$
[R(CHMe=C=NH)]$^+$	4·55	6	1	—	C$_5$H$_5$
SbCl$_6$$^-$ in liquid SO$_2$	4·70		Complex band		=C–H
	7·85	1	1	—	N–H
	8·10	3	2	app. *J* (Me, CH) 6·4	–CH$_3$
[R(CHMe=C=ND)]$^+$	4·53	6	1	—	C$_5$H$_5$
SbCl$_6$$^-$ in liquid SO$_2$	4·70		Complex band		=C–H
	8·10	3	2	app. *J* (Me, CH) 6·4	–CH$_3$

* Relative to SiMe$_4$ as internal standard. † Estimated to nearest whole number by determining areas rel. to π-C$_5$H$_5$ = 5. ‡ Where multiplicity occurs which may be described as first order spin–spin couplings the splittings are recorded as the apparent coupling constants (app. *J*). § R = C$_5$H$_5$Fe(CO)$_2$.

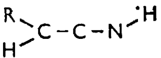
spectra show that the cations (II; R = H or Me) contain a π-cyclopentadienyl group, and the infrared spectra show strong bands which may be assigned to terminal carbonyl stretching frequencies. These bands are of ~50 cm.$^{-1}$ greater frequency than the carbonyl stretches of the neutral complexes (I). The increase is consistent with a higher oxidation state of the metal in the cations (II).[7] No band assignable to an *Fe*-H atom was found in the nuclear magnetic resonance spectra of the cations.

There are marked differences between the infrared spectra of the neutral complexes (I) and their protonated derivatives (II). Bands in the region 2200 cm.$^{-1}$ assigned to the C≡N stretch of the cyanoalkyl group in the spectra of the complexes (I) are absent from the spectra of the cations (II), and new bands are present, notably in the region 3100—3400 cm.$^{-1}$. Spectra of the deuterated cations (II) do not contain the latter bands, but new bands of similar appearance occur at 2600—2400 cm.$^{-1}$. The bands in the regions 3100—3400 and 2600—2400 cm.$^{-1}$ are assigned to N–H and N–D stretches, respectively. Similarly bands at about 1660s and 1470s cm.$^{-1}$ in the spectra of the protonated cations (II), which are shifted to about 1270 and 1145 cm.$^{-1}$ in the spectra of the deuterated derivatives, are assigned to N–H and N–D bending frequencies, respectively. Intensity measurements on the proton magnetic resonance spectra of the cations (II) show that only one proton is added to the neutral complexes (I). Differences between the spectra of the protonated and deuterated cations (II) show that only one deuterium atom is added to the neutral species and therefore that there is no further exchange of other protons on the cyanoalkyl or cyclopentadienyl group. Thus, from the above evidence it is reasonable to state that on protonation of the neutral complex (I; R = H or Me) the cyano-group is protonated, and that there is at least one proton attached to the nitrogen.

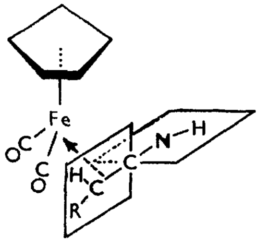
Geometry of the Protonated Cyanoalkyl Group.—The occurrence of at least two fundamental N–H stretches and bending frequencies in the infrared spectra of the cations (II) strongly suggests the presence of an amino-grouping in the protonated 1-cyanoalkyl groups. A structure such as (A) for the protonated cyanoalkyl group would be consistent with this evidence and the formal structure of the group would be R·C≡C–NH$_2$ which could form a π-bond to the metal by donating two electrons. The structure (A) is, however, incompatible with the proton magnetic resonance spectra. For example, the doublet nature of the band assigned to the methyl group in the protonated and the deuterated cation (II; R = Me) is difficult to assign for other than by proposing some spin–spin coupling with another hydrogen atom. Further, since only one deuterium atom is added on deuteration, an NHD group would be expected in the deuterated cations (II), yet there are no bands in the deuterated species which may be assigned to an N–H stretch.



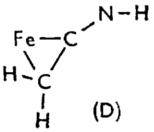
(A)



(B)



(C)



(D)

Although the infrared spectra were mostly determined on mulls, the spectrum of the cation (II; R = H) was also measured for liquid sulphur dioxide solutions. The spectra were practically identical for the mull and the solution, so that the cation (II; R = H) has essentially the same structure in both states; thus the infrared and the proton magnetic resonance spectra refer to the same cationic species.

In view of the above, it is necessary to prefer the nuclear magnetic resonance spectral evidence and to interpret the infrared spectra accordingly.

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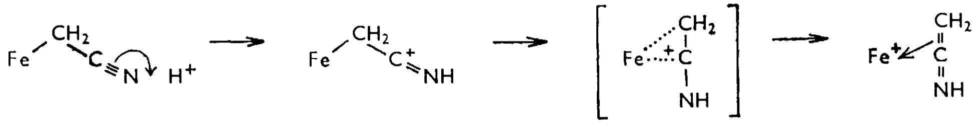
[7] Davison, Green, and Wilkinson, *J.*, 1961, 3172.

The nuclear magnetic resonance spectra of the deuterated and protonated cations (II; R = H or Me) are most readily understood if the protonated cyanoalkyl group has structure (B). Assignments of the spectra on this basis are given in Table 2. An anomaly, namely, that the spectrum of the ion (II; R = H) shows two broad bands assigned to the N–H hydrogen is discussed below. Before the infrared spectra can be assigned it is necessary to consider the spatial arrangement of the group (B) in relation to the metal. The cations are diamagnetic, as shown by the sharpness of the bands in the nuclear magnetic resonance spectra. In view of this and in order to retain the usual " rare-gas " configuration for the metal, it is necessary to postulate that the protonated cyanoalkyl group furnishes the iron with two electrons. By analogy with the manner of protonation of the metal–σ-allyl complexes (see below), and in view of the ease of reversibility of the protonation, a configuration such as (C) is proposed.

In the configuration (C) the H_2C–C group is assumed to bond to the iron as a two-electron ligand and to be held in a plane at right angles to a line from the iron to the C–C bond, as found in ethylene–metal π-complexes.[8] From steric considerations of the ketenimine group it follows that the N–H group may either have an " *endo* "- or an " *exo* "-position relative to the metal. Now, evidence for interaction of hydrogen with the metal and the cyclopentadienyl system, possibly akin to hydrogen bonding, has been presented for some ferrocene derivatives.[9] Therefore it is possible that hydrogen–metal interactions of the *endo*-proton within one molecule or hydrogen-bonding of the *exo*-proton between other molecules may occur. Calculations based on models show that the Fe–H (*endo*) distance in configuration (C) is about 3·0 Å. The presence of *endo*- and *exo*-isomers in approximately equal proportions, differentiated by effects such as described above, could account for the appearance of at least two N–H stretches and bending frequencies in the infrared spectra and the doublet nature of the N–H hydrogen absorption in the proton magnetic resonance spectrum of the cation (II; R = H). The strong bands at 1556 and 1565 cm.$^{-1}$ in the infrared spectra of the cations (II; R = H and Me), respectively, may be assigned to a C=N stretch.[10]

There remain further anomalies in the interpretation of the spectra. The N–H hydrogen of the cation (II; R = H) shows a doublet band in the proton magnetic resonance spectrum, which is interpreted by the postulate of *exo*- and *endo*-isomers. The two components of the band are broad, which may be due to the hydrogen interacting with the ^{14}N nucleus, or to a slow exchange of the hydrogen between the *exo*- and *endo*-positions. The N–H hydrogen of the cation (II; R = Me), however, shows a sharp singlet in the proton magnetic resonance spectrum and yet there are at least two fundamental N–H stretches in the infrared spectrum. This may be explained either by the assumption that the N–H hydrogen exchanges rapidly between the *exo*- and *endo*-positions, or that there is a dissociation equilibrium where the N–H bond is broken, for example: $BH^+SbCl_6^- \rightleftharpoons B + H^+SbCl_6^-$. It is possible that both exchange and dissociation take place. The difference in the proton magnetic resonance and the infrared spectra could then be due to the different time scales of the two measurements.

Discussion.—The mechanism of protonation may be considered to be analogous to that proposed for the protonation of the metal–σ-allyl systems,[2] namely:



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[8] See Coates, " Organometallic Compounds," Methuen and Co. Ltd., London, 2nd edn., 1960, pp. 339, 445.

[9] Trifan and Bachsai, *J. Amer. Chem. Soc.*, 1960, **82**, 5010.

[10] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen and Co., London, 2nd edn., 1958.

On the basis of this mechanism the 2-cyanoethyl complex would not be expected to undergo protonation, which is borne out by experiment. It is not possible to say from our evidence whether the H_2C–H group is bonded to the iron in a manner essentially analogous to that in ethylene–metal π-complexes, or whether there are two σ-bonds forming a 3-membered ring as in (D). A structure such as (D) would be highly strained. It is also conceivable that the protonated 1-cyanoalkyl group may form its bond to the metal through the C=N group. However, the proposal of bonding through the H_2C=C system is preferred on the grounds of the analogy between the protonation of σ-allyl and 1-cyanoalkyl complexes, the ease of reversibility of the protonation, and the difficulty of forming a more satisfactory interpretation of the spectra.

The structure proposed, therefore, is formally represented in (II), which shows the ketenimine forms of acetonitrile and propionitrile stabilised by complex-formation with the iron.

EXPERIMENTAL

Microanalyses were carried out by the Microanalytical Laboratory, Lensfield Road, Cambridge. Preparations, reactions, and purification were carried out under nitrogen or in a vacuum. Light petroleum was "AnalaR" material, of b. p. 30—40°. Analytical data are given in Table 3.

Dicarbonyl-(1-cyanoethyl)cyclopentadienyliron.—A solution of hydridodicarbonylcyclopentadienyliron (3 g.) in light petroleum (100 ml.), prepared as reported,[2] was treated with an excess of acrylonitrile (6 ml.) in tetrahydrofuran. After 2 hr. the solvent was removed under a vacuum and the red oily residue was purified by one of the following procedures. (*a*) Repeated chromatography of the residue on an alumina column made up in light petroleum, elution being with 5 : 1 light petroleum–ether. The deep yellow band which came after the red band of the other main product, namely, the binuclear complex $[C_5H_5Fe(CO)_2]_2$, was collected. (*b*) The reaction residue was extracted with 3N-hydrochloric acid, giving a deep yellow solution which was separated and then re-extracted with ether. (Neutralisation of the acid solution with calcium carbonate increased the efficiency of the re-extraction.) The ether solution was concentrated and chromatographed once, as described above. (*c*) The residue was sublimed in a vacuum at 80°, giving an orange-red sublimate which was dissolved in light petroleum and chromatographed as above.

TABLE 3.

		Found (%)					Required (%)				
Compound	M. p.	C	H	N	Fe	*M* *	C	H	N	Fe	*M*
$C_5H_5Fe(CO)_2(CH_2{\cdot}CN)$	123°	50·2	3·0	6·7	25·6	211	49·8	3·3	6·5	25·7	217
$C_5H_5Fe(CO)_2(CHMe{\cdot}CN)$	86—87	52·3	3·7	6·1	24·1	236	52·0	3·9	6·1	24·2	230
$C_5H_5Fe(CO)_2(CH_2{\cdot}CH_2{\cdot}CN)$	29·5	51·8	4·2	6·4	—	242	52·0	3·9	6·1	—	230
$[C_5H_5Fe(CO)_2(CH_2{=}C{=}NH)]^+SbCl_6^-$	—	19·6	1·6	2·5	9·6		19·6	1·5	2·5	10·1	—
$[C_5H_5Fe(CO)_2(CHMe){=}C{=}NH)]^+SbCl_6^-$	—	20·7	1·6	2·5	9·3		21·2	1·8	2·5	9·9	—
$[C_5H_5Fe(CO)_2(CH_2{=}C{=}NH)]_2{}^+PtCl_6{}^{2-},2H_2O$	—	23·3	2·0	2·9	—		24·6	2·3	3·2	—	—
$[C_5H_5Fe(CO)_2(CHMe){=}C{=}NH)]_2{}^{2+}PtCl_6{}^{2-},2H_2O$	—	26·2	2·5	3·2	—		26·5	2·7	3·1	—	—
$[C_5H_5Fe(CO)_2(CH_2{=}C{=}NH)]^+ClO_4^-$	—	33·8	2·9	4·3	—		34·1	2·5	4·4	—	—
$[C_5H_5Fe(CO)_2(CHMe){=}C{=}NH)]^+ClO_4^-,H_2O$	—	34·0	3·3	3·9	—		34·4	3·5	4·0	—	—
$[C_5H_5Fe(CO)_2(CHMe{=}C{=}NH)]^+CF_3{\cdot}CO_2^-,CF_3{\cdot}CO_2H$	—	36·6	2·4	3·1	—		36·6	2·7	3·1	—	—
$[C_5H_5Fe(CO)_2(CH_2{=}C{=}NH)]^+Cl^-,H_2O$	—	40·2	3·7	4·5	—		39·8	3·7	5·2	—	—

* Cryoscopic in dioxan.

The deep yellow eluates obtained after chromatography from the above purifications were evaporated to dryness, and the orange-red residue was finally recrystallised several times from light petroleum–ether, giving deep orange-yellow crystals (*ca.* 10%).

Dicarbonyl(cyanomethyl)cyclopentadienyliron.—Tetracarbonyldicyclopentadienyldi-iron[5] (10 g.) in tetrahydrofuran was stirred with an excess of 3% sodium amalgam for 1 hr. The resulting solution of the sodium salt $Na^+[C_5H_5Fe(CO)_2]^-$ was slowly added to an excess of chloromethyl cyanide (8 g.), and the mixture was stirred for 1 hr. The solvent and the excess of chloromethyl cyanide were removed under a vacuum, and the crude product was extracted several times with light petroleum. The extract was purified by procedure (*a*) described above. Final recrystallisation of the product from light petroleum affords orange-yellow crystals (*ca.* 10%).

Dicarbonyl(-2-cyanoethyl)cyclopentadienyliron.—The reaction between β-bromopropionitrile and the sodium salt $Na^+[C_5H_5Fe(CO)_2]^-$ was carried out as described above and the product was isolated in the same way. The pure product forms deep orange-yellow crystals (*ca.* 10%).

Protonation of the 1-*Cyanoalkyl Complexes.—Cation* (II) *salts.* A typical reaction is described. Pure dicarbonyl(cyanomethyl)cyclopentadienyliron (0·5 g.) in light petroleum (150 ml.) was treated with dry hydrogen chloride. The bright yellow precipitate formed was washed three times with petroleum by decantation, and, after being dried in a vacuum, was recrystallised from liquid sulphur dioxide–ether. The product formed yellow crystals (*ca.* 90%). The compound is moderately stable to atmospheric oxidation but is hygroscopic and readily forms a monohydrate. The chloride salt of the cation (II; R = Me) was prepared in an analogous manner. Both the chlorides are soluble in water, acetone, and tetrahydrofuran, and these solutions were used to prepare other salts.

Hexachloroplatinates and hexachloroantimonates. Strong aqueous solutions of the cation chlorides, prepared as described above, were treated with concentrated solutions of hexachloroplatinic or hexachloroantimonic acid, giving deep yellow precipitates, which were rapidly separated by filtration. After drying in a vacuum, the precipitates recrystallised from liquid sulphur dioxide, giving deep yellow crystals (*ca.* 80%). The hexachloroplatinates crystallised with water of crystallisation. Heating the pure hexachloroplatinates in a vacuum at 80° for 4 hr. resulted in partial decomposition. The hexachloroantimonates were anhydrous and moderately stable in air.

Perchlorates. Acetone solutions of the cation (II) chlorides, prepared as above, were treated with stoicheiometric amounts of anhydrous silver perchlorate in acetone. The precipitated silver chloride was removed and the filtrate concentrated. Addition of ether to the concentrate precipitated yellow crystals which were recrystallised from liquid sulphur dioxide (yield *ca.* 50%). The perchlorate of cation (II; R = H) was anhydrous and that of cation (II; R = Me) crystallised with one molecule of water of crystallisation.

Trifluoroacetate. Dicarbonyl-(1-cyanoethyl)cyclopentadienyliron (0·1 g.) in ether (2 ml.) was treated with a few drops of trifluoroacetic acid. Addition of light petroleum precipitated yellow crystals which were finally recrystallised from acetone–light petroleum–ether (yield *ca.* 70%). The product appeared to be unchanged when kept in air for several days.

Preparation of Deuterated Salts.—Deuterium chloride was prepared from deuterium oxide and titanium tetrachloride. Hexachlorodeuteroantimonic acid in D_2O was prepared by treating an excess of deuterium chloride in D_2O with antimony pentachloride. The pure 1-cyanoalkyl complexes (I) were dissolved in concentrated deuterochloric acid, and the resulting solution was treated with deuterium hexachloroantimonate. The yellow hexachloroantimonates were precipitated and the precipitate was extracted with liquid sulphur dioxide from which it was recrystallised three times (yield *ca.* 60%). The spectra of the products were determined.

Infrared Spectra.—Measurements were made with a Perkin-Elmer model 21 spectrometer. Neutral complexes were measured in solutions in carbon disulphide and carbon tetrachloride. The salts were determined as mulls in Nujol and hexachlorobutadiene, or on solutions in sulphur dioxide in a special cell.[11]

Conductivity Measurements.—Conductivities were determined by using ~10^{-3}M-solutions in nitrobenzene.

Compound	Concn. (10^{-3}M)	Λ
$[C_5H_5Fe(CO)_2(CH_2{:}C{:}NH)]^+ SbCl_6^-$	0·89	31·1
$[C_5H_5Fe(CO)_2(CHMe{:}C{:}NH]^+ SbCl_6^-)$	1·14	28·8
$[C_5H_5Fe(CO)_2(CH_2{:}C{:}NH)]^+ ClO_4^-$	0·65	27·1

p*K Determination.*—Dicarbonyl(cyanomethyl)cyclopentadienyliron (132 mg.), dissolved in distilled water (75 ml.), was titrated with standard acid. A plot of pH against volume of acid did not show an inflection, presumably since the pK_b of the cyano-complex is comparable with that of water. An estimate of pK_b of the cyano-complex (I; R = H) was made therefore by determining the pH of an aqueous solution, and found to be 13—14.

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[11] Hoyer, *Z. Electrochem.*, 1960, **64**, 631.

High-resolution Nuclear Magnetic Resonance Spectra.—Measurements were made on a Perkin-Elmer spectrometer at 40 Mc./sec. The data and conditions of measurement are given in Table 2.

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