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CHEMISTRY OF THE CYCLOPENTADIENYL METAL CARBONYLS
IV.[*] NEW PERFLUOROALKYL DERIVATIVES OF COBALT[**]

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INTRODUCTION

In an earlier paper[3] we reported cationic derivatives prepared from $C_5H_5Co(CO)C_3F_7I$, a halogen acceptor, and an electron pair donor. We have now extended our work with this perfluoroalkylcobalt system and wish to report the preparation and characterization of other new types of perfluoroalkylcobalt complexes.

EXPERIMENTAL

The preparation of $C_5H_5Co(CO)C_3F_7I$ is described in the literature[4]. Infrared spectra were recorded on a Beckman IR-10 grating spectrophotometer using nujol mulls in most cases. This data is tabulated in Table 1. ^{19}F NMR spectra were run on a Varian H.R.-60 spectrometer at 56.4 Mc and are referenced to CCl_3F (0.0 ppm) (Table 2). The values reported are the average of three calibrated traces. Microanalyses were performed by the A. Bernhardt Microanalytical Laboratory, Mülheim, Germany.

TABLE 1

INFRARED SPECTRA OF PERFLUOROALKYLCOBALT COMPOUNDS IN NUJOL MULLS

$C_5H_5Co(CO)C_3F_7Cl$
3090(w); 2080(s); 1415(w); 1315(s); 1235(m); 1210(s); 1200(s); 1185(s); 1160(s); 1085(s); 1045(m); 1010(m); 945(w); 880(w); 835(m); 825(sh); 800(m); 715(s); 658(m);670(w); 638(w); 608(w); 492(w); 482(w); 458(w) cm^{-1}

$C_5H_5Co(CO)C_3F_7Br$
3100(w); 2080(s); 1415(w); 1315(s); 1235(sh); 1212(s); 1200(s); 1185(sh); 1163(s); 1088(s); 1062(w); 1044(m); 1010(m); 950(w); 880(w); 837(m); 827(m); 800(m); 815(s); 658(m); 620(w); 530(w); 510(w); 492(w); 482(sh); 460(w) cm^{-1}

$[C_5H_5CoC_3F_7CN]_x$
3130(w); 2180(m); 1420(w); 1315(s); 1213(s); 1184(s); 1152(s); 1080(s); 1060(w); 1030(s); 1015(sh); 895(w); 860(w); 833(m); 820(m); 800(m); 715(s); 654(m) cm^{-1}

$[C_5H_5CoC_3F_7SCN]_3$
3100(w); 2267(s); 1414(w); 1317(s); 1212(s); 1190(s); 1180(sh); 1157(m); 1085(m); 1030(m); 1010(m); 838(m); 825(m); 800(m); 658(m); 570(w); 530(w) cm^{-1}

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[*] For previous paper in this series see ref. 1.

[**] Presented in part in ref. 2.

TABLE 1 (continued)

$[C_5H_5CoC_3F_7I]_2$
1410(w); 1320(m); 1230(s); 1215(s); 1190(s); 1165(s); 1152(s); 1110(w); 1072(s); 1020(s); 995(m); 990(sh); 940(w); 870(w); 832(m); 820(m); 800(m); 620(w); 565(w); 530(w) cm^{-1}

$[(n\text{-}C_4H_9)_4N]^+[C_5H_5CoC_3F_7I_2]^-$
1415(w); 1313(s); 1215(s); 1275(s); 1147(s); 1070(m); 1018(s); 998(w); 972(m); 925(w); 875(w); 835(m); 805(sh); 795(m); 712(s); 655(m); 560(w); 528(w) cm^{-1}

$[(n\text{-}C_4H_9)_4N]^+[C_5H_5CoC_3F_7(CN)_2]^-$
1485(m); 1312(m); 1214(s); 1181(s); 1150(m); 1075(m); 1025(s); 987(m); 985(w); 838(m); 825(m); 798(m); 715(s); 655(m); 530(w); 455(w); 415(w) cm^{-1}

$[NH_4]^+[C_5H_5CoC_3F_7IF]^-$
3370(m); 3345(w); 327(w); 3180(vw); 3150(vw); 3120(vw); 3090(vw); 1600(m); 1412(m); 1320(m); 1258(s); 1230(sh); 1210(s); 1195(s); 1182(s); 1150(s); 1080(m); 1025(m); 1215(sh); 980(s); 885(w); 832(s); 825(m); 800(m); 720(m); 655(m); 530(w) cm^{-1}

TABLE 2

^{19}F NMR OF PERFLUOROALKYLCOBALT COMPOUNDS[a]

Compound	*α-CF_2*		*β-CF_2*		*CF_3*	
	[b]	*Multiplicity*	[b]	*Multiplicity*	[b]	*Multiplicity*
$C_5H_5Co(CO)C_3F_7Br$[d]	62.6	broad singlet	114.3	singlet	78.9	broad singlet
$C_5H_5Co(CO)C_3F_7Cl$[d]	65.4	broad singlet	114.5	singlet	89.3	triplet, $J=10.4$ c/s
$(C_5H_5CoC_3F_7SCN)_3$[d]	76.9 79.8	broad singlet broad singlet	115.9[c] 116.1	singlet singlet	78.6[c] 78.8	triplet, $J=10.1$ c/s triplet, $J=10.1$ c/s
$C_5H_5CoC_3F_7I_2^-$[d] $(C_4H_9)_4N^+$	64.9	broad singlet	110.7	singlet	78.6	triplet, $J=10.8$ c/s
$C_5H_5CoC_3F_7(CN)_2^-$[d] $(C_4H_9)_4N^+$	60.6	quartet, $J=11.0$ c/s	114.5	singlet	78.6	triplet, $J=11.0$ c/s
$C_5H_5CoC_3F_7IF^-$[e] NH_4^+	78.9	triplet, $J=78$ c/s	114.2 115.2	doublet, $J=6.1$ c/s doublet, $J=6.1$ c/s	78.9	triplet, $J=12.5$ c/s

[a] Run on a Varian HR-60 spectrometer at 56.4 m.c. [b] Chemical shifts in ppm are upfield from CCl_3F (standard) and are averages of three calibrated traces. [c] Intensity of the first peak is twice that of the second peak in this compound. [d] solution in benzene. [e] solution in methanol.

Preparation of $C_5H_5Co(CO)C_3F_7Br$

To a solution of 0.448 g (1.0 mmole) $C_5H_5Co(CO)C_3F_7I$ in 20 ml benzene under nitrogen was added 9.0 ml of a 0.2 *M* $AgClO_4$ solution in benzene (1.8 mmoles). The reaction mixture was stirred for two hours at room temperature during which time a precipitate of AgI formed and the solution turned red. Then 18.0 ml of a 1.0% solution of NaBr in methanol (1.8 mmoles) was added and the reaction allowed to continue for 4h. The reaction mixture was filtered and the solvent evaporated from the filtrate. The crude residue was dissolved in benzene and chromatographed on silica gel using benzene as an eluent. Four bands were observed to elute. The first band was believed to be a halogen bridged dimer $[(C_5H_5CoC_3F_7X)_2]$ on the basis of its rate of elution and its color, but was present in too small amount to allow identification. The fourth band was also in too small an amount to be identified. The second band was identified as the starting material $C_5H_5Co(CO)C_3F_7I$. The product $C_5H_5Co(CO)C_3F_7Br$ eluted as the third band. It was crystallized from benzene/petroleum ether (b.p. 90–100°)* (0.163 g, 41% yield). (Found: C, 26.95; H, 1.27; F, 33.01; mol. wt.,** 405. $C_9H_5BrCoF_7O$ calcd.: C, 26.95; H, 1.26; F, 33.17%; mol. wt., 401.)

Preparation of $C_5H_5Co(CO)C_3F_7Cl$

A solution of 0.2 *M* $AgClO_4$ in benzene (7.5 ml, 1.5 mmoles) was added to a solution of 0.448 g (1.0 mmole) $C_5H_5Co(CO)C_3F_7I$ in 20 ml of benzene under a nitrogen atmosphere. After stirring for 2 h, 16.0 ml of a 0.5% solution of NH_4Cl in methanol (1.5 mmoles) was added, and stirring continued for one hour. The solution was then filtered and the filtrate evaporated. The residue was recrystallized twice from a benzene/petroleum ether mixture by slow evaporation of the solvent under nitrogen (0.193 g, 53.3% yield). (Found: C, 30.42; H, 1.59; F, 37.17; mol. wt., 389. $C_9H_5ClCoF_7O$ calcd.: C, 30.32; H, 1.41; F, 37.30%; mol. wt., 357.)

Preparation of $(C_5H_5CoC_3F_7SCN)_3$

A solution of 0.2 g (0.45 mmole) $C_5H_5Co(CO)C_3F_7I$ in 10 ml benzene was treated with 2.5 ml of a 0.2 *M* solution of $AgClO_4$ in benzene (0.5 mmoles) under nitrogen. To this was added 5.0 ml of a 0.1 *M* KSCN solution in methanol (0.5 mmoles). The reaction was allowed to proceed at room temperature for 2 h. The solution then was filtered, the solvent evaporated, and the crude product chromatographed on a silica gel column using benzene as eluent. The first band off the column was collected and evaporated to dryness. Purification of the material obtained from this band was effected by crystallization from benzene/petroleum ether; 0.0948 g of brown crystalline $[C_5H_5CoC_3F_7SCN]_3$ was obtained (60% yield). (Found: C, 30.74; H, 1.60; F, 38.05; mol. wt., 1082. $C_{27}H_{15}Co_3F_{21}N_3S_3$ calcd.: C, 30.78; H, 1.44; F, 37.88%; mol. wt., 1053.)

Two other products eluted from the chromatographic column with 30% methanol in benzene. These materials were present in too small an amount to allow identification. However, the necessity to elute with methanol is characteristic of anionic products.

Preparation of $(C_5H_5CoC_3F_7CN)_x$

This reaction was carried out using the procedure outlined in the synthesis of $(C_5H_5CoC_3F_7SCN)_3$, using 0.2 g (0.45 mmoles) $C_5H_5Co(CO)C_3F_7I$, 2.5 ml of a 0.2 *M* $AgClO_4$ solution in benzene (0.5 mmoles), followed by addition of 5.0 ml of a

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* This petroleum ether fraction was used throughout this work. No subsequent mention of the boiling range will be made in this section.

** Molecular weight measurements were made using a Mechrolab Osmometer, on approximately 0.01 molal solutions in benzene.

0.1 *M* KCN solution in methanol (0.5 mmoles). The crude product was chromatographed on silica gel, and the first band collected, evaporated and crystallized twice from a benzene/petroleum ether mixture, giving an orange powder (0.0949 g, 65% yield). (Found: C, 33.87; H, 1.82; F, 41.49. $C_9H_5CoF_7N$ calcd.: C, 33.88; H, 1.58; F, 41.68%.) An approximate molecular weight of this relatively insoluble material gave a value of 1450, corresponding to $x = 4.55$ in the formula $(C_5H_5CoC_3F_7CN)_x$.

Preparation of $[C_5H_5CoC_3F_7I]_2$

A solution of 0.224 g (0.5 mmole) $C_5H_5Co(CO)C_3F_7I$ in 100 ml methanol was allowed to stand for 24 h at room temperature. The solvent was removed by evaporation and the residue chromatographed on a silica gel column using benzene as the eluent. The product was found in the first band eluting from the column. It was crystallized from benzene/petroleum ether by evaporation of benzene from the solution, giving a dark purple, crystalline product (0.082 g, 39% yield). (Found: C, 23.05; H, 1.41; F, 31.73; mol. wt., 628, 622. $C_{16}H_{10}Co_2F_{14}I_2$ calcd.: C, 22.88; H, 1.20; F, 31.67%; mol. wt., 840.

This compound could also be formed by the thermal decomposition of $C_5H_5Co(CO)C_3F_7I$ at 80°/0.1 mm Hg and can be reconverted to $C_5H_5Co(CO)$-C_3F_7I by a reaction with carbon monoxide at 1200 psi at room temperature in benzene solution (54% conversion, 98% yield accounting for unreacted dimer, after 20 h).

Preparation of $[C_5H_5CoC_3F_7I_2]^-[(n\text{-}C_4H_9)_4N]^+$

A solution of 0.4 g (0.476 mmoles) $[C_5H_5CoC_3F_7I]_2$ in 20 ml benzene and 20 ml methanol was treated with 0.7 g (1.9 mmoles) of $(n\text{-}C_4H_9)_4NI$ at room temperature for 1 h. The solvent was evaporated and the unreacted $(n\text{-}C_4H_9)_4NI$ removed by washing the crude product with distilled water. The product was extracted with benzene and precipitated from a benzene/octane solution by evaporation of benzene from the solution, to give a black, crystalline product (0.46 g, 58.4% yield). (Found: C, 36.34; H, 5.22; F, 17.16. $C_{24}H_{41}CoF_7I_2N$ calcd.: C, 36.51; H, 5.25; F, 16.85%.)

Preparation of $[C_5H_5CoC_3F_7(CN)_2]^-[(n\text{-}C_4H_9)_4N]^+$

A solution of 0.4 g (0.476 mmoles) $[C_5H_5CoC_3F_7I]_2$ in 40 ml benzene was treated with 40 ml of a saturated KCN solution in methanol for 5 h at room temperature with agitation. The solvent was evaporated, yielding a yellow solid. The solid was taken up in methanol, benzene added, and the methanol evaporated, precipitating the unreacted KCN. This solution was filtered and the crude $[C_5H_5CoC_3F_7$-$(CN)_2]^-K^+$ separated from a benzene/octane solution as a yellow oil on evaporation of the solvent. This oil was dissolved in 100 ml distilled water and 0.44 g (1.2 mmoles) n-butylammonium iodide added. The water was removed by evaporation, leaving a yellow solid which was separated from the KI and excess n-butylammonium iodide by extraction with benzene and subsequent filtration. The filtrate was dried over $MgSO_4$, refiltered, the solvent removed by evaporation, and the product precipitated from ether/octane solution by evaporation of the ether, yielding a yellow oil. The remaining octane was removed by evaporation at 0.1 mm Hg. The product crystallized at −20°; it was recrystallized twice from an ether/octane mixture (0.34 g, 60.7% yield). (Found: C, 53.25; H, 7.19; F, 22.45; N, 7.33. $C_{26}H_{41}CoF_7N_3$ calcd.: C, 53.14; H, 7.05; F, 22.63; N, 7.15%.)

Preparation of $[C_5H_5CoC_3F_7IF]^-[NH_4]^+$

A solution of 0.2 g (0.238 mmole) $[C_5H_5CoC_3F_7I]_2$ in 100 ml methanol was treated with 0.5 g (13.5 mmole) NH_4F for 4 h at room temperature with constant agitation. The solvent was removed by evaporation and the product crystallized from benzene/petroleum ether by evaporation of the benzene from the solution. The purple-bronze crystals were filtered and allowed to stand in 500 ml of petroleum ether for 16 h to remove the final traces of unreacted starting material. Filtration then gave pure product (0.152 g, 59% yield). (Found: C, 21.26; H, 2.04; Co, 13.04; F, 33.07; I, 27.68; N, 3.17. $C_8H_9CoF_8IN$ calcd.: C, 21.02; H, 1.99; Co, 12.90; F, 33.26; I, 27.77; N, 3.06%.)

This material also prepared by the reaction of $C_5H_5Co(CO)C_3F_7I$ with NH_4F under exactly the same conditions as above, but with slightly lower yields (53 %).

DISCUSSION

The reaction of $AgClO_4$ and $C_5H_5Co(CO)C_3F_7I$ in benzene[3] proceeds with slow precipitation of AgI from the solution, leaving a moisture sensitive, red solution believed to contain the complex $C_5H_5Co(CO)C_3F_7OClO_3$[*]. We did not attempt to characterize this compound but were able to make use of it as an intermediate for the synthesis of other cobalt compounds. Reactions of this material with methanolic solutions of NaBr or NH_4Cl yielded the compounds $C_5H_5Co(CO)C_3F_7X$ ($X = Br$, Cl respectively). The reactions leading to these products are presumably the following equilibria:

$$(1)\quad C_5H_5Co(CO)C_3F_7I + AgClO_4 \rightleftharpoons C_5H_5Co(CO)C_3F_7OClO_3 + AgI\downarrow$$

$$(2)\quad C_5H_5Co(CO)C_3F_7OClO_3 + X^- \rightleftharpoons C_5H_5Co(CO)C_3F_7X + ClO_4^-$$

In the reaction of $C_5H_5Co(CO)C_3F_7OClO_3$ and the thiocyanate ion a monomeric compound was not obtained. Instead the reaction proceeds to give a trimer $(C_5H_5CoC_3F_7SCN)_3$ in which the thiocyanate group serves as the bridging unit. This bridging is presumably through the nitrogen and sulfur ends of the molecule (Fig. 1a) rather than through the sulfur atom only (Fig. 1b) since the infrared spectrum showed no frequency assignable to a free C≡N stretching mode. The thiocyanate group is known to serve such a bridging function in many other systems (see the review in ref. 5).

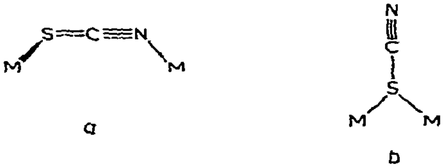

Fig. 1. Possible bridging structures for the thiocyanate group.

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[*] Extreme caution in such reactions which might lead to organometallic σ-perchlorates is recommended because such materials can be extremely dangerous, especially in the solid state. We have not attempted to isolate these postulated reaction intermediates here and have worked generally on millimolar scale. We recommend extreme caution if the scale of the reaction is to be increased or if any attempt to obtain the solid σ-perchlorate is made. In connection with other work we have experienced one explosion of a milligram sample of pure, crystalline $C_5H_5Fe(CO)_2OClO_3$.

The ^{19}F NMR spectrum of this complex consists of two sets of α-CF_2 and β-CF_2, and CF_3 resonances of relative intensities 2:1, indicating that one of the three C_3F_7 groups in this trimer was dissimilar to the other two. This dissimilarity probably arises from the geometry imposed on the system which presumably contains a nonplanar $Co_3(SCN)_3$ unit.

In the reaction of KCN and $C_5H_5Co(CO)C_3F_7OClO_3$ the product was a polymeric material $(C_5H_5CoC_3F_7CN)_x$, where x, by molecular weight measurements, was shown to be approximately 4.5. Since the CN group must bridge in a linear manner, a polymeric species involving such a group is not unexpected.

In several of the reactions mentioned previously the new complex $[C_5H_5CoC_3F_7I]_2$, dimeric via iodine bridges, was isolated as one product. The existence of such a compound is certainly to be expected, and in fact it is surprising that it was not reported earlier. It has its analogy in the dimeric $[R_FFe(CO)_3I]_2$ complexes[6] which are formed from $R_FFe(CO)_4I$ compounds simply by heating.

In fact we have now shown that both $C_5H_5Co(CO)C_3F_7I$ and $(C_5H_5CoC_3F_7I)_2$ are obtained from the reaction of $C_5H_5Co(CO)_2$ and C_3F_7I, in contrast to the previous report[4]. The relative amount of each product depends upon the temperature, and at the low temperatures at which the reaction is usually run the yield of the latter substance is small and observable only if the crude product is chromatographed. The proportion of this substance is greater if higher reaction temperatures are employed. The dimer was shown to be a product of thermal degradation of $C_5H_5Co(CO)C_3F_7I$. The dimer can be recarbonylated to $C_5H_5Co(CO)C_3F_7I$ under carbon monoxide pressure.

$$2\ C_5H_5Co(CO)C_3F_7I \rightleftharpoons (C_5H_5CoC_3F_7I)_2 + 2CO$$

In reactions of halide, cyanide, or thiocyanate ions with $C_5H_5Co(CO)C_3F_7OClO_3$ we sometimes observed substances which appeared to be ionic. On chromatography, such materials could be eluted from silica gel with methanol. The reactants present suggested that these products might reasonably be formulated as halo- or cyanometallates. These observations prompted investigation of possible syntheses of anionic perfluoroalkylcobalt complexes.

We chose to attempt the reaction of $C_5H_5Co(CO)C_3F_7I$ or $(C_5H_5CoC_3F_7I)_2$ with iodide or cyanide ion in order to prepare the expected anionic complexes $C_5H_5CoC_3F_7X_2^-$, (X = I, CN) in reasonable amounts. This type of reaction is similar to that used recently to prepare halocarbonylmetallate ions of the chromium group metals $[M(Co)_5X^-$, M = Cr, Mo, W$]$[7] and dihalocarbonylmanganate anions $[Mn(CO)_4XY^-$, X, Y = Cl, Br, I$]$[8,9], and has also been used to prepare an acetyliodo tetracarbonylmanganate anion[10] $CH_3COMn(CO)_4I^-$. The reactions in methanol proceed rapidly at room temperature to give the products $C_5H_5CoC_3F_7X_2^-$ (X = I, CN) which were eventually isolated as tetrabutylammonium salts. It is interesting to note that no carbonyl insertion into the cobalt–perfluoroalkyl bond has occurred. This contrasts with the previous cited work on acetyliodotetracarbonylmanganate anion[10] but is more or less in accord with other observations on fluoroalkyltransition metal complexes[11].

There have been only a few reports of other alkyl-, acyl- or fluoroalkylcarbonylmetallate anions previous to this work. Fischer and Maasböl[12] report the isolation of the benzoylpentacarbonylmetallate anions of the chromium group metals. A number of alkyl-[13] and fluoroalkyl-[14]pentacyanocobaltate derivatives have recently been prepared.

The ^{19}F NMR spectra of the anionic perfluoroalkylcobalt complexes, and of the other reported derivatives $C_5H_5Co(CO)C_3F_7X$, were quite similar to those of other C_3F_7-transition metal complexes reported[11]. These values are listed in Table 2. Three sets of peaks corresponding to α- and β-CF_2 and the CF_3 group were observed. The latter two resonances were fairly consistent in position (~114 ppm and 80 ppm respectively from CCl_3F), and the CF_3 resonance usually had a triplet structure due to a $J(\alpha-\gamma)$ coupling of approximately 10 c/s. The α-CF_2 resonance was rather broad due to relaxation caused by the cobalt quadrupole moment however, so that the expected quartet splitting was seldom resolved.

The ionic compound $NH_4^+C_5H_5CoC_3F_7IF^-$, related to the above anionic complexes, arose unexpectedly in another reaction. Attempting to prepare the compound $C_5H_5Co(CO)(C_3F_7)F$ we investigated the reaction of $C_5H_5Co(CO)$-$C_3F_7OClO_3$ and ammonium fluoride. From this reaction the anionic complex in the form of the ammonium salt was obtained. Later investigation showed that this compound could be obtained from $C_5H_5Co(CO)C_3F_7I$ or $(C_5H_5CoC_3F_7I)_2$ rather than from the perchlorate.

This unusual complex was soluble in methanol and acetone (to a lesser extent) and slightly soluble in benzene. It was insoluble in saturated petroleum solvents and most surprisingly for an ammonium salt, it was quite insoluble in water. This latter fact and the unusual ^{19}F NMR spectrum observed for this compound proved most puzzling features, though the analytical data leave no doubt about its composition.

The ^{19}F NMR is sketched schematically in Fig. 2. The spectrum consists of two major patterns of peaks near 78.9 ppm and 114.7 ppm, upfield from CCl_3F standard. The high field resonance consists of two doublets separated by 59 c/s, each doublet being split by 6.1 c/s. The pattern at lower field consists of two overlapping triplets of unequal intensity. One triplet $\delta = 78.9$ ppm, $J(\alpha-\gamma) = 12.5$ c/s is similar to the CF_3 absorptions in other C_3F_7 compounds, and reasonably assigned to this group in this compound. A second triplet, whose center peak is coincident with the same peak in the former pattern ($\delta = 78.9$ ppm) has a splitting value $J = 78$ c/s.

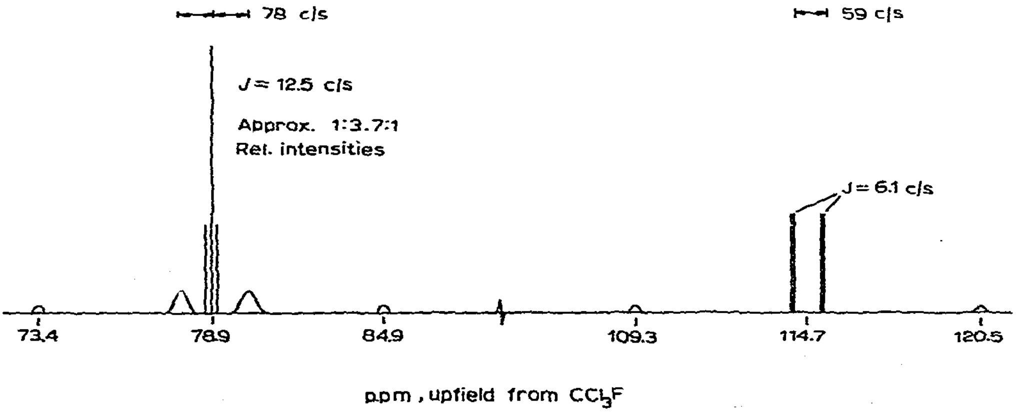

Fig. 2. ^{19}F NMR spectrum of $C_5H_5CoC_3F_7IF^-NH_4^+$.

In addition to these peaks, two very weak lines symmetrically placed at about 327 c/s on either side of each of the above patterns are observed. These lines appear reproducibly but their low intensity and broadness do not allow us to observe if any splitting occurs.

The physical and spectral properties of this compound suggest that the best formulation for this compound might involve a strongly held cation–anion pair; one possible structure is shown in Fig. 3. Strong hydrogen bonding in addition to the normal electrostatic attraction of the cation and anion might account for the insolubility of this substance in water. Assuming this model, then the second triplet at 78.9 ppm would be assignable to the α-CF_2 group which is strongly coupled to two of the ammonium protons. The resonance at 114.7 ppm is in the normal region for a β-CF_2 and assignable to this group. The larger doublet splitting could result from coupling of the fluorine bonded to cobalt (a 1–3 splitting in fluorocarbons sometimes being rather large) the further 6.1 c/s coupling might come from one proton of the ammonium group in close proximity to this group.

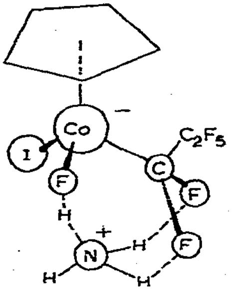

Fig. 3. Proposed structure of $C_5H_5CoC_3F_7IF^-NH_4^+$.

It is difficult to predict the pattern expected for the fluorine bonded to cobalt. Perhaps it would not be seen at all, the resonance been very broad due to the quadrupole broadening due to the cobalt atom. Alternatively the small peaks observed in the spectrum might be part of a pattern associated with this fluorine, perhaps even coupled with the cobalt nucleus (spin = 7/2).

A proton NMR spectrum of this compound showed only the C_5H_5 resonance at 7.33 τ. The ammonium proton resonance was not observed but this is not unexpected since N-H protons in assymmetrically substituted nitrogen compounds are often broadened to the extent of not being observed because of the nitrogen quadrupole moment[15].

SUMMARY

New compounds of the formula $C_5H_5Co(CO)C_3F_7X$ (X = Br, Cl) can be prepared from sodium bromide or chloride and $C_5H_5Co(CO)C_3F_7OClO_3$, the latter reagent being prepared *in situ* from $C_5H_5Co(CO)C_3F_7I$ and $AgClO_4$ in benzene. A similar reaction with sodium cyanide or sodium thiocyanate did not give the monomeric cyanide or thiocyanate compounds; from the thiocyanate reaction a trimer $[C_5H_5CoC_3F_7SCN]_3$ was formed, and from the cyanide ion reaction the product obtained was a polymeric species $[C_5H_5CoC_3F_7CN]_x$ ($x \sim 4.5$). The structures of

these two species involve bridging CN and SCN groups. A dimeric halogen bridge species $[C_5H_5CoC_3F_7I]_2$ is also described; this material is interconvertible with $C_5H_5Co(CO)C_3F_7I$ by the equilibrium:

$$2\ C_5H_5Co(CO)C_3F_7I \rightleftharpoons 2\ CO + (C_5H_5CoC_3F_7I)_2$$

Several ionic compounds containing perfluoropropyl groups are formed in reactions of $C_5H_5Co(CO)C_3F_7I$ or $[C_5H_5CoC_3F_7I]_2$ and $(C_4H_9)_4N^+I^-$, KCN, or $NH_4^+F^-$. These compounds contain anions of the general formula $C_5H_5Co\text{-}C_3F_7(X,Y)^-$ [$X,Y = I_2$, $(CN)_2$, IF] and arise from displacement of a carbonyl or iodine bridge by the halide or cyanide anion.

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