

basis we obtain for the heat of the complete transition -2740 ± 200 cal. (monomer mole) $^{-1}$. Similarly a value of -1800 ± 250 cal. (monomer mole) $^{-1}$ is obtained from the data summarized in Fig. 3 for the heat of the transition at 10°

TABLE II
EXTINCTION COEFFICIENT OF POLY A IN 0.1 M KCl

Temp., °C.	pH	$\epsilon_{259} \times 10^{-4}$, $M^{-1} \text{ cm.}^{-1}$	Helix, % ^a
10	4.00	0.760	100 (assumed)
25	4.00	.760	100 (assumed)
10	7.00	.944	58.5
25	7.00	1.010	43.5
40	7.00	1.085	26.5
80	7.00	1.202	0 (assumed)

^a NOTE ADDED IN PROOF.—A correction has not been applied for the effect of protonation in lowering the extinction coefficient of the monomer and presumably also of the polymer. When this effect is included, the estimated values of the helical content are raised about 3% and the calculated heats are unchanged within the experimental errors cited above.

The above interpretation of the poly A data is weakened by the fact that there is less experimental justification for the assumption that poly A exists in only one ordered conformation than there is in the case of the 1:1 poly (A + U) complex.

The heat of the poly A transition can be employed in conjunction with the apparent percentage of helical structure given in Table II to evaluate on a tentative basis corrected heats for the formation of helical poly (A + U) from two random coil polymers. These corrected heats are given in the third row of Table I. The correction at 40° was calculated using the value -3680 cal. (monomer mole) $^{-1}$ for the poly A transition, derived on the assumption of a constant change in apparent heat capacity in the transition of -60 cal. deg. $^{-1}$ (monomer mole) $^{-1}$. The uncertainty limits given in Table I include the experimental uncertainty in the corrections applied. The corrected heats are plotted in Fig. 1 (filled circles), and extrapolate to a value of approximately -8700 cal. (mole of base pairs) $^{-1}$ at the melting temperature of poly (A + U).

The data presented in this paper for poly (A + U) would lead to values of 3 to 4 kcal. per hydrogen bond if all of the observed heat changes accompanying polynucleotide helix formation were attributed to hydrogen bonding between the base pairs. Values of 1–2 kcal. are usually estimated for hydrogen bonds of the types occurring in polynucleotides in aqueous solution. This work, therefore, lends support to the view that forces other than those due to hydrogen bonds are involved in the stabilization of polynucleotide helices.

In earlier work¹⁷ the heats of the acid denaturation of salmon testes DNA in 0.1 M NaCl at 5° , 25° and 40° have been measured calorimetrically. At 25° it was found that 4880 cal. (mole of base pairs) $^{-1}$ was absorbed when the pH was lowered from 7 to 2.8 or lower; that is, when the native helical conformation was changed to that of random coils. If we assume, with DeVoe and Tinoco,¹⁸ that the heats of ionization of the bases in denatured DNA are the same as found¹⁶ for the 5'-deoxymononucleotides, and take the base pairs in the DNA to be 59.2% adenine-thymine pairs, we may compute the heat for the hypothetical process DNA (denatured, pH 7) = DNA (native, pH 7) to be -8260 cal. (mole of base pairs) $^{-1}$. This value is slightly lower than the value -8700 found for the coil to helix transition in poly (A + U) at its melting temperature but considerably higher than the value -5780 cal. found for the interaction of poly A and poly U at 25° .

The data presented in this paper together with the data of Steiner and Kitzinger⁵ suggest that for poly (A + U) the heat of transition at T_m is independent of the value of T_m . For the same to hold with respect to the heats of denaturation of DNA it would be necessary for the ionizations of the bases in denatured DNA to be accompanied by a decrease in heat capacity of approximately 100 cal. deg. $^{-1}$ mole $^{-1}$. Lewin and Tann¹⁹ found $\Delta C_p = -110$ cal. deg. $^{-1}$ mole $^{-1}$ for adenine ionization. From our data on poly A we estimate $\Delta C_p = -80$ cal. deg. $^{-1}$ mole $^{-1}$ for the ionization of adenine residues in helical poly A.

(18) H. DeVoe and I. Tinoco, Jr., *J. Mol. Biol.*, **4**, 500 (1962).

(19) S. Lewin and N. W. Tann, *J. Chem. Soc.*, 1466 (1962).

[CONTRIBUTION FROM THE MELLON INSTITUTE, PITTSBURGH, PENNSYLVANIA]

Reactions of Alkali Metal Derivatives of Metal Carbonyls. II. Reactions between Acid Chloride Derivatives and the Sodium Derivative of Cyclopentadienyliron Dicarboxyl¹

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RECEIVED DECEMBER 21, 1962

The iron complexes $C_5H_5Fe(CO)_2CO(CH_2)_nCOFe(CO)_2C_5H_5$ ($n = 3$ and 4), $C_5H_5Fe(CO)_2(CH_2)_3COFe(CO)_2C_5H_5$ and $C_5H_5Fe(CO)_2CO(CF_2)_3COFe(CO)_2C_5H_5$ have been prepared as stable orange crystalline solids by reactions between $NaFe(CO)_2C_5H_5$ and the appropriate acid chloride derivative. Reaction between the carbonyl chloride derivatives R_2NCOCl ($R = CH_3$ and C_2H_5) and $NaFe(CO)_2C_5H_5$ yields the relatively unstable orange volatile crystalline solids $R_2NCOFe(CO)_2C_5H_5$ ($R = CH_3$ and C_2H_5). Reaction between $[C_5H_5Fe(CO)_2]_2$ and thiolbenzoic acid yields the thiolbenzoate $C_6H_5C(O)SFe(CO)_2C_5H_5$ as a stable orange crystalline solid.

Although several compounds of general formula $RFe(CO)_2C_5H_5$ ($R = CH_3$, C_2H_5 , etc.) have been prepared by the reaction between alkyl halides and the sodium salt $NaFe(CO)_2C_5H_5$ ² and several compounds of general formula $C_5H_5Fe(CO)_2(CH_2)_nFe(CO)_2C_5H_5$ by the reactions between certain polymethylene dibromides and $NaFe(CO)_2C_5H_5$,¹ the reactions between acid chlorides and $NaFe(CO)_2C_5H_5$ have been little investigated. The only reported example of such a

reaction is the reaction between $NaFe(CO)_2C_5H_5$ and acetyl chloride to give the acetyl derivative $CH_3COFe(CO)_2C_5H_5$.³ The experimental details of this reaction, however, do not yet seem to have been described. This paucity of acyl derivatives of general formula $RCOFe(CO)_2C_5H_5$ is in contrast to the existence of numerous acyl derivatives of manganese of general formula $RCOMn(CO)_5$.^{3,4}

(1) For part I of this series see R. B. King, *Inorg. Chem.*, **2**, 531 (1963).

(2) G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

(3) T. H. Coffield, J. Kozikowski and R. D. Closson, Chemical Society, Special Publication 13, Abstracts of Papers submitted at the International Conference on Coordination Chemistry, London, April 6–11, 1959, p. 126.

Since numerous acyl derivatives of general formula $\text{RCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ should be capable of existence, the reactions between the sodium salt $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ and various acid chloride derivatives were investigated in attempts to prepare a variety of acyl derivatives. One aim of this research was the preparation of diacyl derivatives of general formula $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CO}(\text{CH}_2)_n\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ in order to compare their properties with those of the polymethylene derivatives $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{CH}_2)_n(\text{CO})_2\text{C}_5\text{H}_5$.¹

Experimental

In general infrared spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer model 21 double-beam machine with NaCl optics. In addition, the metal and acyl carbonyl regions of the infrared spectra of selected compounds (Table I) were taken in halocarbon oil mulls and recorded on a Perkin-Elmer model 112 single-beam machine with CaF_2 optics. Proton n.m.r. spectra were taken in chloroform solution on a Varian Associates model A-60 machine. Hexamethyldisiloxane was used as an internal standard. Microanalyses and molecular weight determinations (Mechrolab vapor pressure osmometer in benzene) were performed by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, Max-Planck-Institut für Kohlenforschung, Mülheim (Ruhr), Germany; Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.; and Huffman Microanalytical Laboratory, Wheatridge, Colo. Melting points were taken in capillaries and are uncorrected.

Materials.—Cyclopentadienyliron dicarbonyl dimer was prepared from iron pentacarbonyl and dicyclopentadiene by the usual procedure.⁵ All of the acid chloride derivatives were commercial samples. Tetrahydrofuran was redistilled over lithium aluminum hydride. All reactions were carried out under nitrogen.

General Procedure for the Reactions between $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ and Diacid Chlorides.—A solution of 0.1 mole of $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ in ~300 ml. of redistilled tetrahydrofuran was prepared from $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ and excess ~1% sodium amalgam by the usual procedure.^{1,2} After removing excess amalgam through a stopcock on the bottom of the reaction flask, this $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ solution was treated dropwise with 0.05 mole of the diacid dichloride. The reaction mixture was stirred overnight (~15 hours) at room temperature. Solvent was then removed at ~20 mm., leaving a brownish residue. This was extracted with three 100-ml. portions of dichloromethane. These dichloromethane extracts were filtered by suction through ~20 g. of alumina (Fisher chromatographic grade) and then refiltered by gravity, collecting the final filtrate under nitrogen. Solvent was removed from this filtrate at ~20 mm. leaving an orange crystalline residue which was purified by recrystallizing from dichloromethane-hexane mixtures and by washing with pentane, in which the solubility of the diacyl derivatives was limited. Since solutions of the iron derivatives are slightly air-sensitive, it was found advisable to recrystallize them under nitrogen to obtain samples for n.m.r. spectra absolutely free of paramagnetic oxides of iron.

The properties of the individual compounds prepared by this general procedure are given below:

A. $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CO}(\text{CH}_2)_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ was prepared in 45% yield from $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ and glutaryl dichloride; m.p. 110–111.5°; infrared spectrum: C–H bands at 3120(vw), 3080(w), 2930(vw), 2900(vw) and 2880(vw) cm^{-1} ; see Table I for metal and acyl carbonyl bands; other bands at 1450(vw), 1435(vw), 1410(m), 1405(m), 1350(vw), 1296(vw), 1255(vw), 1210(w), 1062(vw), 1037(w), 1015(w), 1000(w), 930(w), 900(s), 841(m), 828(m), 728(m), and 710(m) cm^{-1} ; proton n.m.r. spectrum: sharp peak at $\tau = 5.18$ due to the ten cyclopentadienyl protons; triplet ($J = 7$ cycles) at $\tau = 7.17$ due to the four methylene protons adjacent to the acyl carbonyl groups split by the two other center methylene protons; and a complex multiplet at $\tau = 8.41$ due to the remaining two center methylene protons.

Anal. Calcd. for $\text{C}_{19}\text{H}_{16}\text{Fe}_2\text{O}_6$: C, 50.5; H, 3.6; Fe, 24.7; O, 21.2; mol. wt., 452. Found: C, 50.0; H, 3.9; Fe, 24.4; O, 21.9; mol. wt., 450.

B. $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CO}(\text{CH}_2)_4\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ was prepared in 46% yield from $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ and adipyl dichloride; m.p. 143–143.5°; infrared spectrum: C–H bands at 3100(w), 2925(w), and 2850(w) cm^{-1} ; see Table I for metal and acyl carbonyl bands; other bands at 1465(w), 1430(w), 1410(m), 1400(m), 1352(vw), 1330(w), 1205(w), 1060(w), 1035(m), 1010(w), 995(w),

TABLE I
INFRARED SPECTRA OF $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2$ DERIVATIVES IN THE CARBONYL REGION^a

Compound	Metal carbonyl bands, cm^{-1}	Acyl carbonyl bands, cm^{-1}
$(\text{CH}_2)_3(\text{CO})_2[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$	1945, 1953, 2010, 2018	1651
$(\text{CF}_2)_3(\text{CO})_2[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$	1981, 2030	1651
$(\text{CH}_2)_4(\text{CO})_2[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$	1949, 1998	1651
$(\text{CH}_2)_3\text{CO}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$	1936, 1964, 1997, 2014	1646
$\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$	1963, 2018	1655
$(\text{C}_2\text{H}_5)_2\text{NCOFe}(\text{CO})_2\text{C}_5\text{H}_5$	1942, 1964, 2004, 2017	1534
$[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$	1940, 1955, 1756	..
$\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}^6$	1979, 2034	..
$(\text{CH}_2)_3[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2^1$	1949, 2002	..
$\text{C}_5\text{N}_3\text{Cl}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2^1$	1950, 1970, 1995, 2035	..

^a Halocarbon oil mulls, CaF_2 optics.

930(w), 895(m), 866(vw), 845(m), 830(m), 735(m) and 728(m) cm^{-1} ; proton n.m.r. spectrum: sharp peak at $\tau = 5.16$ due to the ten cyclopentadienyl protons; triplet at $\tau = 7.17$ due to the four methylene protons adjacent to the acyl carbonyl groups; and an apparent quintet at $\tau = 8.64$ due to the remaining four methylene protons.

Anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{Fe}_2\text{O}_6$: C, 51.5; H, 3.9; Fe, 24.0; O, 20.6; mol. wt., 466. Found: C, 51.0; H, 3.8; Fe, 23.3; O, 22.1; mol. wt., 389.

C. $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{CH}_2)_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ was prepared in 46% yield from $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ and the acid chloride $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{COCl}$; m.p. 133–134°; infrared spectrum: C–H bands at 3075(w), 2915(vw) and 2875 (vw) cm^{-1} ; see Table I for metal and acyl carbonyl bands; other bands at 1430(w), 1410(w), 1390(w), 1242(w), 1110(vw), 1055(vw), 1020(w), 995(w), 898(m), 842(m), 833(m), 760(w) and 714(w) cm^{-1} ; proton n.m.r. spectrum: sharp peak at $\tau = 5.17$ due to the five protons of the cyclopentadienyl group bonded to the iron atom to which the acyl group is bonded; sharp peak at $\tau = 5.27$ due to the five protons of the cyclopentadienyl group bonded to the iron atom to which the alkyl group is bonded; triplet at $\tau = 7.09$ due to the two methylene protons adjacent to the acyl carbonyl group; and a complex multiplet at $\tau = 8.61$ due to the remaining four methylene protons.

Anal. Calcd. for $\text{C}_{18}\text{H}_{16}\text{Fe}_2\text{O}_6$: C, 51.0; H, 3.8; Fe, 26.4; O, 18.9; mol. wt., 424. Found: C, 51.0; H, 3.9; Fe, 26.1; O, 18.5; mol. wt., 430.

Reaction between $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ and Perfluoroglutaryl Dichloride.—Owing to the tendency for large amounts of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ to form in the reaction between $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ and perfluoroglutaryl dichloride it was necessary to prepare $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CO}(\text{CF}_2)_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ by a modified procedure.

A solution of 0.1 mole of $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ in 300 ml. of redistilled tetrahydrofuran prepared from $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ and sodium amalgam was cooled to -78° after removal of the excess amalgam. It was treated dropwise with 13.85 g. (0.05 mole) of perfluoroglutaryl dichloride at such a rate that the temperature did not exceed -70° . The reaction mixture was then allowed to warm slowly overnight to room temperature. Solvent was removed from the reaction mixture at ~30 mm. leaving a red-purple residue. This residue was extracted with three 100-ml. portions of dichloromethane and the extracts filtered through ~20 g. of alumina. Removal of solvent from the filtrate left a dark red solid. This solid was dissolved in ~200 ml. of thiophene-free benzene and after filtration chromatographed on a 6 × 60 cm. alumina column. A yellow band⁷ followed by a red-purple band appeared. The red-purple band was eluted with benzene. Evaporation of this eluate at ~30 mm. gave 4.0 g. (23% yield) of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ identical with the starting material. After eluting this red-purple band the column was eluted with an additional 500 ml. of benzene giving a weak yellow eluate. Solvent was removed from this eluate at ~30 mm. to give yellow crystals of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CO}(\text{CF}_2)_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$. This product was recrystallized once from dichloromethane-hexane to give 3.86 g. (14% yield) of orange crystals which were washed with pentane and dried; m.p. 112–113°; infrared spectrum: C–H bands at 3100(w) cm^{-1} ; see Table I for metal and acyl carbonyl bands; other bands at 1430(m), 1410(w), 1355(vw), 1265(sh), 1250(w), 1230(vw), 1160(sh), 1140(s), 1074(w), 1060(w), 1015(w), 1000(w), 925(m), 865(w), 848(m), 738(sh, br), 725(w) and 703(m) cm^{-1} ; proton n.m.r. spectrum: single sharp peak at $\tau = 5.04$ due to the ten cyclopentadienyl protons; F^{19}

(6) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 38 (1956).

(7) This yellow band containing only very small quantities of material is probably due to traces of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{Hg}$ formed from traces of mercury remaining from the amalgam. Related reactions will be described in a forthcoming paper.

(4) R. D. Closson, J. Kozikowski and T. H. Coffield, *J. Org. Chem.*, **22**, 598 (1957); W. Hieber and G. Wagner, *Ann.*, **618**, 24 (1958); W. Hieber, G. Braun and W. Beck, *Ber.*, **93**, 901 (1960); H. D. Kaesz, R. B. King and F. G. A. Stone, *Z. Naturforsch.*, **15b**, 763 (1960); W. R. McClellan, *J. Am. Chem. Soc.*, **83**, 1598 (1961).

(5) B. F. Hallam, O. S. Mills and P. L. Pauson, *J. Inorg. Nucl. Chem.*, **1**, 313 (1955); see also R. B. King and F. G. A. Stone, "Inorganic Syntheses," Vol. VII, in press.

n.m.r. spectrum⁸: resonance at 109 p.p.m.⁸ due to the four fluorine atoms of the two CF₂ groups adjacent to the acyl groups; resonance at 122 p.p.m.⁸ due to the two fluorine atoms of the center CF₂ group; no fine structure of these resonances could be observed.

Anal. Calcd. for C₁₉H₁₀F₆Fe₂O₆: C, 40.7; H, 1.8; F, 20.4; Fe, 20.0; mol. wt., 560. Found: C, 40.0; H, 1.8; F, 20.7; Fe, 19.4; mol. wt., 585.

Reaction between NaFe(CO)₂C₅H₅ and Acetyl Chloride.—This reaction has been reported,⁸ but the experimental details have not been published. The procedure used in this Laboratory for carrying out the reaction is therefore described.

A solution of 0.1 mole of NaFe(CO)₂C₅H₅ in 300 ml. of redistilled tetrahydrofuran was treated dropwise with 7.85 g. (0.1 mole) of acetyl chloride. A slightly exothermic reaction occurred. The originally brown solution first became dark red and then brown again. After stirring for 16 hr. at room temperature solvent was removed at ~30 mm. leaving a brownish residue. This residue was extracted with three 100-ml. portions of dichloromethane and this extract filtered through ~20 g. of alumina by the usual procedure. Solvent was removed from this filtrate at ~30 mm. leaving a brown crystalline residue. This residue was sublimed at 70–90° (0.3 mm.) to give 13.9 g. (63% yield) of orange crystalline CH₃COFe(CO)₂C₅H₅, m.p. 56–57°; infrared spectrum: C–H bands at 3050(w), 2940(vvw) and 2900(vvw) cm.⁻¹; see Table I for metal and acyl carbonyl bands; other bands at 1430(w), 1415(m), 1352(w), 1318(m), 1065(s), 1018(w), 1004(w), 945(vw), 930(w), 910(m), 885(vw), 840(m) and 828(s) cm.⁻¹; proton n.m.r. spectrum: sharp peak at $\tau = 5.13$ due to the five cyclopentadienyl protons; sharp peak at $\tau = 7.43$ due to the three methyl protons.

Anal. Calcd. for C₉H₈FeO₃: C, 49.1; H, 3.6; Fe, 25.4. Found: C, 49.1; H, 3.8; Fe, 25.1.

Reactions between NaFe(CO)₂C₅H₅ and Dialkylcarbonyl Chlorides.—A solution of 0.1 mole of NaFe(CO)₂C₅H₅ in 300 ml. of redistilled tetrahydrofuran was treated dropwise with 0.1 mole of the dialkylcarbonyl chloride. The reaction mixture was allowed to stir overnight (~16 hr.) at room temperature. Solvent was removed at ~30 mm. leaving a brown residue to which nitrogen was admitted. This residue was extracted with three 100-ml. portions of dichloromethane and the extracts filtered through ~20 g. of alumina by the usual procedure. Solvent was removed from the filtrate at ~30 mm. An orange crystalline residue remained.

The crude products could be purified either by recrystallization from dichloromethane–hexane or by sublimation at 80° (0.1 mm.). Recrystallized products, however, decomposed completely at room temperature within 1 day in a closed container giving purple [C₅H₅Fe(CO)₂]₂ and developing pressure. Sublimed samples, on the other hand, could be stored for several weeks in sealed vials under nitrogen before decomposition was appreciable. This difference in stability between the recrystallized and the sublimed materials occurred both with (CH₃)₂NCOFe(CO)₂C₅H₅ and with (C₂H₅)₂NCOFe(CO)₂C₅H₅. Analogous iron derivatives of higher molecular weight carbonyl chloride derivatives of which the volatility would not be sufficient for the compound to be sublimed without decomposition were therefore not investigated.

The individual compounds prepared by this method are described below:

A. (CH₃)₂NCOFe(CO)₂C₅H₅ was prepared in 42% yield from NaFe(CO)₂C₅H₅ and dimethylcarbonyl chloride; m.p. 111–112°; infrared spectrum: C–H bands at 3060(w) and 2910(w) cm.⁻¹; metal carbonyl bands at 2020(s) and 1933(s) cm.⁻¹; carbonyl band from [C₅H₅Fe(CO)₂]₂ formed from partial decomposition at 1760 cm.⁻¹; acyl carbonyl bands at 1545(m) and 1530(m) cm.⁻¹; other bands at 1475(w), 1430(vw), 1415(w), 1390(vw), 1355(vw), 1330(m), 1255(sh), 1238(m), 1072(m), 1052(m), 1030(m), 1002(w), 874(w), 858(w), 840(m) and 832(m) cm.⁻¹; proton n.m.r. spectrum: sharp peak at $\tau = 5.12$ due to the five cyclopentadienyl protons; sharp peak at $\tau = 7.02$ due to the six methyl protons.

Anal. Calcd. for C₁₀H₁₁NFeO₃: C, 48.2; H, 4.4; N, 5.6; Fe, 22.4; O, 19.3; mol. wt., 249. Found: C, 47.9; H, 4.2; N, 5.2; Fe, 21.9; O, 20.0; mol. wt., 241.

B. (C₂H₅)₂NCOFe(CO)₂C₅H₅ was prepared in 59% yield from NaFe(CO)₂C₅H₅ and diethylcarbonyl chloride; m.p. 75–76.5°; infrared spectrum: C–H bands at 3025(vw), 2925(w) and 2850(sh) cm.⁻¹; see Table I for metal and acyl carbonyl bands; other bands at 1450(w), 1438(w), 1410(w), 1378(w), 1368(w), 1350(w), 1295(w), 1230(m), 1208(m), 1085(m), 1050(m), 1015(vw), 997(w), 935(vw), 856(w), 840(m), 835(m) and 828(m) cm.⁻¹; proton n.m.r. spectrum: sharp peak at $\tau = 5.15$ due to the five cyclopentadienyl protons; quartet ($J = 7$ cycles) at $\tau = 6.57$ due to

the CH₂ protons of the ethyl group; triplet ($J = 7$ cycles) at $\tau = 8.91$ due to the CH₃ protons of the ethyl group.

Anal. Calcd. for C₁₂H₁₃NFeO₃: C, 52.0; H, 5.4; N, 5.1; Fe, 20.2. Found: C, 52.2; H, 5.5; N, 5.3; Fe, 20.0.

Hydrolysis of the Compounds R₂NCOFe(CO)₂C₅H₅.—A 0.50-g. (2.0 mmoles) sample of (CH₃)₂NCOFe(CO)₂C₅H₅ was stirred for several minutes with 20 ml. of water, a yellow solution being observed which deposited a brown precipitate. After the reaction appeared to be complete the pH of the resulting solution was ~10. The solution was filtered by gravity to remove the brown insoluble material and the filtrate treated with a solution of 1.0 g. of sodium tetraphenylborate in 20 ml. of water. A white precipitate formed immediately. After a few minutes, this precipitate was filtered, washed with water, methanol, and pentane and sucked dry to give 0.25 g. (35% yield) of dimethylammonium tetraphenylborate. The product was identified by comparison of its infrared spectrum with that of an authentic sample of dimethylammonium tetraphenylborate obtained by mixing aqueous solutions of dimethylammonium chloride and sodium tetraphenylborate.

By a similar procedure 0.50 g. (1.8 mmoles) of (C₂H₅)₂NCOFe(CO)₂C₅H₅ gave 0.46 g. (65% yield) of diethylammonium tetraphenylborate.

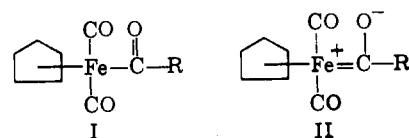
Reaction between [C₅H₅Fe(CO)₂]₂ and Thiolbenzoic acid.—A mixture of 4.0 g. (11.3 mmoles) of [C₅H₅Fe(CO)₂]₂, 6 ml. of thiolbenzoic acid and 40 ml. of methylcyclohexane was heated 6 hr. at the boiling point under nitrogen. The reaction mixture was allowed to cool to room temperature and the brown residue filtered. This brown material was recrystallized twice from hexane–dichloromethane mixtures and washed with pentane to give 1.82 g. (26% yield) of orange crystals of C₆H₅C(O)SFe(CO)₂C₅H₅, m.p. 125–126°; infrared spectrum: C–H bands at 3060(vw) cm.⁻¹; metal carbonyl bands at 2030(s) and 1990(s) cm.⁻¹; thiolbenzoate carbonyl bands at 1590(m) and 1568(m) cm.⁻¹; other bands at 1418(vw), 1195(m), 1165(m), 920(m), 845(w), 775(m) and 692(m) cm.⁻¹.

Anal. Calcd. for C₁₄H₁₆SFeO₃: C, 53.5; H, 3.1; S, 10.2; Fe, 17.9; O, 15.3; mol. wt., 314. Found: C, 53.4; H, 3.2; S, 10.2; Fe, 18.0; O, 15.4; mol. wt., 273.

Discussion

A. Acyl Derivatives.—The acyl derivatives described in this paper are yellow to orange crystalline solids fairly stable to air in the solid state but somewhat air-sensitive in solution. They are soluble in benzene and dichloromethane but only sparingly soluble in saturated hydrocarbons, such as pentane or hexane. Their properties are entirely consistent with structures where an iron atom is σ -bonded to the carbon atom of the acyl carbonyl group (I).

A characteristic feature of the acyl derivatives described in this paper as well as of previously reported acyl derivatives of manganese and rhenium^{3,4} is the presence of a strong absorption at ~1650 cm.⁻¹ in the infrared spectrum due to the acyl carbonyl group. This absorption occurs at a lower frequency than the carbonyl absorption in ketones. A possible explanation is the significant contribution of resonance structures with metal–carbon double bonding (II) which reduce the carbon–oxygen bond order.⁹ Such a metal–carbon double bond could be formed by overlap of a d-orbital of the transition metal with a p-orbital of the carbon atom and would be somewhat similar in nature to the metal–carbon partial double bonding which occurs in the transition metal–carbon monoxide bond in metal carbonyls. Resonance contributions of



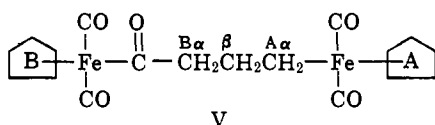
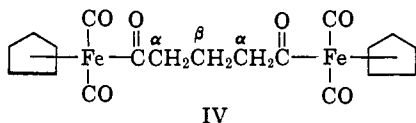
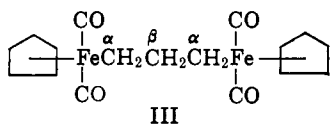
structures of type II may have the effect of stabilizing acyl derivatives of transition metals as compared with similar acyl derivatives of non-transition metals since

(8) This F¹⁹ n.m.r. spectrum was recorded at 56.4 Mc. on a Varian Associates machine in dichloromethane solution. CFCl₃ was used as an internal standard and chemical shifts are given in p.p.m. upfield from CFCl₃.

(9) The possibility of partial metal–carbon double bonding in transition metal acyl compounds has been previously mentioned by E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, **18**, 585 (1962).

non-transition metals are incapable of forming the type of double bond postulated for structures similar to II.

It is interesting to compare the proton n.m.r. spectra of the acyl derivatives $C_5H_5Fe(CO)_2CO(CH_2)_nCOFe(CO)_2C_5H_5$ with those of the corresponding alkyl derivatives $C_5H_5Fe(CO)_2(CH_2)_nFe(CO)_2C_5H_5$. It



was previously found that in the compound $C_5H_5Fe(CO)_2(CH_2)_3Fe(CO)_2C_5H_5$ (III) the protons of both the α - and the β -methylene groups were found to have identical chemical shifts and exhibited a single sharp resonance at $\tau = 8.5$. In the diacyl derivative $C_5H_5Fe(CO)_2CO(CH_2)_3COFe(CO)_2C_5H_5$ (IV), however, the four protons of the α -methylene groups exhibit a resonance at $\tau = 7.17$ and the two protons of the β -methylene group at $\tau = 8.41$. These resonances are split in a manner consistent with a coupling of ~ 7 cycles between these two sets of protons. Moreover, in the alkyl derivatives such as III the sharp resonance due to the cyclopentadienyl protons appears at $\tau = 5.27 \pm 0.02$, whereas in the acyl derivatives such as IV the sharp resonance due to the cyclopentadienyl protons appears at $\tau = 5.17 \pm 0.04$. This suggests that the position of the resonance due to the cyclopentadienyl protons in the compounds $C_5H_5Fe(CO)_2R$ is dependent on the electronegativity of R. This is also confirmed by the occurrence of the cyclopentadienyl resonance of the perfluoroglutaryl derivative $C_5H_5Fe(CO)_2CO(CF_2)_3COFe(CO)_2C_5H_5$ at $\tau = 5.04$ as would be expected since the perfluoroglutaryl group due to the inductive effect of the very electronegative fluorine atoms is more electronegative than hydrocarbon acyl groups such as the glutaryl group. In addition, the cyclopentadienyl resonance of $C_5H_5Fe(CO)_2I$,⁶ where an electronegative halogen atom rather than a less electronegative carbon atom is directly bonded to the iron atom, appears at $\tau = 4.93$, which is at an even lower field than that of the perfluoroglutaryl derivative.

In view of these interesting differences in the spectra of the alkyl and the acyl derivatives of cyclopentadienyliron dicarbonyl it seemed of interest to study a cyclopentadienyliron dicarbonyl derivative which contains both an iron-acyl and an iron-alkyl bond. In this connection the reaction between $ClCH_2CH_2CH_2COCl$ and $NaFe(CO)_2C_5H_5$ was found to yield the compound $C_5H_5Fe(CO)_2COCH_2CH_2CH_2Fe(CO)_2C_5H_5$ (V) which contains one of the cyclopentadienyliron dicarbonyl groups bonded to an alkyl carbon atom and the other cyclopentadienyliron dicarbonyl group bonded to an acyl carbon atom. This compound exhibits two sharp cyclopentadienyl resonances as would be expected for structure V. By comparison with the cyclopentadienyl resonances of other alkyl and acyl derivatives the cyclopentadienyl resonance at $\tau = 5.17$ may be assigned to the five protons of the

cyclopentadienyl group (B in V) which is bonded to the iron atom which is bonded to the acyl group and the cyclopentadienyl resonance at $\tau = 5.27$ to the five protons of the cyclopentadienyl group (A in V) which is bonded to the iron atom which is bonded to the alkyl group. Comparison with the n.m.r. spectrum of the glutaryl derivative IV leads to the assignment of the resonance at $\tau = 7.09$ to the protons of the methylene group adjacent to the acyl carbonyl group (B_α in V) and the remaining complex resonance at $\tau = \sim 8.61$ to the remaining four methylene protons (β and A_α in V) which have almost identical chemical shifts like the α - and β -methylene protons in the trimethylene derivative III.

A characteristic feature of the acyl compounds of manganese $RCOMn(CO)_5$ is their tendency to lose one mole of carbon monoxide on heating to produce the corresponding alkyl derivatives $RMn(CO)_5$.^{3,4} In this connection it is of interest that both $C_5H_5Fe(CO)_2CO(CH_2)_3COFe(CO)_2C_5H_5$ and $C_5H_5Fe(CO)_2CO(CF_2)_3COFe(CO)_2C_5H_5$ remained unchanged after being heated to $\sim 130^\circ$ (0.25 mm.) for 2 hr., conditions much more vigorous than those necessary for the decarbonylation of related manganese compounds. This is consistent with the reported inability to decarbonylate $CH_3COFe(CO)_2C_5H_5$ to $CH_3Fe(CO)_2C_5H_5$.³ Studies with labeled carbon monoxide have indicated that in the decarbonylation of the acyl derivatives of manganese the mole of carbon monoxide which is lost does not come from the acyl carbonyl group but from one of the carbonyl groups bonded only to the manganese atom.³ Therefore the ease of decarbonylation of acyl derivatives of metal carbonyls should be dependent on the strength of the metal-carbon monoxide bond and should be related to the ease of displacement of carbonyl groups from the same metal carbonyl derivatives by other ligands. Thus the failure for the acyl derivatives $RCOFe(CO)_2C_5H_5$ to undergo decarbonylation to the corresponding alkyl derivatives $RFe(CO)_2C_5H_5$ under conditions where the compounds $RCOMn(CO)_5$ undergo such decarbonylation may be related to the failure to synthesize $C_5H_5FeCO(\pi\text{-allyl})$ by decarbonylation of $C_5H_5Fe(CO)_2(\sigma\text{-allyl})$ in a manner similar to the synthesis of $(\pi\text{-allyl})Mn(CO)_4$ by the decarbonylation of $(\sigma\text{-allyl})Mn(CO)_5$ ¹⁰ and to the failure to synthesize $C_5H_5FeCONO$ by methods analogous to the synthesis of $Mn(CO)_4NO$,¹¹ although such cyclopentadienyliron carbonyl derivatives should be quite stable and preparable by other methods.^{11a}

B. Dialkylcarbonyl Derivatives.—The dialkylcarbonyl derivatives described in this paper are orange crystalline solids volatile at about 80° (0.1 mm.). They are soluble in benzene and dichloromethane, but only sparingly soluble in saturated aliphatic hydrocarbons such as pentane and hexane. As described in the Experimental section their stability depends greatly on the method of purification, but even the most stable samples decompose completely after a few months. Their properties are entirely consistent with the expected structure VI.

The dialkylcarbonyl derivatives VI react with water to give a brown solution of $pH \sim 10$. This

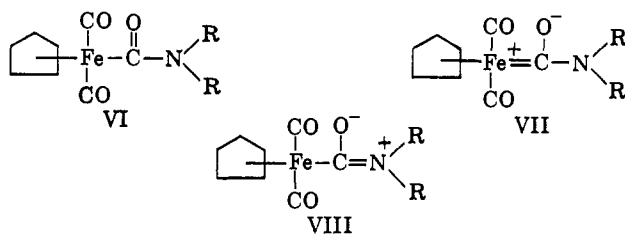
(10) H. D. Kaesz, R. B. King and F. G. A. Stone, *Z. Naturforsch.*, **15b**, 682 (1960); W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties and B. W. Howk, *J. Am. Chem. Soc.*, **83**, 1601 (1961).

(11) P. M. Treichel, E. Pitcher, R. B. King and F. G. A. Stone, *ibid.*, **83**, 2593 (1961).

(11a) NOTE ADDED IN PROOF.—Since this paper was accepted, the preparation of the compound $C_5H_5FeCO(\pi\text{-allyl})$ by decarbonylation of $C_5H_5Fe(CO)_2(\sigma\text{-allyl})$ was described.^{11b} Unlike the analogous manganese system,¹⁰ however, ultraviolet irradiation was necessary for this decarbonylation to occur, mere heating of $C_5H_5Fe(CO)_2(\sigma\text{-allyl})$ failing to produce any $C_5H_5FeCO(\pi\text{-allyl})$.^{11b}

(11b) M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963).

contains the free amine R_2NH identified by precipitation of the amine as the tetraphenylborate and comparison of this precipitate with an authentic sample of the amine tetraphenylborate. The iron appeared to be present in a brown insoluble material which was not further investigated. The compounds $C_5H_5Fe(CO)_2CONR_2$ are therefore unusual among cyclopentadienyliron dicarbonyl derivatives in being decomposed by water at room temperature. This sensitivity to water may account for the difficulty in obtaining reproducible infrared spectra in potassium bromide pellets (which are extremely difficult to have absolutely dry) and possibly for the presence of a band of variable intensity at $\sim 1760\text{ cm}^{-1}$ in such infrared spectra arising from the bridging carbonyl group in $[C_5H_5Fe(CO)_2]_2$ produced in decomposition.



It is of interest that in the compounds $C_5H_5Fe(CO)_2CONR_2$ the carbamoyl carbonyl group appears at extremely low wave numbers ($1535 \pm 10\text{ cm}^{-1}$). This is much lower than even the acyl carbonyl group in the compounds $RCOFe(CO)_2C_5H_5$ ($\sim 1650\text{ cm}^{-1}$). This suggests that not only is the carbon-oxygen bond order reduced by resonance contributions of structures with partial iron-carbon double bonding (VII) similar to that postulated above for the acyl derivatives (II) but also by resonance contributions of structures with partial nitrogen-carbon double bonding (VIII) as in other amide derivatives.

C. Cyclopentadienyliron Dicarbonyl Thiolbenzoate.—Cyclopentadienyliron dicarbonyl dimer and thiolbenzoic acid were found to react at $\sim 100^\circ$ in an inert solvent to give the brown-orange compound $C_6H_5C(O)SFe(CO)_2C_5H_5$. This compound appears to be a covalent derivative similar to the recently reported covalent trifluoroacetates $CF_3CO_2W(CO)_3C_5H_5$, $CF_3CO_2Mo(CO)_3C_5H_5$ and $CF_3CO_2Re(CO)_5$.¹² The presence of thiolbenzoate carbonyl bands at 1590 and 1568 cm^{-1} suggests that there is a carbon-oxygen double bond in the molecule and therefore that the iron atom is bonded to the sulfur atom rather than to the oxygen atom. It will be noted that this organosulfur derivative of cyclopentadienyliron carbonyl is of a different type from the recently prepared compounds $[C_5H_5FeCOSR]_2$ ($R = \text{methyl}^{13}$ and $t\text{-butyl}^{14}$) with bridging sulfur atoms.

Other reactions of thiolacids and metal carbonyl derivatives have been investigated, but in most cases the reaction mixtures have been found to be more complex. In certain reactions involving iron pentacarbonyl or triiron dodecacarbonyl and thiolacids compounds of the type $[Fe(CO)_3SR]_2$ ¹⁵ have been isolated in low yield. Molybdenum hexacarbonyl and cyclopentadienylmolybdenum tricarbonyl dimer appear to react with thiolacids with complete loss of carbonyl and cyclopentadienyl groups to form black crystalline products of as yet uncertain composition. Some of these materials are being investigated further.

Acknowledgment.—The author is indebted to Mr. M. Bisnette for experimental assistance in carrying out the reactions described in this paper and for taking most of the infrared spectra.

(12) A. Davison, W. McFarlane, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 3653 (1962).

(13) R. B. King, P. M. Treichel and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3600 (1961).

(14) R. B. King, unpublished results.

(15) See R. B. King, *J. Am. Chem. Soc.*, **84**, 2460 (1962), and references given there.

[CONTRIBUTION FROM THE MELLON INSTITUTE, PITTSBURGH, PENNA.]

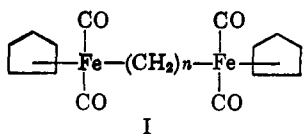
Reactions of Alkali Metal Derivatives of Metal Carbonyls. III. Reaction between Sodium Pentacarbonylmanganate(−I) and Certain Organic Polyhalides¹

BY R. B. KING

RECEIVED DECEMBER 21, 1962

The yellow crystalline manganese derivative $(CH_2)_3[Mn(CO)_5]_2$ has been prepared by the reaction between $NaMn(CO)_5$ and 1,3-dibromopropane or $ClCH_2CH_2CH_2COCl$. The reaction between $NaMn(CO)_5$ and 1,3-dibromobutane yields a similar yellow compound $CH_3C_3H_5[Mn(CO)_5]_2$. Proton n.m.r. studies suggest an unusual structure for these compounds. Reaction between $NaMn(CO)_5$ and perfluoroglutaryl dichloride yields the pale yellow diacyl derivative $(CO)_5MnCOCF_2CF_2CF_2COMn(CO)_5$ which undergoes facile decarbonylation on heating to give white $(CO)_5MnCF_2CF_2CF_2Mn(CO)_5$. Reaction between $NaMn(CO)_5$ and cyanuric chloride yields white crystalline $C_3N_3Cl[Mn(CO)_5]_2$.

Recently the reactions between $NaFe(CO)_2C_5H_5$ and various polymethylene dibromides of general formula $Br(CH_2)_nBr$ ($n = 3, 4, 5, 6$) were investigated and found to yield stable crystalline products of the general formula $(CH_2)_n[Fe(CO)_2C_5H_5]_2$ with the expected properties for materials with iron-carbon σ -bonds and the obvious structure I.² Another sodium



derivative capable of reacting with certain organic halogen derivatives to form compounds with stable transition metal-carbon σ -bonds is the manganese derivative $NaMn(CO)_5$.³ It therefore seemed of interest to investigate the reactions between $NaMn(CO)_5$ and various organic polyhalogen derivatives in order to compare the properties of the resulting products with those of the previously prepared iron compounds.^{1,2}

(2) R. B. King, *Inorg. Chem.*, **2**, 531 (1963).

(3) (a) R. D. Closson, J. Kozikowski and T. H. Coffield, *J. Org. Chem.*, **22**, 598 (1957); (b) W. Hieber and G. Wagner, *Ann.*, **618**, 24 (1958); (c) W. Hieber, G. Braun and W. Beck, *Ber.*, **93**, 901 (1960); (d) H. D. Kaesz, R. B. King and F. G. A. Stone, *Z. Naturforsch.*, **15b**, 763 (1960); (e) W. R. McClellan, *J. Am. Chem. Soc.*, **83**, 1598 (1961).

(1) For part II see R. B. King, *J. Am. Chem. Soc.*, **85**, 1918 (1963).