groups at 2.34, 1.54, 0.95, and 0.91 p.p.m.; other resonances centered at 6.21 (singlet), 6.17 (doublet, J = 10 cycles), 5.75 (doublet, J = 10 cycles), 2.75 (singlet), and 2.55 (singlet) p.p.m., each of which may be attributed to a single proton.

The Palladium Compound $C_{10}H_{12}OCH_3PdC_5H_5$.—The $[C_{10}H_{12}OCH_3PdCl]_2$[9] required for this preparation was prepared in quantitative yield from commercially available sodium palladium(II) chloride (Englehard Industries) by treatment with excess dicyclopentadiene in methanol solution. The resulting pale yellow crystalline precipitate was filtered after several hours; washed with water, methanol, and pentane; and dried overnight in a vacuum desiccator.

Sodium cyclopentadienide was prepared under nitrogen from 0.8 ml. of 30% sodium dispersion in xylene (~10 mmoles of sodium) and 2.0 ml. (1.6 g., 24 mmoles) of cyclopentadiene in 150 ml. of tetrahydrofuran. After all of the sodium had dissolved, 2.0 g. (6.5 mmoles) of $[C_{10}H_{12}OCH_3PdCl]_2$ was added. The reaction mixture was stirred 2 hr. at room temperature and then refluxed for 3 hr., becoming dark red. After the reaction period was over, solvent was removed at ~50 mm., leaving a rather sticky residue. Nitrogen was admitted and this residue was extracted with three 50-ml. portions of dichloromethane. The extract was filtered. Solvent was removed from the deep orange filtrate at ~50 mm., leaving a dark yellow liquid. This liquid was extracted with two 15-ml. portions of pentane and the extracts filtered. Cooling the orange filtrate in a −78° bath for 1.5 hr. precipitated orange crystals of the product. These were filtered and dried giving 980 mg. (45% yield) of crude $C_{10}H_{12}OCH_3PdC_5H_5$. Sublimation of this material at 80–110° (0.1 mm.) for 2 hr. through glass wool to a water-cooled probe gave 800 mg. (37% yield) of pure $C_{10}H_{12}OCH_3PdC_5H_5$, m.p. 74–75.5°.

Anal. Calcd. for $C_{16}H_{20}OPd$: C, 57.3; H, 6.0; Pd, 31.9; OCH_3, 9.0; mol. wt., 334. Found (two independent preparations): C, 56.8, 56.4; H, 6.1, 6.2; Pd, 31.4, 31.1; OCH_3, 7.8, 7.4; mol. wt., 352 (Mechrolab osmometer in benzene solution).

Infrared Spectrum.—C–H bands at 2980 (sh), 2950 (m), and 2900 (m) cm.$^{-1}$; other bands at 1455 (w), 1450 (sh), 1440 (w), 1365 (w), 1333 (w), 1291 (w), 1279 (sh), 1272 (w), 1259 (w), 1240 (vw), 1230 (vw), 1202 (w), 1179 (w), 1162 (sh), 1157 (m), 1120 (m), 1083 (s), 1057 (w), 1039 (m), 1019 (sh), 1011 (w), 988 (m), 969 (sh), 961 (m), 940 (m), 928 (m), 920 (sh), 885 (w), 854 (w), 849 (sh), 836 (m), 817 (w), 798 (w), 763 (sh), 757 (s), 747 (m), 710 (w), and 673 (w) cm.$^{-1}$.

Proton N.m.r. Spectrum.—Sharp peak at 5.53 p.p.m. due to the five cyclopentadienyl protons; sharp peak at 3.14 p.p.m. due to the three methyl protons of the methoxy group; other resonances centered at 5.03 (doublet, J ~ 6 cycles), 3.43 (singlet), 3.35 (doublet, J ~ 6 cycles), 2.53 (very broad), 2.21 (broad and asymmetric), 1.53 (doublet, J = 10 cycles), and 0.92 (doublet, J = 10 cycles) p.p.m.

Acknowledgment.—The author acknowledges the helpful advice of Dr. R. D. Cramer in the preparation of $[(C_2H_4)_2RhCl]_2$.

CONTRIBUTION FROM E. I. DU PONT DE NEMOURS AND CO.,
EXPLOSIVES DEPARTMENT, EXPERIMENTAL STATION LABORATORY,
WILMINGTON, DELAWARE

Reactions of Alkali Metal Derivatives of Metal Carbonyls. I. Reactions between $C_5H_5Fe(CO)_2Na$ and Certain Organic Polyhalogen Compounds

BY R. B. KING[1]

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Reactions between the sodium derivative $C_5H_5Fe(CO)_2Na$ and the α,ω-dibromides, $Br(CH_2)_nBr$ (n = 3, 4, 5, and 6) have been found to yield the stable orange crystalline solids $(CH_2)_n[C_5H_5Fe(CO)_2]_2$. Reaction between 1,4-dichlorobutyne-2 and $C_5H_5Fe(CO)_2Na$ yields the acetylenic derivative $C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_2Fe(CO)_2C_5H_5$ as well as significant quantities of $[C_5H_5Fe(CO)_2]_2$. Reaction between $C_5H_5Fe(CO)_2Na$ and cyanuric chloride has been found to yield orange crystalline $C_3N_3Cl[C_5H_5Fe(CO)_2]_2$.

Recently several organometallic derivatives of transition metals with metal–carbon σ-bonds have been synthesized by the reaction of alkali metal salts of carbonyl hydride derivatives with various alkyl and aryl halides. These include such compounds as the methyl derivatives $Mn(CO)_5CH_3$[2] and $C_5H_5Fe(CO)_2CH_3$[3] prepared by reaction between the appropriate sodium derivatives and methyl iodide. It seemed of interest to investigate reactions between various sodium derivatives and various organic polyhalogen derivatives in attempts to synthesize organometallic derivatives containing more than one transition metal atom bonded to a single organic residue. This paper reports reactions between the readily available sodium derivative, $C_5H_5Fe(CO)_2Na$,[3] and various organic polyhalogen derivatives which have resulted in the syntheses of a variety of new compounds containing two $-Fe(CO)_2C_5H_5$ residues bonded to a single organic molecule.

Experimental

Infrared spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Infracord machine unless otherwise indicated. Proton n.m.r. spectra were taken in carbon disulfide solution and recorded on a Varian A-60 machine. Chemical shifts are given in p.p.m. downfield from tetramethylsilane and were reproducible to ±0.02 p.p.m. Molecular weight determinations were carried out in benzene solution in a Mechrolab vapor pressure osmometer. Melting and decomposition points were determined in sealed capillaries and are uncorrected.

Preparation of the Compounds $(CH_2)_n[C_5H_5Fe(CO)_2]_2$ (n = 3, 4, 5, and 6).—The reaction was conducted under nitrogen in a

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[1] Mellon Institute, Pittsburgh 13, Pennsylvania.

[2] R. D. Closson, J. Kozikowski, and T. H. Coffield, *J. Org. Chem.*, **22**, 598 (1957).

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

Table I

Compounds of the Type $(CH_2)_n[C_5H_5Fe(CO)_2]_2$

Compound	Color	M.p., °C.	Yield, %		Analyses, %			Mol. wt.
					C	H	Fe	
$(CH_2)_3[C_5H_5Fe(CO)_2]_2$	Orange	103–105	47	Calcd.	51.5	4.0	28.3	396
				Found	51.9	4.2	28.3	385
$(CH_2)_4[C_5H_5Fe(CO)_2]_2$	Orange	123–124	46	Calcd.	52.7	4.4	27.3	410
				Found	52.4	4.9	27.1	402
$(CH_2)_5[C_5H_5Fe(CO)_2]_2$	Orange	82–83	15	Calcd.	53.7	4.7	26.4	424
				Found	53.8	5.3	26.6	428
$(CH_2)_6[C_5H_5Fe(CO)_2]_2$	Orange	98–100	39	Calcd.	54.8	5.0	25.5	438
				Found	54.5	5.1	25.3	431

1-l. three-necked flask equipped with a stopcock at the bottom for removal of excess mercury. Sodium amalgam was prepared under nitrogen by adding 3.0 g. (0.13 mole) of sodium metal in ~0.4-g. portions to 23 ml. of mercury. After the sodium amalgam had formed it was treated with 17.7 g. (0.05 mole) of cyclopentadienyliron dicarbonyl dimer[4] and 300 ml. of tetrahydrofuran which had been redistilled over lithium aluminum hydride. The reaction mixture then was stirred for about 1 hr. at room temperature to form a brownish solution of the sodium derivative $C_5H_5Fe(CO)_2Na$. Excess amalgam then was drained from the reaction mixture through the stopcock at the bottom of the reaction flask.

The resulting brownish solution then was treated with ~0.06 mole of the α,ω-dibromoalkane and the mixture was stirred overnight at room temperature and then refluxed 3–7 hr. at the boiling point.

Solvent then was removed from the reaction mixture at ~30 mm., leaving an orange to brown residue. This residue was extracted with three 100-ml. portions of dichloromethane and the extracts were treated with about 20 g. of alumina (Merck) and filtered. The addition of the alumina seemed to make the filtration less difficult.

The resulting orange filtrate was concentrated at 30 mm., hexane being added. As the volume of the solution decreased, crystals of the product separated. These were filtered when the volume of remaining solution was about 20 ml. The resulting orange crystals after washing with a minimum amount of pentane and drying were analytically pure.

The properties of the compounds $(CH_2)_n[C_5H_5Fe(CO)_2]_2$ are listed in Table I.

Infrared Spectra of $(CH_2)_n[C_5H_5Fe(CO)_2]_2$.—A. $(CH_2)_3[C_5H_5Fe(CO)_2]_2$.—C–H bands at 3140 (vw), 2930 (m), and 2830 (w) cm.$^{-1}$; carbonyl bands at 2020 (s) and 1940 (s) cm.$^{-1}$; other bands at 1430 (w), 1411 (m), 1354 (w), 1280 (w), 1140 (m), 1114 (vw), 1084 (m), 1063 (m), 1015 (w), 1004 (m), 922 (vw), 858 (m), 847 (m), and 835 (s) cm.$^{-1}$.

B. $(CH_2)_4[C_5H_5Fe(CO)_2]_2$.—C–H bands at 3140 (vw), 2980 (m), and 2880 (w) cm.$^{-1}$; carbonyl bands at 2030 (vs) and 1960 (vs) cm.$^{-1}$; other bands at 1458 (vw), 1437 (vw), 1420 (w), 1360 (vw), 1260 (w), 1102 (w), 1069 (vw), 1065 (sh), 1039 (vw), 1022 (vw), 1007 (w), 863 (w), 851 (w), 838 (s), and 786 (w) cm.$^{-1}$.

C. $(CH_2)_5[C_5H_5Fe(CO)_2]_2$.—C–H bands at 3160 (vw), 2960 (m), and 2880 (w) cm.$^{-1}$; carbonyl bands at 2020 (s) and 1960 (s) cm.$^{-1}$; other bands at 1490 (vw), 1458 (w), 1431 (w), 1418 (w), 1358 (vw), 1240 (w), 1138 (w), 1106 (m), 1066 (w), 1019 (w), 1005 (w), 858 (m), 835 (s), 747 (vw), and 702 (w) cm.$^{-1}$.

D. $(CH_2)_6[C_5H_5Fe(CO)_2]_2$.—C–H bands at 3150 (vw), 2960 (m), and 2875 (m) cm.$^{-1}$; carbonyl bands at 2020 (s) and 1950 (s) cm.$^{-1}$; other bands at 1462 (w), 1434 (w), 1419 (w), 1358 (vw), 1223 (w), 1105 (m), 1066 (w), 1020 (w), 1005 (w), 863 (m), 855 (m), 848 (m), 840 (s), and 733 (w) cm.$^{-1}$.

Proton N.m.r. Spectra.—(Resonances given in p.p.m. downfield from tetramethylsilane.)

A. $(CH_2)_3[C_5H_5Fe(CO)_2]_2$.—Resonances at 4.64 p.p.m. due to the ten cyclopentadienyl protons and at 1.42 p.p.m. due to the six methylene protons.

B. $(CH_2)_4[C_5H_5Fe(CO)_2]_2$.—Resonances at 4.65 p.p.m. due to the ten cyclopentadienyl protons and at 1.35 p.p.m. due to the eight methylene protons.

C. $(CH_2)_5[C_5H_5Fe(CO)_2]_2$.—Resonances at 4.64 p.p.m. due to the ten cyclopentadienyl protons and at 1.40 p.p.m. due to the ten methylene protons.

D. $(CH_2)_6[C_5H_5Fe(CO)_2]_2$.—Resonances at 4.65 p.p.m. due to the ten cyclopentadienyl protons and at 1.36 p.p.m. due to the twelve methylene protons.

Preparation of the Compound $C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_2Fe(CO)_2C_5H_5$.—A tetrahydrofuran solution of $C_5H_5Fe(CO)_2Na$ was prepared from 17.7 g. (0.05 mole) of cyclopentadienyliron dicarbonyl dimer and excess ~1% sodium amalgam using the same technique and apparatus as described above for the preparations of the compounds $(CH_2)_n[C_5H_5Fe(CO)_2]_2$. After removing excess amalgam the reaction mixture was treated with 6.0 ml. (~0.05 mole) of 1,4-dichlorobutyne-2 over a period of a few minutes. An exothermic reaction occurred. After stirring for 18 hr. at room temperature solvent was removed at ~30 mm., leaving a brown residue.

After admitting nitrogen this residue was extracted with three 100-ml. portions of dichloromethane. The extracts were first filtered by suction through ~25 g. of alumina and the alumina was washed with two 75-ml. portions of dichloromethane. This filtrate was filtered a second time by gravity collecting the final filtrate under nitrogen. Evaporation of this filtrate at ~30 mm. left an orange solid consisting of approximately equal quantities of $C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_2Fe(CO)_2C_5H_5$ and $[C_5H_5Fe(CO)_2]_2$.

In order to separate these two materials the orange solid was dissolved in ~50 ml. of thiophene-free benzene and chromatographed on a 5 × 60 cm. alumina column. The chromatogram was developed with benzene. A yellow-orange band of $C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_2Fe(CO)_2C_5H_5$ followed by a red-brown band of $[C_5H_5Fe(CO)_2]_2$ appeared. Each band was eluted with benzene and the eluates evaporated at 30 mm. The orange $C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_2Fe(CO)_2C_5H_5$ was recrystallized from a mixture of dichloromethane and hexane to give 2.3 g. (11% yield) of pure material. From the red-brown band 1.7 g. (9.6% yield) of $[C_5H_5Fe(CO)_2]_2$ was obtained.

Anal. Calcd. for $C_{18}H_{14}O_4Fe_2$: C, 53.2; H, 3.5; Fe, 27.6. Found: C, 52.9; H, 3.5; Fe, 27.3.

Infrared Spectrum (Perkin-Elmer Model 21, KBr Pellet).—C–H bands at 3060 (vw) and 2900 (w) cm.$^{-1}$; carbonyl bands at 1995 (s), 1945 (sh), and 1930 (s) cm.$^{-1}$; other bands at 1430 (w), 1415 (w), 1050 (sh), 1045 (m), 1013 (vw), 999 (vw), and 832 (m) cm.$^{-1}$.

Proton N.m.r. Spectrum.—Resonances at 4.72 p.p.m. due to the ten cyclopentadienyl protons and at 1.70 p.p.m. due to the four methylene protons.

Preparation of the Compound $C_3N_3Cl[C_5H_5Fe(CO)_2]_2$).—A tetrahydrofuran solution of $C_5H_5Fe(CO)_2Na$ was prepared from 17.7 g. (0.05 mole) of cyclopentadienyliron dicarbonyl dimer and excess ~1% sodium amalgam using the same technique and apparatus as described above for the preparations of the compounds $(CH_2)_n[C_5H_5Fe(CO)_2]_2$. After removing excess amalgam the reaction mixture was treated with 9.2 g. (0.05 mole) of cyanuric chloride, a slightly exothermic reaction occurring. The reaction mixture was stirred at room temperature for 20 hr. and then re-

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[4] B. F. Hallam, O. S. Mills, and P. L. Pauson, *J. Inorg. Nucl. Chem.*, **1**, 313 (1955).

fluxed for 3 hr. Solvent then was removed from the reaction mixture at ~30 mm., leaving a brown residue.

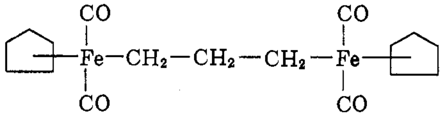
This residue was extracted with three 100-ml. portions of dichloromethane; the extracts were treated with ~50 g. of alumina (Merck) and the brownish extracts filtered by suction, this filtration being extremely slow. The filtrate was treated with dichloromethane to replace solvent that had evaporated during the slow filtration process. Hexane then was added and the solution filtered again. Slow removal of the solvent at ~30 mm. caused orange crystals of the product to separate from the solution. When the volume of the solution was ~40 ml. the evaporation was discontinued. The resulting crystals were filtered, washed with six 50-ml. portions of pentane, and dried to give 9.0 g. (39% yield) of orange crystalline $C_3N_3Cl[C_5H_5Fe(CO)_2]_2$. On heating this material darkened at about 150°.

Anal. Calcd. for $C_{17}H_{10}O_4N_3ClFe$: C, 43.7; H, 2.1; N, 9.0; Cl, 7.6; Fe, 23.9; mol. wt., 467. Found: C, 43.4; H, 2.3; N, 8.8; Cl, 7.7; Fe, 23.2; mol. wt., 483.

Infrared Spectrum.—C–H at 3120 (w) $cm.^{-1}$; carbonyl bands at 2040 (s) and 1970 (s) $cm.^{-1}$; other bands at 1770 (w), 1468 (s), 1435 (m), 1418 (m), 1390 (m), 1363 (s), 1350 (s), 1210 (s), 1190 (s), 1118 (vw), 1063 (vw), 1023 (w), 1009 (w), 965 (m), 855 (m), 839 (m), 806 (m), 786 (s), and 743 (s) $cm.^{-1}$.

Discussion

$(CH_2)_3[Fe(CO)_2C_5H_5]_2$ and higher homologs exhibit properties entirely compatible with σ-bonded structures such as I for the trimethylene derivative. The proton n.m.r. spectrum of $(CH_2)_3[Fe(CO)_2C_5H_5]_2$ shows in addition to a sharp peak for the ten cyclopentadienyl protons a second single sharp peak for all six of the methylene protons. The chemical shifts of both the α- and β-CH_2 groups thus appear to be identical. This is perhaps somewhat surprising but certainly not impossible for structure I.



I

The physical properties of the compounds $(CH_2)_n$-$[Fe(CO)_2C_5H_5]_2$ resemble those of other compounds in which a $-Fe(CO)_2C_5H_5$ group is σ-bonded to a hydrocarbon residue such as the methyl derivative $CH_3Fe(CO)_2C_5H_5$.[3] Thus the trimethylene compound $(CH_2)_3[Fe(CO)_2C_5H_5]_2$ can be sublimed unchanged at 80° (0.1 mm.) and is soluble in organic solvents such as pentane, benzene, and dichloromethane. As compared with the methyl and ethyl derivatives which are reported to be rather air-sensitive, the compounds $(CH_2)_n[Fe(CO)_2C_5H_5]_2$ appear to be fairly stable in air, especially in the solid state. It is to be noted that the melting points of the $(CH_2)_n[Fe(CO)_2C_5H_5]_2$ compounds alternate with increasing values for *n*.

An attempt to prepare the compound $(CH_2)_2[Fe(CO)_2C_5H_5]_2$ from 1,2-dibromoethane and $C_5H_5Fe(CO)_2Na$ under conditions similar to those used for the preparation of the compounds $(CH_2)_n[Fe(CO)_2C_5H_5]_2$ described in this paper gave a quantitative yield of $[C_5H_5Fe(CO)_2]_2$ rather than the desired compound.

1,4-Dichlorobutyne-2 was found to react with $C_5H_5Fe(CO)_2Na$ to give a mixture of $[C_5H_5Fe(CO)_2]_2$ and the compound $C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_2Fe(CO)_2C_5H_5$, an unsaturated analog of the $(CH_2)_n[Fe(CO)_2C_5H_5]_2$ compounds. An attempt to hydrogenate this compound to $(CH_2)_4[Fe(CO)_2C_5H_5]_2$ instead gave $[C_5H_5Fe(CO)_2]_2$. The reaction between 1,4-dichlorobutene-2 and $C_5H_5Fe(CO)_2Na$ gave only $[C_5H_5Fe(CO)_2]_2$.

In an attempt to prepare a compound containing three $-Fe(CO)_2C_5H_5$ residues cyanuric chloride was allowed to react with $C_5H_5Fe(CO)_2Na$. The product, however, had the composition $C_3N_3Cl[Fe(CO)_2C_5H_5]_2$, only two of the three chlorine atoms being replaced with $-Fe(CO)_2C_5H_5$ groups. This material is an orange crystalline solid. Its air stability is comparable to that of the compounds $(CH_3)_n[Fe(CO)_2C_5H_5]_2$, but its solubility in organic solvents such as pentane is somewhat less.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY OF CHEMICAL AND
SOLID STATE PHYSICS, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS

Vibrational Spectra and Bonding in Metal Carbonyls. II. Infrared Spectra of Amine-Substituted Group VI Carbonyls in the CO Stretching Region[1a]

BY C. S. KRAIHANZEL AND F. A. COTTON[1b]

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The method presented earlier for interpreting the CO stretching frequencies of substituted metal carbonyls of the type $ML_n(CO)_{6-n}$ in terms of CO stretching and stretch–stretch interaction force constants is applied to molecules in which M = Cr, Mo, and W and the L's are supplied by cyclohexylamine, ethylenediamine, diethylenetriamine, pyridine, and α,α-dipyridyl. The results are discussed in terms of the π-bonding abilities of these ligands. Several of the compounds studied are new and their preparation and characterization are described in detail.

Introduction

In part I[2] a method of analyzing and correlating the CO stretching modes of substituted group VI carbonyls was developed on the basis of valence theory and its applicability demonstrated by applying it to a variety of phosphine-substituted compounds. In this paper we report data and analysis thereof, using the same princi-

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(1) (a) Supported by the U. S. Atomic Energy Commission. (b) Fellow of the Alfred P. Sloan Foundation.

(2) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).