

ORGANOMETALLIC CHEMISTRY OF THE TRANSITION METALS

NII*. SOME ALKOXYCARBONYL DERIVATIVES OF THE CYCLOPENTADIENYLMETAL CARBONYLS**

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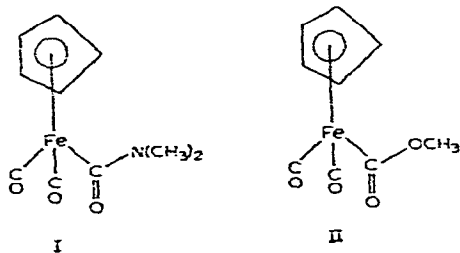
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INTRODUCTION

Several years ago³ the dimethylcarbamoyl derivative $(\text{CH}_3)_2\text{NCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ (I) was prepared from dimethylcarbamoyl chloride and $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$. Characteristic of $(\text{CH}_3)_2\text{NCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ is its facile decomposition in aqueous solution giving a mixture containing dimethylamine and $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$.

This dimethylcarbamoyl derivative $(\text{CH}_3)_2\text{NCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ may also be considered as the dimethylamide of the unknown carboxylic acid $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{COOH}$. Reaction between $(\text{CH}_3)_2\text{NCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ (I) and water may first produce $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{COOH}$ which then decarboxylates to give the hydride $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{H}$ which in turn loses hydrogen in the known manner^{4,5} to give the observed $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$. This possibility suggested the reaction between $(\text{CH}_3)_2\text{NCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ and methanol to give the methyl ester $\text{CH}_3\text{OCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ (II) with a methoxycarbonyl group directly bonded to the iron atom. Similar alkoxy-carbonyl derivatives of the types $\text{ROCOC}(\text{CO})_3\text{L}$ [$\text{R} = (\text{CH}_3)_3\text{C}$ and C_2H_5 , $\text{L} = (\text{C}_6\text{H}_5)_3\text{P}$]^{6,7} $\text{ROCOC}(\text{CO})_2\text{L}_2$ [$\text{R} = \text{CH}_3$ and C_2H_5 , $\text{L} = (\text{C}_6\text{H}_5)_3\text{P}$]⁷ and $\text{ROCOMn}(\text{CO})_3\text{L}_2$ [$\text{R} = \text{CH}_3$, C_2H_5 , C_5H_{11} , and $\text{C}_6\text{H}_5\text{CH}_2$, $\text{L} = (\text{C}_6\text{H}_5)_3\text{P}$; $\text{R} = \text{C}_2\text{H}_5$, $\text{L} = \text{CO}$]⁸ have been prepared either by treatment of a metal carbonyl cation with an alkoxide anion, treatment of a metal carbonyl anion with ethyl chloroformate, or treatment of a metal carbonyl anion with *tert*-butyl hypochlorite.



As discussed in our communication² the reaction between $(\text{CH}_3)_2\text{NCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ did indeed yield this ester $\text{CH}_3\text{OCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ (II), the first alkoxy-

* For Part XI of this series see ref. 1.

** For a preliminary communication of some of this work see ref. 2.

TABLE I

NEW COMPOUNDS DESCRIBED IN THIS PAPER

No.	Compound	Color	M. p.	Preparation	Yield	Analyses					
						C	H	O	Metal Other		
<i>A. Iron compounds</i>											
(1)	$\text{CH}_3\text{OCOFe}(\text{CO})_2\text{C}_6\text{H}_5$	yellow-orange	34-36°	$(\text{CH}_3)_2\text{NCOFe}(\text{CO})_2\text{C}_6\text{H}_5 + \text{CH}_3\text{OH}$	63%	Calcd. Found	45.8 46.1 48.0 47.4 51.8 34.6 34.4 36.0	3.4 3.6 4.0 3.9 5.0 2.2 2.6 2.7	27.1 26.5 25.6 25.4 23.0 17.3 20.1 18.4	23.7 23.6	23.6 (mol. wt.) 248 (mol. wt.)
(2)	$\text{CH}_3\text{OCOC}_2\text{H}_5\text{Fe}(\text{CO})_2\text{C}_6\text{H}_5$	yellow-orange	34-36°	$\text{NaFe}(\text{CO})_2\text{C}_6\text{H}_5 + \text{C}_2\text{H}_5\text{CO}_2\text{CH}_3$	5.1%	Calcd. Found	48.0 47.4 51.8 34.6 34.4 36.0	4.0 3.9 5.0 2.2 2.6 2.7	25.6 25.4 23.0 17.3 20.1 18.4	23.6	
(3)	$\text{C}_2\text{H}_5\text{OCOC}(\text{CH}_3)_2\text{Fe}(\text{CO})_2\text{C}_6\text{H}_5$	orange-brown	liquide	$\text{NaFe}(\text{CO})_2\text{C}_6\text{H}_5 + \text{C}_2\text{H}_5\text{CO}_2\text{C}(\text{CH}_3)_2$	17%	Calcd. Found	51.8 34.6 34.4 36.0	5.0 2.2 2.6 2.7	23.0 17.3 20.1 18.4		25.6 (Cl) 23.6 (Cl)
(4)	$[\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2][\text{HCl}]_2$	light yellow	129-130° (dec.)	$\text{C}_2\text{H}_5\text{OCOCFe}(\text{CO})_2\text{C}_6\text{H}_5 + \text{HCl}$	83%	Calcd. Found ^b	34.6 34.4 36.0	2.2 2.6 2.7	17.3 20.1 18.4		25.6 (Cl) 23.6 (Cl) 22.6 (Cl)
<i>B. Manganese compounds</i>											
(1)	$\text{CH}_3\text{OCOMn}(\text{CO})(\text{NO})\text{C}_6\text{H}_5$	orange	56-58°	$[\text{C}_6\text{H}_5\text{Mn}(\text{CO})_2\text{NO}][\text{PF}_6] + \text{NaOCH}_3$	23%	Calcd. Found	40.5 39.9 43.4 42.7	3.4 3.0 3.6 3.8	27.0 27.3 21.7 24.5	23.2 23.6 24.9 22.9	5.9 (N) 5.9 (N) 6.3 (N) 5.8 (N)
(2)	$\text{CH}_3\text{COMn}(\text{CO})(\text{NO})\text{C}_6\text{H}_5$	orange-brown	liquide	$\text{CH}_3\text{OCOMn}(\text{CO})(\text{NO})\text{C}_6\text{H}_5 + \text{CH}_3\text{MgBr}$	low	Calcd. Found	40.5 39.9 43.4 42.7	3.4 3.0 3.6 3.8	27.0 27.3 21.7 24.5	23.2 23.6 24.9 22.9	5.9 (N) 5.9 (N) 6.3 (N) 5.8 (N)
<i>C. Molybdenum compounds</i>											
(1)	$\text{CH}_3\text{OCOC}_2\text{H}_5\text{Mo}(\text{CO})_2\text{C}_6\text{H}_5$	yellow	47-49°	$\text{NaMo}(\text{CO})_2\text{C}_6\text{H}_5 + \text{C}_2\text{H}_5\text{CO}_2\text{CH}_3$	37%	Calcd. Found	41.5 41.6 43.6 43.8	3.1 2.8 3.0 3.3	25.2 24.8 24.2 25.7	31.8 (mol. wt.) 32.4 (mol. wt.)	
(2)	$\text{C}_2\text{H}_5\text{OCOC}_2\text{H}_5\text{Mo}(\text{CO})_2\text{C}_6\text{H}_5$	yellow	33-34°	$\text{NaMo}(\text{CO})_2\text{C}_6\text{H}_5 + \text{C}_2\text{H}_5\text{CO}_2\text{C}_6\text{H}_5$	86%	Calcd. Found	43.6 43.8 42.7	3.0 3.3 4.0	24.2 25.7 24.4		
(3)	$[(\text{C}_2\text{H}_5)_4\text{N}][\text{Mo}(\text{CO})_2\text{C}_6\text{H}_5]$	pale yellow	182-185° (dec.) 180-182° (dec.)	$\text{C}_2\text{H}_5\text{OCOC}_2\text{H}_5\text{Mo}(\text{CO})_2\text{C}_6\text{H}_5 + \text{KOH} + (\text{C}_2\text{H}_5)_4\text{NBr}$ $\text{NaMo}(\text{CO})_2\text{C}_6\text{H}_5 + (\text{C}_2\text{H}_5)_4\text{NBr}$	25% 37%	Calcd. Found	51.2 50.1	6.7 6.7	12.8 13.1		3.7 (N) 3.6 (N)

^a Solid in freezer at -15°. ^b This compound apparently has some tendency to absorb water and to lose hydrogen chloride.

carbonyl derivative of a *cyclopentadienyl*metal carbonyl. We therefore proceeded further both to investigate the reactions of $\text{CH}_3\text{OCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ and to prepare other alkoxy-carbonyl derivatives both with the alkoxy-carbonyl group directly bonded to the transition metal atom (*e.g.* $\text{CH}_3\text{OCOMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$) and with the alkoxy-carbonyl group bonded to a carbon atom (*e.g.* $\text{CH}_3\text{OCOCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$). This paper discusses these results in detail amplifying and extending the results outlined in our communication².

EXPERIMENTAL

Microanalyses (Table 1) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Molecular weight determinations were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, New York, using the Mechrolab vapor pressure osmometer in benzene solution. Infrared spectra (Table 2) were generally taken in potassium bromide pellets (solids) or liquid films (liquids) and recorded on a Perkin-Elmer Model 21 spectrometer. In addition the carbonyl regions of many compounds were investigated in cyclohexane solution or halocarbon oil mulls and recorded on a Beckman IR-9 spectrometer using a scale expanded by a factor of 2.5 or 4. Unless otherwise indicated, proton NMR spectra (Table 3) were taken in carbon disulfide solution using a Varian A-60 spectrometer. Ultraviolet spectra were taken in cyclohexane solution and recorded on a Cary Model 14 spectrometer.

The dimethylcarbamoyl derivative $(\text{CH}_3)_2\text{NCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ (I) was prepared from equimolar quantities of $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ and dimethylcarbamoyl chloride using the previously published procedure³. To prevent destructive hydrolysis of the $(\text{CH}_3)_2\text{NCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ by moisture condensed from the atmosphere, it was most desirable to subject the orange-brown residue obtained from evaporation of the dichloromethane extracts directly to sublimation at $90^\circ/0.1$ mm without any intervening washing with pentane or similar solvents.

The salt $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{NO}][\text{PF}_6]$ was obtained from the commercially available $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ (Ethyl Corporation, New York City) by the previously published procedure⁹. Unless otherwise specified, solutions of $\text{NaMo}(\text{CO})_3\text{C}_5\text{H}_5$ were obtained by boiling hexacarbonylmolybdenum with a 20% excess of sodium cyclopentadienide in tetrahydrofuran solution under reflux^{10,11}. Diethyl ether solutions of the alkylmagnesium halides (3 M) were purchased from the Arapahoe Chemicals, Inc., Boulder, Colorado. Other required materials were purchased from several routine sources.

Tetrahydrofuran was always redistilled over lithium aluminum hydride before use. Besides where indicated, a nitrogen atmosphere was routinely provided to exclude oxygen from the following three types of operations: (1) carrying out reactions with organometallic compounds; (2) handling filtered solutions of organometallic compounds; (3) admitting to evacuated vessels containing organometallic compounds.

Preparation of $\text{CH}_3\text{OCOFe}(\text{CO})_2\text{C}_5\text{H}_5$

A mixture of 1.0 g (4 mmoles) of $(\text{CH}_3)_2\text{NCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ (I) and 50 ml of nitrogen-saturated C. P. methanol was boiled under reflux 1 h with magnetic stirring. After cooling to room temperature methanol was removed at $\sim 25^\circ/30$ mm leaving a crystalline residue. This residue was extracted with ~ 30 ml of pentane in three portions. Cooling the filtered pentane extracts overnight in a -78° bath precipitated

TABLE 2
INFRARED SPECTRA (cm⁻¹)

No.	Compound	ν _{CO}	Medium ^a Metal	ν _{NO}	ν _{Fe-Cl} ^b	Other ^b
<i>A. Iron compounds</i>						
(1)	C ₁₁ H ₉ OCOFe(CO) ₃ C ₈ H ₆	CH	2046 (s), 1995 (s) ^c	1665 (s)	3060 (vvw)	1425 (vw), 1410 (w), 1165 (w), 1025 (s), 915 (m), 835 (m, br), 768 (w)
(2)	C ₁₁ H ₉ OCCOCH ₂ Fe(CO) ₃ C ₈ H ₆	CH	2030 (s), 1979 (s)	1706 (m)	3080 (w)	1430 (m), 1418 (sh) 1250-1230 (s, br), 1090 (s), 1060 (m), 1017 (m), 1001 (w), 844 (m), 833 (m), 750 (w)
(3)	C ₂₁ H ₁₅ OCCO(CH ₂) ₄ Fe(CO) ₃ C ₈ H ₆	CH	2016 (s), 1963 (s)	1740 (w)	3060 (w)	1472 (w), 1453 (m), 1435 (m), 1427 (m), 1412 (m), 1381 (w), 1360 (m), 1316 (m), 1280 (m), 1220 (s), 1185 (s), 1105 (s), 1031 (m), 1014 (m), 1000 (m), 922 (w), 842 (s), 828 (s)
(4)	CH ₃ COFe(CO) ₂ C ₈ H ₆	CH	2035 (s), 1969 (s)	1673 (s)	d	f
(5)	C ₈ H ₆ COFe(CO) ₂ C ₈ H ₆	CH	2033 (s), 1976 (s)	1633 (m)	e	r
(6)	[C ₈ H ₆ Fe(CO) ₃][HCl]	KBr	2110 (s), 2050 (vs)	...	3020 (vw)	1414 (w), 1002 (vw, br), 874 (w)
<i>B. Manganese compounds</i>						
(1)	CH ₃ COMn(CO)(NO) ₂ C ₈ H ₆	CH	2023 (m)	1653 (m)	3070 (vw)	1455 (vw), 1430 (w), 1413 (m), 1350 (vw), 1258 (vw), 1168 (w), 1067 (w), 1018 (vs), 995 (m), 920 (m), 846 (m), 838 (w), 832 (w), 765 (w)
(2)	CH ₃ COMn(CO)(NO) ₂ C ₈ H ₆	liq.	1990 (s)	1630 (s)	3060 (w)	1493 (vw), 1430 (w), 1410 (m), 1324

*ν*_{max} (cm⁻¹)

(1)	CH ₃ COCCl ₂ Mo(CO) ₃ C ₆ H ₆	C-H	2041 (s), 1959 (vs)	1708 (m)	2975 (vvw)	1440 (vs), 1102 (s), 1063 (w), 1054 (w), 1027 (m), 1015 (w), 1007 (w), 947 (w), 862 (m), 840 (s), 835 (m), 827 (w), 724 (w)
(2)	C ₂ H ₅ OCCOCH ₂ Mo(CO) ₃ C ₆ H ₆	C-H	2036 (m), 1957 (s)	1702 (w)	3060 (w)	1475 (w), 1460 (w), 1435 (m), 1422 (m), 1416 (m), 1380 (w), 1357 (w), 1293 (vw), 1235 (vs), 1088 (s), 1077 (s), 1035 (s), 1010 (m), 1003 (m), 949 (w), 922 (w), 847 (sh), 820 (s), 755 (vw)
(3)	[(C ₂ H ₅) ₄ N][Mo(CO) ₃ C ₆ H ₆]	H-C	2053 (m), 1983 (s), 1939 (m), 1889 (s), 1782 (s), 1748 (s)		3030 (w)	1490 (s), 1480 (s), 1450 (s), 1435 (s), 1420 (m), 1390 (s), 1364 (s), 1293 (w), 1267 (w), 1235 (w), 1185 (m), 1170 (s), 1101 (m), 1090 (m), 1053 (m), 997 (s), 774 (s)

^a This refers to the medium in which the carbonyl and nitrosyl bands were observed. Abbreviations: CH = cyclohexane solution, HC = halo-carbon oil (ml), KBr = KBr pellet, and liq. = liquid film. Spectra in this region were generally studied on more dilute samples than in the other regions. ^b This region was studied in KBr pellets for solid compounds and in liquid films for liquid compounds. ^c Weaker bands due to [C₆H₆Fe(CO)₂]₂ were observed in this solution. ^d For a description of the spectrum of CH₃CO)₂e(CO)₂C₆H₆ in these regions see ref. 3. ^e For a description of the spectrum of C₆H₅COFe(CO)₂C₆H₆ in these regions see ref. 10.

TABLE 3

PROTON NMR SPECTRA (τ)

No.	Compound	Solvent	π -C ₅ H ₅ ^a	CH ₃ ^b	CH ₂ ^b	Remarks
(1)	CH ₃ OCOF _e (CO) ₂ C ₅ H ₅	CS ₂	5.14	6.61	—	
(2)	CH ₃ OCOMn(CO)(NO)C ₅ H ₅	CS ₂	4.90	6.54	—	
(3)	CH ₃ COFe(CO) ₂ C ₅ H ₅	CS ₂	5.13	7.43	—	
(4)	CH ₃ COMn(CO)(NO)C ₅ H ₅	CS ₂	4.96	7.43	—	
(5)	CH ₃ OCOCH ₂ Fe(CO) ₂ C ₅ H ₅	CS ₂	5.20	6.54	8.60	
(6)	CH ₃ OCOCH ₂ Mo(CO) ₃ C ₅ H ₅	CS ₂	4.65	6.52	8.30	
(7)	C ₂ H ₅ OCOCH ₂ Mo(CO) ₃ C ₅ H ₅	CS ₂	4.63	—	8.31	
(8)	C ₂ H ₅ OCOCH ₂ CH ₂ Fe(CO) ₂ C ₅ H ₅	CS ₂	5.24	—	8.82 (t) 6.07 (q) 7.76 (t) 8.40 (t)	$J_{HH} = 7$ cps $J_{HH} = 8$ cps
(9)	[(C ₂ H ₅) ₄ N] ⁺ Mo(CO) ₂ C ₅ H ₅ ⁻	(CD ₃) ₂ CO	5.00	8.81 (t) 8.53 (tt)	6.00 (q) 6.53 (q)	$J_{HH} = 7$ cps $J_{HH} = 8$ cps $J_{NH} = 2$ cps

^a All of the resonances were singlets. ^b Singlets unless otherwise indicated. Abbreviations: t = triplet, q = quartet, tt = triple triplet.

~ 0.6 g (63% yield) of pale red crystals of crude CH₃OCOF_e(CO)₂C₅H₅ which were removed by filtration and dried. Sublimation of this crude product at 60–90°/0.1 mm onto a -78° probe gave 0.466 g (49% yield) of orange crystals, m.p. 34–36°.

Larger quantities of CH₃OCOF_e(CO)₂C₅H₅ were obtained by treating crude unsublimed (CH₃)₂NCOFe(CO)₂C₅H₅ with methanol. Thus 200 mmoles each of NaFe(CO)₂C₅H₅ and dimethylcarbonyl chloride were reacted 3 h in 600 ml of tetrahydrofuran at room temperature. After removal of the tetrahydrofuran at ~ 25°/30 mm, the residue was extracted with ~ 500 ml of dichloromethane in several portions. Solvent was removed from the dichloromethane extracts at ~ 25°/30 mm leaving an orange-brown residue of crude (CH₃)₂NCOFe(CO)₂C₅H₅. This residue was boiled under reflux with 250 ml of C. P. methanol for 2 h. After cooling to room temperature, solvent was removed at 25°/30 mm. The residue was sublimed at ~ 85°/~ 0.5 mm collecting the orange sublimate on a probe cooled with circulating isopropanol at -2°. A total of 22 g (46% yield based on [C₅H₅Fe(CO)₂]₂) of CH₃OCOF_e(CO)₂C₅H₅ was obtained.

Upon storage in a closed container, CH₃OCOF_e(CO)₂C₅H₅ appeared to decompose slowly over a period of weeks even in a freezer at -10°.

Analogous treatment of (CH₃)₂NCOFe(CO)₂C₅H₅ with ethanol gave an orange-brown viscous liquid, probably C₂H₅OCOF_e(CO)₂C₅H₅, which was not investigated in detail.

Reaction between CH₃OCOF_e(CO)₂C₅H₅ and HCl

A solution of 1.15 g (5 mmoles) of CH₃OCOF_e(CO)₂C₅H₅ in ~ 50 ml of pure benzene or diethyl ether was treated with excess gaseous hydrogen chloride for several minutes. The pale yellow precipitate was filtered under nitrogen, washed with diethyl ether and pentane, and dried in a stream of nitrogen to give ~ 1.15 g (83% yield) of pale yellow solid [C₅H₅Fe(CO)₃][HCl₂].

In a larger scale preparation a mixture of 200 mmoles each of $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ and dimethylcarbamoyl chloride was converted to crude $\text{CH}_3\text{OCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ as described above. The unsublimed methoxycarbonyl derivative was dissolved in ~ 225 ml of pure benzene and treated with gaseous hydrogen chloride for 30 minutes. The resulting pale yellow precipitate was filtered under nitrogen and washed with diethyl ether and pentane to give 25.8 g (47 % yield based on $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$) of pale yellow $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3][\text{HCl}_2]$.

Water dissolved $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3][\text{HCl}_2]$ readily and completely to form a pale yellow solution. Treatment of this solution with an aqueous solution of ammonium hexafluorophosphate gradually gave a pale yellow crystalline precipitate indicated by its infrared spectrum to be $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3][\text{PF}_6]$ previously¹²⁻¹⁴ prepared by other reactions.

Reaction between $\text{CH}_3\text{OCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ and methylmagnesium bromide

A mixture of 1.18 g (5 mmoles) of $\text{CH}_3\text{OCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ and ~ 43 ml of diethyl ether containing 10 mmoles of methylmagnesium bromide was stirred ~ 16 h at room temperature. The reaction mixture was then hydrolyzed with 20 ml of saturated aqueous ammonium chloride. The ether layer was separated, dried (anhydrous Na_2SO_4), and filtered. Solvent was removed from the filtrate at $\sim 25^\circ/30$ mm. The crystalline residue of crude $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ was extracted with five 15 ml portions of pentane and the filtered extracts cooled in a -78° bath for 4 h to precipitate 0.854 g (78 % yield) of orange crystalline $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$. Sublimation of a portion of this material at $55-65^\circ/0.1$ mm gave an 85 % recovery of yellow-orange crystals, m.p. $57-59^\circ$ (lit.³ m.p. $56-57^\circ$), identified by comparison of its infrared spectrum with that of an authentic sample obtained from $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ and acetyl chloride.

Reaction between $\text{CH}_2\text{OCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ and phenylmagnesium bromide

The reaction between 1.18 g (5 mmoles) of $\text{CH}_2\text{OCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ and 10 mmoles of phenylmagnesium bromide was carried out exactly as for the reaction with methylmagnesium bromide described above except that the reaction time was only ~ 1 h prior to hydrolysis (similar results were obtained with longer reaction times). Evaporation of the ether layer after hydrolysis gave a yellow-brown liquid. This liquid product was chromatographed on a 2×50 cm alumina column in diethyl ether solution. After development with $(\text{C}_2\text{H}_5)_2\text{O}$ the yellow-orange band was eluted with diethyl ether. Evaporation of the filtered eluate left yellow-orange crystals. These were dissolved in 40 ml of pentane and the filtered solution cooled overnight in a -78° bath. After filtration and drying 0.043 g (3.1 % yield) of $\text{C}_6\text{H}_5\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$, m.p. $63-64^\circ$ (lit.¹⁰, m.p. $59-62^\circ$) was obtained. The infrared spectrum of this product was identical to that of an authentic sample of $\text{C}_6\text{H}_5\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ obtained from $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ and benzoyl chloride¹⁶.

Preparation of $\text{CH}_3\text{OCOMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$

A solution of 0.28 g (12.2 mmoles) of sodium metal spheres in 50 ml of methanol was stirred 18 h with 3.5 g (10 mmoles) of $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{NO}][\text{PF}_6]$. Methanol was removed from the resulting reaction mixture at $\sim 25^\circ/30$ mm. The product could be extracted from the residue with pentane but use of diethyl ether was preferable since

it dissolved more of the product. Evaporation of the pentane or diethyl ether extracts gave orange crystals. These crystals were dissolved in the minimum necessary quantity of pentane and the filtered solution cooled in a -78° bath. The resulting orange crystals were filtered and dried to give up to 0.555 g (23% yield) of orange $\text{CH}_3\text{OCOMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$, m.p. $56-58^\circ$.

Attempts to scale up this reaction were relatively unsatisfactory. In larger scale experiments cooling (0° bath) is desirable during the addition of the $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{NO}]^-\text{PF}_6^-$ to the sodium methoxide solution since the exothermic reaction otherwise raises significantly the temperature of the reaction mixture. In some cases reaction times of as little as 30 min prior to methanol removal were tried with similar results. Despite these precautions the maximum yield of $\text{CH}_3\text{OCOMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ obtained from 50 mmoles of $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{NO}]^-\text{PF}_6^-$ and 60 mmoles of sodium methoxide was only $\sim 11\%$.

The orange crystals of $\text{CH}_3\text{OCOMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ darkened appreciably upon exposure to air for ~ 1 h especially when wet or impure. Upon heating at $\sim 80^\circ/0.1$ mm rapid sublimation of $\text{CH}_3\text{OCOMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ occurred to give an orange crystalline sublimate; however, the recovery of sublimed material was only $\sim 22\%$. Much of the $\text{CH}_3\text{OCOMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ decomposed to give a black residue insoluble even in dichloromethane. Even storage of $\text{CH}_3\text{OCOMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ at -10° in closed nitrogen-flushed vials caused noticeable decomposition after several days.

Preparation of $\text{CH}_3\text{COMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$

A solution of 1.38 g (60 mmoles) of sodium metal spheres in 150 ml of pure methanol was cooled in an ice bath and treated with 17.5 g (50 mmoles) of solid $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{NO}]^-\text{PF}_6^-$ at such a rate that the temperature remained below $+5^\circ$. After all of the manganese compound had been added, stirring was continued for 30 min. Methanol was then removed from the deep red reaction mixture at $\sim 25^\circ/30$ mm. The residue was then dried ~ 16 h at $25^\circ/0.1$ mm to assure complete removal of the methanol.

This residue was stirred for a few minutes with ~ 150 ml of anhydrous diethyl ether. After cooling the resulting mixture to -78° , it was treated dropwise with 20 ml (60 mmoles) of a 3 M solution of methylmagnesium bromide in diethyl ether. The reaction mixture was allowed to warm to room temperature and stirred ~ 16 h at room temperature. The resulting reaction mixture was then hydrolyzed with 100 ml of saturated aqueous ammonium chloride. The diethyl ether layer was separated and the aqueous layer extracted with 50 ml portions of diethyl ether until the extracts were no longer colored. The combined diethyl ether solutions were dried over anhydrous sodium sulfate, filtered, and solvent removed from the filtrate at $\sim 25^\circ/30$ mm giving a yellow-brown liquid residue. A filtered solution of this residue in 40 ml of pentane was cooled 2 days at -78° . Orange crystals separated. Supernatant liquid was removed from these crystals with a syringe and the crystals then dried in a vigorous stream of nitrogen while warming to room temperature. They melted to give ~ 0.15 g (1.4% yield) of orange-brown liquid $\text{CH}_3\text{COMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$. This material appeared to decompose upon standing.

Treatment with methylmagnesium bromide of a pure sample of $\text{CH}_3\text{OCOMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ as well as one prepared *in situ* as described above gave $\text{CH}_3\text{COMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$.

Preparation of $C_2H_5OCOCH_2Mo(CO)_3C_5H_5$

A solution of 100 mmoles of $NaMo(CO)_3C_5H_5$ in ~ 350 ml of tetrahydrofuran was stirred ~ 20 h with 12.2 g (100 moles) of ethyl chloroacetate at room temperature. Solvent was then removed from the reaction mixture at ~ 25°/30 mm. The residue was extracted with ~ 250 ml of dichloromethane in four portions. Solvent was removed from the filtered extracts at ~ 25°/30 mm. The yellow-orange liquid residue was extracted with ~ 300 ml of pentane in three portions. The filtered pentane extracts were cooled to -78° for ~ 17 h. The resulting yellow-orange crystals were filtered and dried to give 28.26 g (86 % yield) of crude $C_2H_5OCOCH_2Mo(CO)_3C_5H_5$, m.p. 30-32°.

A sample of this crude product was purified further for analysis by chromatography on 2 × 50 cm alumina column in diethyl ether solution followed by low-temperature crystallization from pentane.

The same compound $C_2H_5OCOCH_2Mo(CO)_3C_5H_5$ could also be obtained from ethyl diazoacetate and $C_5H_5Mo(CO)_3H$. In this case a solution of 10 mmoles of $NaMo(CO)_3C_5H_5$ in ~ 150 ml of redistilled tetrahydrofuran was prepared from $[C_5H_5Mo(CO)_3]_2$ and dilute sodium amalgam. This solution was treated with excess glacial acetic acid or *tert*-butyl chloride to generate $C_5H_5Mo(CO)_3H$. The resulting mixture was stirred at least 16 h with excess ethyl diazoacetate. After isolation by dichloromethane extraction, alumina chromatography in diethyl ether solution, and low-temperature pentane crystallization, a 3 % yield of $C_2H_5OCOCH_2Mo(CO)_3C_5H_5$ was obtained.

Preparation of $CH_3OCOCH_2Mo(CO)_3C_5H_5$

The reaction between 100 mmoles of $NaMo(CO)_3C_5H_5$ and 10.85 g (100 mmoles) of methyl chloroacetate was carried out in a manner exactly analogous to the reaction between $NaMo(CO)_3C_5H_5$ and ethyl chloroacetate cited above until the first low-temperature pentane crystallization which yielded 11.68 g (37 % yield) of crude $CH_3OCOCH_2Mo(CO)_3C_5H_5$. Final purification (92 % recovery) of some of this sample was carried out by sublimation at 100°/0.1 mm collecting the yellow crystalline sublimate on a probe cooled to 25°.

Preparation of $CH_3OCOCH_2Fe(CO)_2C_5H_5$

A mixture of 50 mmoles of $NaFe(CO)_2C_5H_5$ and 5.4 g (50 mmoles) of methyl chloroacetate in 200 ml of redistilled tetrahydrofuran was stirred ~ 16 h at room temperature. The tetrahydrofuran was then removed at ~ 25°/30 mm. The residue was extracted with three 100 ml portions of dichloromethane and solvent removed from the filtered dichloromethane extracts at ~ 25°/30 mm. A solution of the residue in ~ 150 ml of diethyl ether was chromatographed on a 5 × 50 cm alumina column. The chromatogram was developed with diethyl ether. A brown-violet band of $[C_5H_5Fe(CO)_2]_2$ was observed followed by a yellow band of $CH_3OCOCH_2Fe(CO)_2C_5H_5$. Both bands were eluted with diethyl ether. Solvent was removed from the filtered eluates at ~ 25°/30 mm. After pentane washing the residue from evaporation of the eluate of the first band yielded 0.649 g of $[C_5H_5Fe(CO)_2]_2$. Evaporation of solvent from the eluate of the second band left a yellow-orange liquid which gradually crystallized on standing. A filtered solution of this liquid in 50 ml of pentane de-

posited yellow-orange crystals at -78° which were filtered and dried after several hours to give 0.634 g (5.1% yield) of $\text{CH}_3\text{OCOCH}_2\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$, m.p. $34-36^{\circ}$.

Preparation of $\text{C}_2\text{H}_5\text{OCOCH}_2\text{CH}_2\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$

The preparation of $\text{C}_2\text{H}_5\text{OCOCH}_2\text{CH}_2\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ was carried in an identical manner to that of $\text{CH}_3\text{OCOCH}_2\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ except for the following two changes: (a) During the chromatography the yellow band of $\text{C}_2\text{H}_5\text{OCOCH}_2\text{CH}_2\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ preceded rather than followed the brown-violet band of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$. (b) Since $\text{C}_2\text{H}_5\text{OCOCH}_2\text{CH}_2\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ is a liquid rather a solid at room temperature, supernatant liquid from the final low-temperature pentane crystallization was removed with a syringe rather than by suction filtration to prevent melting of the product and its passage through the filter.

Reaction between $\text{CH}_3\text{OCOCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ and methanolic potassium hydroxide

A solution of 1.0 g (15.2 mmoles) of 85% potassium hydroxide pellets in 2.5 ml of methanol was treated with 1.0 g (3.15 mmoles) of $\text{CH}_3\text{OCOCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$. The resulting dark mixture was kept for 20 h in a test tube at room temperature without any protection from the air. The reaction mixture was then filtered and the filtrate diluted to ~50 ml with methanol. The clear solution was treated with a filtered solution of 1.0 g (4.75 mmoles) of tetraethylammonium bromide in 30 ml of methanol. After storage under nitrogen at -10° for two weeks, the pale yellow well-formed crystals were filtered and dried to give 0.266 g (25% yield) of pale yellow $[(\text{C}_2\text{H}_5)_4\text{N}^+][\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5]^-$, m.p. $182-185^{\circ}$ (dec.).

The salt $[(\text{C}_2\text{H}_5)_4\text{N}^+][\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5]^-$ was also obtained from $\text{NaMo}(\text{CO})_3\text{C}_5\text{H}_5$ and tetraethylammonium bromide. A solution of $\text{NaMo}(\text{CO})_3\text{C}_5\text{H}_5$ in 250 ml of tetrahydrofuran was prepared from 100 mmoles of hexacarbonylmolybdenum and 120 mmoles of sodium cyclopentadienide by the usual procedure. Tetrahydrofuran was removed from the solution at ~30 mm and the residue dissolved in 250 ml of methanol. The filtered dark-brown solution was treated with a solution of 25.2 g (120 mmoles) of tetraethylammonium bromide in 150 ml of methanol. After stirring at room temperature for 2 h the yellow slightly air-sensitive crystalline precipitate was filtered and dried to give 14.0 g (37% yield) of $[(\text{C}_2\text{H}_5)_4\text{N}^+][\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5]^-$, m.p. $180-182^{\circ}$ (dec.).

Ultraviolet spectra

A. $\text{CH}_3\text{OCOCH}_2\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$: Maxima at 256 μm ($\epsilon = 9150$) and 360 μm ($\epsilon = 731$) in cyclohexane solution (pale yellow).

B. $\text{CH}_3\text{OCOCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$: Maxima at 254 μm ($\epsilon = 11400$) and 310 μm ($\epsilon = 2390$) in cyclohexane solution (yellow).

C. $\text{C}_2\text{H}_5\text{OCOCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$: Maximum at 310 μm ($\epsilon = 3620$) in cyclohexane solution (yellow).

Molar conductance measurements

A. $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2][\text{HCl}_2]$: 229 to 195 $\text{ohm}^{-1}\cdot\text{cm}^2\cdot\text{mole}^{-1}$ (1.12×10^{-3} to 3.46×10^{-3} molar acetone solution); 775 to 705 $\text{ohm}^{-1}\cdot\text{cm}^2\cdot\text{mole}^{-1}$ (1.06×10^{-3} to 4.83×10^{-3} molar aqueous solution).

B. $[(\text{C}_2\text{H}_5)_4\text{N}^+][\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5]^-$: 169 to 145 $\text{ohm}^{-1}\cdot\text{cm}^2\cdot\text{mole}^{-1}$ (2.35×10^{-4} to 1.58×10^{-3} molar acetone solution).

DISCUSSION

The properties of $\text{CH}_3\text{OCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ are entirely in accord with those expected for the expected structure (II). Thus the proton NMR spectrum exhibits sharp singlet resonances at τ 5.14 and τ 6.61 of approximate relative intensities 5:3 which may be assigned to the π -cyclopentadienyl and methyl protons, respectively. The infrared spectrum of $\text{CH}_3\text{OCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ besides exhibiting the usual strong terminal metal carbonyl bands (KBr pellet) at 2020 and 1950 cm^{-1} exhibits an additional strong band at 1615 cm^{-1} which may be assigned to the carbonyl group of the σ -bonded methoxycarbonyl group. Like other $\text{RFe}(\text{CO})_2\text{C}_5\text{H}_5$ compounds, the methoxycarbonyl derivative $\text{CH}_3\text{OCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ is a volatile yellow-orange solid readily soluble even in non-polar organic solvents. The volatility of $\text{CH}_3\text{OCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ was sufficient to permit purification of small quantities by sublimation at 90°/0.1 mm but not of larger quantities by distillation under these conditions. Upon storage $\text{CH}_3\text{OCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ gradually decomposed into $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$.

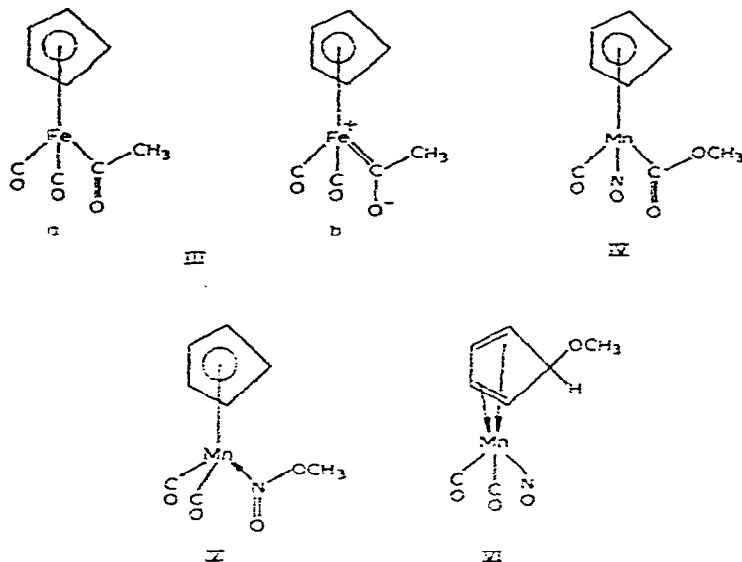
Kruck and Noack⁸ found their alkoxy carbonyl derivatives of manganese to react with hydrogen chloride and other acids to give salts of manganese carbonyl cations. Similarly $\text{CH}_3\text{OCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ reacts with hydrogen chloride in ether or benzene solution to form pale yellow hygroscopic water-soluble $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3][\text{HCl}_2]$ completely analogous to the manganese salt $[\text{Mn}(\text{CO})_6][\text{HCl}_2]$ prepared by Kruck and Noack. On the basis of their composition both of these salts appear to be derivatives of the hydrogen dichloride anion*. Analyses of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3][\text{HCl}_2]$ suggested that upon attempted thorough drying ($\sim 25^\circ/1$ mm) a loss of some of the hydrogen chloride occurred. The nature of the cation in $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3][\text{HCl}_2]$ was demonstrated by conversion with aqueous ammonium hexafluorophosphate to the known $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3][\text{PF}_6]^{12,13}$. This synthesis of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3][\text{HCl}_2]$ is the first synthesis of a derivative of the $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3]^+$ cation^{12,13} from $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ which does not require the use of carbon monoxide under pressure; in this synthesis of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3]^+$ the "extra" carbonyl group originates from the dimethylcarbamyl chloride.

The reaction between $\text{CH}_3\text{OCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ and methylmagnesium bromide did not give the expected tertiary alcohol $(\text{CH}_3)_2\text{C}(\text{OH})\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$. Instead, a good yield of the known³ acetyl derivative $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ (III) was obtained. Evidently this acetyl derivative unlike a typical ketone is resistant to further addition of methylmagnesium bromide. This is readily understandable when the significant contribution of the resonance structure (IIIb) is considered^{3,17}. The negative charge on the oxygen atom resulting from this resonance structure would act as a barrier towards addition of the anionic methyl fragment from the methylmagnesium bromide. The acetyl derivative (III) was also obtained in moderate yield (41%) from methylmagnesium bromide and the dimethylcarbamoyl derivative $(\text{CH}_3)_2\text{NCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ (I). The benzoyl derivative $\text{C}_6\text{H}_5\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ was analogously obtained but in low yield ($\sim 3\%$) from $\text{CH}_3\text{OCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ and phenylmagnesium bromide. However, several attempts to prepare the formyl derivative $\text{HCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ from $\text{CH}_3\text{OCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ and complex metal hydrides such as LiAlH_4 or NaBH_4 always failed; $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ was the major product containing iron.

In 1956 Piper and Wilkinson¹¹ reported alkyl derivatives of the types RFe -

* For a description of other salts of the HCl_2^- anion see refs. 15 and 16.

$(\text{CO})_2\text{C}_5\text{H}_5$ and $\text{RCr}(\text{NO})_2\text{C}_5\text{H}_5$. They predicted the eventual discovery of compounds of the intermediate type $\text{RMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ but failed to report any such compounds. Even in the subsequent literature compounds of the type $\text{RMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ remained unreported. In one of the most recent attempts⁹ to prepare such compounds, the binuclear compound $[\text{C}_5\text{H}_5\text{MnCONO}]_2$ was reduced with sodium amalgam and



the resulting brown solution (assumed but not proved to contain the anion $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})(\text{NO})]^-$) treated with methyl iodide or acetyl chloride. However, no $\text{RMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ compounds were obtained.

Using a different approach to the preparation of $\text{RMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ compounds suggested by the work of Kruck and Noack⁸ and by the iron chemistry discussed above, the reaction between $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{NO}]^+\text{PF}_6^-$ and methanolic sodium methoxide was investigated. From the resulting mixture orange crystals of the expected composition $\text{C}_5\text{H}_5\text{NO}_4\text{Mn}$ were obtained.

Three possible structures must be considered for a product of this composition $\text{C}_5\text{H}_5\text{NO}_4\text{Mn}$ obtained from the $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{NO}]^+$ cation and the methoxide anion. The first possibility is $\text{CH}_3\text{OCOMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ (IV), a σ -methoxycarbonyl complex of the type $\text{RMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$. The second possibility is $\text{CH}_3\text{ONOMn}(\text{CO})_2\text{C}_5\text{H}_5$ (V), a methyl nitrite complex of the type $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{L}^*$. The third and final possibility is $(\text{C}_5\text{H}_5\text{OCH}_3)\text{Mn}(\text{CO})_2\text{NO}$ (VI), a diene complex derived from methoxycyclopentadiene.

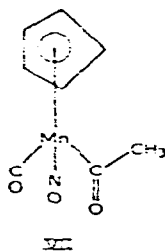
The spectroscopic properties of $\text{C}_5\text{H}_5\text{NO}_4\text{Mn}$ are in accord with the formulation $\text{CH}_3\text{OCOMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ (IV) unambiguously excluding both of the alternative possibilities. Thus the infrared spectrum exhibits a terminal metal carbonyl band at 2023 cm^{-1} ; a terminal metal nitrosyl band at 1786 cm^{-1} ; and an ester carbonyl band at 1653 cm^{-1} . This excludes formulation as the methyl nitrite complex (V) which, like other $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{L}$ compounds¹⁹ would be expected to have *two* terminal metal

* For a discussion of $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{L}$ complexes see ref. 18.

carbonyl frequencies separated by at least 55 cm^{-1} . Moreover, the methyl nitrite derivative would be expected to exhibit neither terminal metal nitrosyl bands nor ester carbonyl bands but instead bands at ~ 1680 and $\sim 1625\text{ cm}^{-1}$ due to ν_{NO} of the methyl nitrite ligand²⁰. The proton NMR spectrum of $\text{C}_5\text{H}_5\text{NO}_4\text{Mn}$ exhibits sharp singlet resonances at τ 4.90 and τ 6.54 of approximate relative intensities 5:3 which may be assigned to the η -cyclopentadienyl and methyl protons, respectively. If the compound $\text{C}_5\text{H}_5\text{NO}_4\text{Mn}$ was the methoxycyclopentadiene diene complex (VI), the π -bonded diene ligand would be expected to exhibit two resonances rather than the single observed resonance. Thus the compound $\text{C}_5\text{H}_5\text{NO}_4\text{Mn}$ clearly must be formulated as $\text{CH}_3\text{OCOMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ (IV) thereby representing the first known example of an $\text{RMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ compound.

Characteristic of $\text{CH}_3\text{OCOMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ is its instability*. Upon storage the orange crystals gradually become brown. Sublimation at $\sim 80^\circ/0.1\text{ mm}$ led only to a poor recovery of orange sublimate; the bulk of the $\text{CH}_3\text{OCOMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ turned to an insoluble black material. Attempted scaling up of this preparation led to a drastic reduction of the yield even when cooling was used to moderate the exothermic reaction between $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{NO}][\text{PF}_6^-]$ and methanolic sodium methoxide. Thus only small quantities of $\text{CH}_3\text{OCOMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ were available.

The formation of $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ in good yield from $\text{CH}_3\text{OCOFc}(\text{CO})_2\text{C}_5\text{H}_5$ and methylmagnesium bromide suggested the preparation of the acetyl derivative $\text{CH}_3\text{COMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ from $\text{CH}_3\text{OCOMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ and methylmagnesium bromide. These materials were indeed found to react vigorously in diethyl ether solution to give a mixture from which a small quantity of an air-sensitive orange-brown liquid could be isolated after hydrolysis. Larger quantities of this material were obtained by treating the crude product obtained from $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{NO}][\text{PF}_6^-]$ and sodium methoxide after removal of the methanol with methylmagnesium bromide avoiding isolation of the intermediate $\text{CH}_3\text{OCOMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$. The proton NMR spectrum of this liquid was distinctly different from that of $\text{CH}_3\text{OCOMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ exhibiting singlet resonances at τ 4.96 and τ 7.43 of relative intensities 5:3. This and the similarity of the $1400\text{--}700\text{ cm}^{-1}$ region of the infrared spectrum to that of $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ support formulation of this orange-brown liquid as $\text{CH}_3\text{COMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ (VII). The rarity and instability of $\text{CH}_3\text{COMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ discouraged

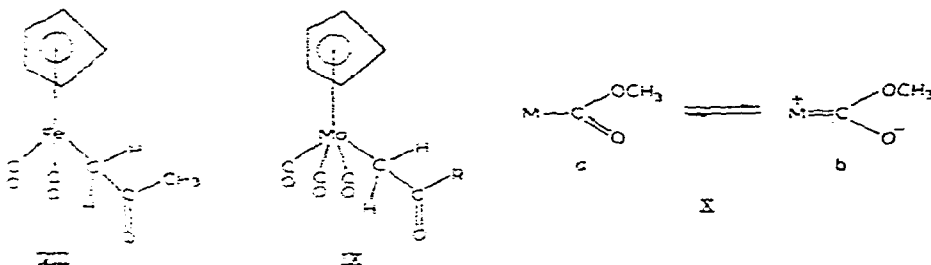


studies other than those required for its characterization. Curiously anomalous is the higher melting point of $\text{CH}_3\text{OCOMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ ($56\text{--}58^\circ$) relative to $\text{CH}_3\text{OCOFc}(\text{CO})_2\text{C}_5\text{H}_5$ ($34\text{--}36^\circ$) but the lower melting point of $\text{CH}_3\text{COMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ ($< 20^\circ$) relative to $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ ($57\text{--}59^\circ$). One clear indication from these studies on

* The cyclopentadienylmanganese nitrosyl carbonyl $[\text{C}_5\text{H}_5\text{MnCONO}]_2$ is also rather unstable⁹.

$\text{CH}_3\text{OCOMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ (IV) and $\text{CH}_3\text{COMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ (VII) is the instability of $\text{RMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ compounds relative to analogous $\text{RFe}(\text{CO})_2\text{C}_5\text{H}_5$ compound and probably also analogous $\text{RCr}(\text{NO})_2\text{C}_5\text{H}_5$ compounds.

The compounds $\text{CH}_3\text{OCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ (II) and $\text{CH}_3\text{OCOMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$ (IV) contain methoxycarbonyl groups directly bonded to a transition-metal atom. For comparison the compounds $\text{CH}_3\text{OCOCH}_2\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ (VIII) and $\text{CH}_3\text{OCOCH}_2\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5$ (IX, $\text{R} = \text{CH}_3$) were synthesized from methyl chloroacetate and the sodium salt of the appropriate metal carbonyl anion. The physical and spectroscopic properties of these materials are entirely those expected for $\text{RFe}(\text{CO})_2\text{C}_5\text{H}_5$ and $\text{RMo}(\text{CO})_2\text{C}_5\text{H}_5$ compounds. The ester carbonyl frequencies (Table 2) in compounds of the type CH_3OCOM [(II) and (IV)] are lower than those in compounds of the type $\text{CH}_3\text{OCOCH}_2\text{M}$ [(VIII) and (IX)]. In compounds of the type CH_3OCOM [(II) and (IV)] the carbon-oxygen bond order of the carbonyl group can be lowered by significant contributions of the dipolar resonance structure (Xb)*. A similar effect is not possible in the $\text{CH}_3\text{OCOCH}_2\text{M}$ compounds owing to the "insulating" CH_2 group.



Piper and Wilkinson¹¹ prepared the methyl compounds $\text{CH}_3\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5$ in low yield ($\sim 3\%$) from $\text{HMo}(\text{CO})_2\text{C}_5\text{H}_5$ and diazomethane. The reaction between ethyl diazoacetate and $\text{HMo}(\text{CO})_2\text{C}_5\text{H}_5$ to give the ethyl ester $\text{C}_2\text{H}_5\text{OCOCH}_2\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5$ (IX, $\text{R} = \text{C}_2\text{H}_5$) also in only $\sim 3\%$ yield is entirely analogous. Much more efficient is the preparation of $\text{C}_2\text{H}_5\text{OCOCH}_2\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5$ (IX, $\text{R} = \text{C}_2\text{H}_5$) from $\text{NaMo}(\text{CO})_2\text{C}_5\text{H}_5$ and ethyl chloroacetate.

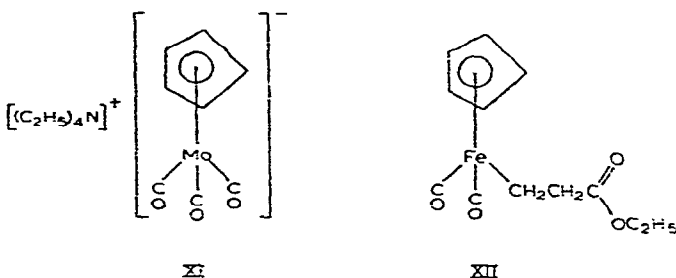
Attempts to prepare other organomolybdenum compounds from $\text{C}_2\text{H}_5\text{OCOCH}_2\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5$ (IX, $\text{R} = \text{C}_2\text{H}_5$) were generally unsuccessful. Treatment of (IX, $\text{R} = \text{C}_2\text{H}_5$) with methylmagnesium bromide or lithium aluminum hydride led to production of only $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2]_2$; no $\text{RMo}(\text{CO})_2\text{C}_5\text{H}_5$ compounds were observed. Attempts to decarbonylate $\text{C}_2\text{H}_5\text{OCOCH}_2\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5$ either thermally or photochemically gave only $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2]_2$ as an identifiable organomolybdenum compound. No compound such as $\text{C}_2\text{H}_5\text{OCOCH}_2\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5$ was observed.

In an attempt to prepare salts of the unknown carboxylic acid $\text{HOOCCH}_2\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5$, the methyl ester $\text{CH}_3\text{OCOCH}_2\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5$ was treated with methanolic potassium hydroxide. After removal of insoluble materials, treatment of the filtrate with tetraethylammonium bromide yielded ultimately a crystalline tetraethylammonium salt. Investigation of this salt showed it to be $[(\text{C}_2\text{H}_5)_4\text{N}][\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5]$ (XI). Thus the proton NMR spectrum of this material in acetone- d_6 solution exhibited (after subtracting the solvent impurity resonances) only a resonance at $\tau 5.00$ (singlet)

* This effect is entirely analogous to that observed in acyl compounds such as $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ (refs. 3 and 17); see structure (III).

due to the five π -cyclopentadienyl protons and resonances at τ 6.53 (quartet, $J = \sim 8$ cps) and τ 8.53 [1:2:1 triplet ($J = 8$ cps) of 1:1:1 triplets* ($J = 2$ cps)] due to the eight methylene protons and twelve methyl protons, respectively, of the tetraethylammonium cation. Potassium hydroxide thus degrades $\text{CH}_3\text{OCOCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ to the $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]^-$ anion.

Despite the ready availability of both the tetraethylammonium cation and the $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]^-$ anion, this salt $[(\text{C}_2\text{H}_5)_4\text{N}][\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5]$ (XI) has never been described in the literature. Treatment of a methanol solution of $\text{NaMo}(\text{CO})_3\text{C}_5\text{H}_5$ with a methanol solution of tetraethylammonium bromide gave a yellow precipitate with an infrared spectrum identical to that of the product (XI) obtained by the degradation of $\text{CH}_3\text{OCOCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$. The tetraethylammonium salt $[(\text{C}_2\text{H}_5)_4\text{N}][\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5]$ (XI) is oxidized by air only relatively slowly; usual manipulations with it may be carried out in the air but storage under nitrogen is recommended.



The reactions between other haloesters of the general type $\text{ROCO}(\text{CH}_2)_n\text{X}$ ($\text{R} = \text{methyl or ethyl}$; $n = 2$ or 3 ; $\text{X} = \text{Cl or Br}$) and the sodium salts $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ and $\text{NaMo}(\text{CO})_3\text{C}_5\text{H}_5$ were investigated. The molybdenum derivative $\text{NaMo}(\text{CO})_3\text{C}_5\text{H}_5$ failed to react at room temperature with these haloesters in which the halogen atom and the ester group are separated by two or more carbon atoms. The more reactive iron derivative $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ reacted with ethyl 3-chloropropionate, $\text{C}_2\text{H}_5\text{OCOCH}_2\text{CH}_2\text{Cl}$, to form orange-brown air-sensitive liquid $\text{C}_2\text{H}_5\text{OCOCH}_2\text{CH}_2\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ (XII). The proton NMR spectrum was entirely in accord with the proposed formulation.

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SUMMARY

Reaction between $(\text{CH}_3)_2\text{NCOFe}(\text{CO})_2\text{C}_5\text{H}_5^3$ and methanol gives the yellow-orange methyl ester $\text{CH}_3\text{OCOFe}(\text{CO})_2\text{C}_5\text{H}_5$. Cleavage of this iron-containing ester with hydrogen chloride in ether or benzene solution gives the yellow hygroscopic salt $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3][\text{HCl}_2]$. Reaction between $\text{CH}_3\text{OCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ and the alkylmagnesium bromides RMgBr ($\text{R} = \text{methyl or phenyl}$) gives the acyl derivatives $\text{RCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ previously prepared from $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ and acyl halides^{3,10}.

* The 1:1:1 triplets in this spectrum apparently arise from coupling of the methyl protons with the ^{14}N nucleus ($I = 1$).

Treatment of $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{NO}][\text{PF}_6]$ with methanolic sodium methoxide gives orange crystalline $\text{CH}_3\text{OCOMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$. Treatment of this manganese-containing ester with methylmagnesium bromide in diethyl ether gives the brown liquid acetyl derivative $\text{CH}_3\text{COMn}(\text{CO})(\text{NO})\text{C}_5\text{H}_5$.

By reaction of the appropriate sodium salt $[\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5]$ or $[\text{NaMo}(\text{CO})_3\text{C}_5\text{H}_5]$ with the appropriate halogenated ester the previously unreported compounds $\text{CH}_3\text{OCOCH}_2\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$, $\text{C}_2\text{H}_5\text{OCOCH}_2\text{CH}_2\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$, $\text{CH}_3\text{OCOCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$, and $\text{C}_2\text{H}_5\text{OCOCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ were prepared. Degradation of $\text{CH}_3\text{OCOCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ with methanolic potassium hydroxide followed by treatment with tetraethylammonium bromide gives the previously unreported tetraethylammonium salt $[(\text{C}_2\text{H}_5)_4\text{N}][\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5]$ rather than a salt of the corresponding carboxylic acid.

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