PREPARATION AND DECARBONYLATION OF ACYL DERIVATIVES OF CYCLOPENTADIENYL METAL CARBONYLS*

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INTRODUCTION

Numerous acyl derivatives of manganese carbonyl of general formula $RCOMn(CO)_5$ have been prepared[3,4,5,6,7]. A characteristic reaction of these acyl derivatives is the facile thermal decarbonylation to produce the corresponding alkyl derivatives $RMn(CO)_5$. Many $RMn(CO)_5$ derivatives such as those with aryl and perfluoroalkyl groups not readily accessible by other methods may be easily obtained by thermal decarbonylation of the corresponding $RCOMn(CO)_5$ compounds. Some $R_fCOCo(CO)_4$ (R_f = perfluoroalkyl) compounds have also been obtained[8], but generally undergo spontaneous decarbonylation even at room temperature to produce the corresponding perfluoroalkyl derivatives $R_fCo(CO)_4$ (refs. 7 and 8). In addition the acyl derivatives $(R_fCO)_2Fe(CO)_4$ are undoubtedly unstable intermediates in the preparation of the perfluoroalkyl derivatives $(R_f)_2Fe(CO)_4$ from $Na_2Fe(CO)_4$ and the perfluoroacyl halides R_fCOCl (ref. 9).

The corresponding acyl derivatives of various cyclopentadienyl metal carbonyls have been investigated in much less detail. Several compounds of the type $RCOFe(CO)_2C_5H_5$ have been prepared[3,10,11], but unlike analogous derivatives of metal carbonyls without cyclopentadienyl groups listed above, could not be decarbonylated on heating[3,10]. This inability to decarbonylate the $RCOFe(CO)_2C_5H_5$ derivatives made them much less useful for syntheses of organometallic derivatives and thus discouraged detailed investigations. The molybdenum derivative $C_3F_7COMo(CO)_3C_5H_5$ has also been briefly described[6], but was prepared only once in low yield and characterized only by carbon and hydrogen analyses and its infrared spectrum[12]. Compounds of the type $RCOMo(CO)_3C_5H_5$, however, in general, are unstable[3,11]. The analogous tungsten compound $C_2H_5COW(CO)_3C_5H_5$ is considerably more stable[11].

The carbon monoxide lost in the decarbonylation of $RCOMn(CO)_5$ derivatives has been demonstrated by radiochemical techniques[3] to arise from one of the carbonyl groups bonded to the metal atom rather than from the acyl carbonyl group. Thus, the acyl carbonyl group rather than being lost is converted into a metal carbonyl group. This mechanism suggests that the case of decarbonylation of acyl metal carbonyl derivatives depends on the strength of the metal–carbon monoxide bond. It is, therefore, not surprising that the $RCOFe(CO)_2C_5H_5$ derivatives fail to undergo de-

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[*] Reactions of alkali metal derivatives of metal carbonyls, IV; for Part III of this series see ref. 1. Organometallic chemistry of the transition metals, X; for Part IX of this series see ref. 2.

carbonylation on heating just as the isoelectronic $C_5H_5Mn(CO)_3$ fails to undergo substitution reactions with loss of carbon monoxide on heating with Lewis bases such as triphenylphosphine[13]. On the other hand, the facile thermal decarbonylation of the $RCOMn(CO)_5$ derivatives parallels the thermal reaction of the isoelectronic $Cr(CO)_6$ with Lewis bases to produce substitution products with loss of carbon monoxide[14].

Although $C_5H_5Mn(CO)_3$ fails to undergo substitution reactions on heating with ligands such as Lewis bases and olefins, ultraviolet irradiation of $C_5H_5Mn(CO)_3$ with these ligands[15] has produced numerous substitution products primarily of the general type $C_5H_5Mn(CO)_2L$. These results suggested that ultraviolet irradiation might be effective in causing the decarbonylation of the acyl derivatives $RCOFe(CO)_2C_5H_5$ to the corresponding alkyl derivatives. This idea received further support from the recent decarbonylation by Green and Nagy[16] of the σ-allyl derivative $C_3H_5Fe(CO)_2C_5H_5$ to the corresponding π-allyl derivative $C_3H_5FeCOC_5H_5$.

Initial experiments with $CH_3COFe(CO)_2C_5H_5$ indicated that it could be readily decarbonylated to $CH_3Fe(CO)_2C_5H_5$ by ultraviolet irradiation. This discovery prompted preparation of several previously unreported acyl compounds of the type $RCOFe(CO)_2C_5H_5$ and preparation of new perfluoroalkyl and vinyl derivatives of the type $RFe(CO)_2C_5H_5$ by their photochemical decarbonylation. In addition, photochemical decarbonylation of $C_6H_5COFe(CO)_2C_5H_5$ provided an improved synthesis of $C_6H_5Fe(CO)_2C_5H_5$ previously obtained by Piper and Wilkinson[17] in very low yield either by treatment of the iodide $C_5H_5Fe(CO)_2I$ with phenylmagnesium bromide or by treatment of $NaFe(CO)_2C_5H_5$ with iodobenzene.

Experiments with the corresponding molybdenum derivatives $RCOMo(CO)_3C_5H_5$ indicated that like the $RCOMn(CO)_5$ derivatives and unlike the $RCOFe(CO)_2C_5H_5$ derivatives, decarbonylation may be carried out by heating without irradiation. Unfortunately, like previous workers[3,11] we were unable to obtain stable compounds of the type $RCOMo(CO)_3C_5H_5$ except where R is a perfluoroalkyl group. The corresponding acyl tungsten compounds $RCOW(CO)_3C_5H_5$ appear to be more stable than their molybdenum analogous, but were neither decarbonylated by irradiation like the $RCOFe(CO)_2C_5H_5$ derivatives nor by heating like the $RCOMo(CO)_3C_5H_5$ derivatives.

This paper describes the details of our research in these areas.

EXPERIMENTAL

Microanalyses and molecular weight determinations (Table 1) (Mechrolab vapor pressure osmometer in benzene solution) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, and Schwarzkopf Microanalytical Laboratory, Woodside, New York. In general, infrared spectra were taken in potassium bromide pellets or liquid films and recorded on a Perkin-Elmer Model 21 spectrometer. In addition, the carbonyl regions of the infrared spectra of selected compounds (Table 2) were investigated in greater detail in Halocarbon oil mulls on a Beckman IR-9 spectrometer with grating optics. Ultraviolet spectra (Table 3) were taken in cyclohexane solution and recorded on a Cary Model 14 spectrometer. Ultraviolet irradiations were carried out under nitrogen in quartz vessels placed ~30 cm from a mercury lamp of ~1000 watts input power with a reflector directing the light towards the sample tube.

TABLE I

COMPOUNDS DESCRIBED IN THIS PAPER

Compound	*Color*	*M.p.*	*Preparation*	*Yield*		*Analyses*			
						C	*H*	*O or F*[a]	*Metal*
			A. Iron Compounds						
1) $C_6H_5COFe(CO)_2C_5H_5$	orange	59–62°	$NaFe(CO)_2C_5H_5 + C_6H_5COCl$	75%	Calcd.	59.5	3.5	17.1 (O)	19.9
					Found	59.3	4.0	18.0 (O)	20.8
2) $C_6H_5CH{=}CHCOFe(CO)_2C_5H_5$	orange	91–92°	$NaFe(CO)_2C_5H_5 + C_6H_5CH{=}CHCOCl$	80%	Calcd.	62.3	3.9	15.6 (O)	18.2
					Found	62.2	4.1	15.9 (O)	18.1
3) $CH_2{=}CHCOFe(CO)_2C_5H_5$	orange	liquid[b]	$NaFe(CO)_2C_5H_5 + CH_2{=}CHCOCl$	5%	Calcd.	51.7	3.4	20.7 (O)	24.1
					Found	51.7	3.5	20.9 (O)	23.5
4) $CF_3COFe(CO)_2C_5H_5$	orange	33–34°	$NaFe(CO)_2C_5H_5 + (CF_3CO)_2O$	9%	Calcd.	39.4	1.8	20.8 (F)	20.5
					Found	39.7	1.7	21.1 (F)	20.4
5) $C_2F_5COFe(CO)_2C_5H_5$	orange	54–57°	$NaFe(CO)_2C_5H_5 + C_2F_5COCl$	12%	Calcd.	37.1	1.5	29.3 (F)	17.3
					Found	37.3	1.3	29.8 (F)	17.6
6) $C_3F_7COFe(CO)_2C_5H_5$	orange	liquid[b]	$NaFe(CO)_2C_5H_5 + C_3F_7COCl$	11%	Calcd.	35.3	1.3	35.6 (F)	15.0
					Found	35.2	1.4	35.4 (F)	15.2
7) $C_6H_5Fe(CO)_2C_5H_5$	yellow	35–36° (lit.[17] 26–30°)	Irradiation of $C_6H_5COFe(CO)_2C_5H_5$	17%	Calcd.	61.4	3.9	12.6 (O)	22.0
					Found	60.6	3.8	13.1 (O)	22.2
8) $CH_2{=}CHFe(CO)_2C_5H_5$	orange	liquid[b]	Irradiation of $NaFe(CO)_2C_5H_5 + CH_2{=}CHCOCl$	2%	Calcd.	52.9	3.9	15.7 (O)	27.4
					Found	52.8	4.5	16.0 (O)	26.5
9) $CF_3Fe(CO)_2C_5H_5$	pale yellow	137–139°	Irradiation of $CF_3COFe(CO)_2C_5H_5$	33%	Calcd.	39.0	2.0	23.2 (F)	22.7
					Found	39.3	1.7	23.7 (F)	23.0
10) $C_2F_5Fe(CO)_2C_5H_5$	orange	43–45°	Irradiation of $C_2F_5COFe(CO)_2C_5H_5$	58%	Calcd.	36.5	1.7	32.1 (F)	18.9
					Found	36.9	2.0	31.1 (F)	18.7
11) $C_3F_7Fe(CO)_2C_5H_5$	orange	31–32°	Irradiation of $C_3F_7COFe(CO)_2C_5H_5$	46%	Calcd.	34.7	1.4	38.4 (F)	16.2
					Found	34.7	1.5	37.2 (F)	16.9
12) $(CF_2)_3[Fe(CO)_2C_5H_5]_2$[c]	yellow	168–172°	Irradiation of $(CF_2)_3(CO)_2[Fe(CO)_2C_5H_5]_2$	44%	Calcd.	40.5	2.0	22.6 (F)	22.2
					Found	41.5	1.9	21.5 (F)	21.7

(continued on p. 18).

TABLE 1 (*continued*)

Compound	Color	M.p.	Preparation	Yield	Analyses				
						C	*H*	*O or F*[a]	*Metal*
			B. Molybdenum Compounds						
13) $CF_3COMo(CO)_3C_5H_5$	yellow	64–65°	$NaMo(CO)_3C_5H_5 + (CF_3CO)_2O$	31 %	Calcd.	35.1	1.5	16.7 (F)	28.0
					Found	35.5	0.9	16.9 (F)	27.9
14) $C_3F_7COMo(CO)_3C_5H_5$	yellow	46–47°	$NaMo(CO)_3C_5H_5 + C_3F_7COCl$	34 %	Calcd.	32.6	1.1	30.5 (F)	
					Found	33.1	1.2	30.0 (F)	
15) $(CF_2)_3(CO)_2[Mo(CO)_3C_5H_5]_2$	dirty yellow	129–132°	$NaMo(CO)_3C_5H_5 + (CF_2)_3(COCl)_2$	47 %	Calcd.	36.2	1.4	16.4 (F)	
					Found	35.8	1.5	16.4 (F)	
16) $CF_3Mo(CO)_3C_5H_5$	yellow	153°	Pyrolysis of $CF_3COMo(CO)_3C_5H_5$	50 %	Calcd.	34.4	1.6	18.1 (F)	30.6
					Found	34.6	1.7	18.0 (F)	30.6
17) $C_3F_7Mo(CO)_3C_5H_5$	yellow	81–83°	Pyrolysis of $C_3F_7COMo(CO)_3C_5H_5$	41 %	Calcd.	31.8	1.2	32.1 (F)	
					Found	32.1	1.3	32.3 (F)	
18) $(CF_2)_3[Mo(CO)_3C_5H_5]_2$[d]	yellow	blackens above ~ 200°	Pyrolysis of $(CF_2)_3(CO)_2[Mo(CO)_3C_5H_5]_2$	28 %	Calcd.	35.6	1.6	17.8 (F)	
					Found	34.5	2.4	15.0 (F)	
			C. Tungsten Compounds						
19) $CF_3COW(CO)_3C_5H_5$[c]	yellow	80–82°	$NaW(CO)_3C_5H_5 + (CF_3CO)_2O$	53 %	Calcd.	27.9	1.1	13.2 (F)	42.8
					Found	27.7	1.4	13.6 (F)	43.3
20) $C_3F_7COW(CO)_3C_5H_5$	yellow	53–55°	$NaW(CO)_3C_5H_5 + C_3F_7COCl$	32 %	Calcd.	27.2	0.9	25.1 (F)	
					Found	27.4	1.2	24.6 (F)	
21) $CH_2{=}CHCOW(CO)_3C_5H_5$	yellow	57–59°	$NaW(CO)_3C_5H_5 + CH_2{=}CHCOCl$	8 %	Calcd.	34.0	2.1	16.5 (O)	47.4
					Found	33.4	2.2	17.9 (O)	46.6

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[a] The techniques used by the commercial microanalytical laboratories for the direct analysis of oxygen could not be used in the presence of fluorine.

[b] Solidified in freezer at ~ −15°.

[c] The infrared spectrum of even the purest material indicated the presence of an acyl metal carbonyl derivative as an impurity. This impurity could not be detected in the ^{19}F NMR spectrum.

[d] Not obtained pure. Compound identified by infrared and NMR spectra.

[e] Molecular weight: Calcd., 430. Found, 436.

TABLE 2

INFRARED SPECTRA (cm⁻¹) OF SOME CYCLOPENTADIENYL METAL CARBONYL DERIVATIVES

Compound	*Metal Carbonyl Bands*[a]	*Acyl Carbonyl Bands*[a]	*C-H Bands*[b]	*Other Bands*[b]
		A. Iron Compounds		
1) $C_6H_5COFe(CO)_2C_5H_5$	2029 (s), 1972 (s), 1943 (w)	1603 (m)	3080 (w)	1582 (s), 1570 (s), 1480 (w), 1440 (m), 1415 (m), 1358 (w), 1305 (w), 1175 (m), 1155 (s), 1110 (w), 1072 (m), 1065 (w), 1020 (m), 1000 (m), 926 (w, br), 883 (m), 850 (vs), 843 (vs), 833 (s), 762 (m), 732 (w), 694 (s)
2) $C_6H_5CH{=}CHCOFe(CO)_2C_5H_5$	$\left\{\begin{matrix}2031\ (s)\\2009\ (s)\end{matrix}\right\}$, 1963 (s)	1634 (m)	3080 (w), 3050 (sh), 3020 (vs)	1582 (s)[d], 1562 (m), 1493 (w), 1445 (w), 1430 (vw), 1410 (w), 1325 (vw), 1305 (vw), 1288 (vw), 1255 (w), 1198 (vw), 1108 (vw), 1070 (vw), 1060 (vw), 1028 (w), 1018 (w), 997 (w), 974 (m), 965 (s), 875 (w), 865 (w), 845 (m), 841 (m), 831 (m), 755 (m), 732 (m), 693 (m)
3) $CH_2{=}CHCOFe(CO)_2C_5H_5$[c]	2010 (vs), 1960 (vs)	1622 (vs)	3080 (w)	1587 (vs)[d], 1430 (m), 1410 (m), 1380 (m), 1354 (vw), 1280 (w), 1112 (m), 1058 (w), 1014 (m), 996 (m), 975 (s), 924 (vs), 914 (vs), 845 (s), 830 (s), 718 (s), 690 (s)
4) $CF_3COFe(CO)_2C_5H_5$	2046 (s), 1995 (s)	1654 (m)	3090 (w)	1430 (m), 1415 (m), 1220 (vs), 1175 (vs), 1125 (vs), 1060 (w), 1015 (w), 1000 (w), 940 (vw, br), 860–840 (vs, br), 716 (s), 686 (s)
5) $C_2F_5COFe(CO)_2C_5H_5$	2048 (s), 1998 (s)	1659 (m)	3120 (m)	1570 (w), 1430 (s), 1415 (s), 1355 (m), 1330 (vs), 1205 (vs), 1182 (vs), 1155 (vs), 1130 (vs), 1062 (s), 1050 (s), 1015 (s), 1002 (s), 945 (w), 880 (m), 870 (w), 852 (vs), 836 (s), 788 (vs), 714 (vs)
6) $C_3F_7COFe(CO)_2C_5H_5$[c]	2030 (vs), 1980 (vs)	1645 (s)	3100 (w)	1430 (w), 1416 (w), 1338 (m), 1220–1200 (vs, br), 1176 (s), 1162 (s), 1065 (w, sh), 1015 (w), 1000 (w), 975 (w), 845 (m), 835 (m), 772 (m), 728 (m), 698 (m), 688 (m)
7) $C_6H_5Fe(CO)_2C_5H_5$[17]	2021 (s), 1969 (s)	none	3070 (vvw), 3010 (vw)	1555 (m), 1468 (m), 1425 (vs), 1415 (w), 1355 (vw), 1185 (vw), 1148 (vw), 1060 (w), 1050 (w), 1007 (s), 993 (w), 860 (sh), 850 (sh), 842 (m), 826 (m), 738 (m), 728 (s)

(continued on p. 20).

TABLE 2 (*continued*)

Compound	*Metal Carbonyl Bands*[a]	*Acyl Carbonyl Bands*[a]	*C–H Bands*[b]	*Other Bands*[b]
8) $CH_2{=}CHFe(CO)_2C_5H_5$[c]	2020 (vs), 1950 (vs)	none	3080 (w), 3010 (w), 2920 (m), 2850 (sh)	1770 (w)[d], 1550 (m)[d], 1465 (sh), 1428 (w), 1415 (w), 1370 (m), 1232 (s), 1104 (w), 1059 (w), 1014 (m), 1000 (m), 985 (sh), 972 (vw, br), 880 (m), 839 (sh), 828 (s)
9) $CF_3Fe(CO)_2C_5H_5$	2053 (s), 2003 (s)	none	3100 (w)	1430 (m), 1415 (m), 1360 (vw), 1068 (s), 1042 (vs), 1015 (s), 985 (vs), 942 (s), 870 (w), 850 (s), 835 (s)
10) $C_2F_5Fe(CO)_2C_5H_5$	2054 (s), 1999 (s)	none	3100 (w)	1432 (m), 1418 (m), 1360 (w), 1295 (s), 1270 (m), 1185 (vs), 1160 (vs), 1130 (m), 1065 (m), 1010 (vs), 960 (vs), 905 (vs), 850 (s), 836 (s), 726 (s)
11) $C_3F_7Fe(CO)_2C_5H_5$[e]	2040 (s), 1990 (s)	none	3100 (vw)	1435 (m), 1417 (m), 1360 (w), 1320 (s), 1315 s), 1186 (s), 1154 (s), 1080 (s), 1065 (m), 1020 (s), 990 (s), 846 (s), 837 (m), 810 (s), 806 (s), 742 (w), 722 (s)
12) $(CF_2)_3[Fe(CO)_2C_5H_5]_2$	2026 (s), 1977 ± 7 (vs, br)	1635 (w)	3100 (w)	1430 (m), 1416 (m), 1358 (vw), 1185 (vw), 1135 (m, sh), 1119 (s), 1065 (m), 1040 (s), 1010 (s), 930 (vw), 910 (vw), 865 (sh), 846 (s), 836 (m), 760 (vw), 744 (w), 732 (w)
		B. Molybdenum Compounds		
13) $CF_3COMo(CO)_3C_5H_5$	2047 (s), $\left\{\begin{matrix}1970\ (s)\\1956\ (s)\end{matrix}\right\}$, 1926 (s)	1627 (s)	3080 (w)	1420 (m), 1220 (s), 1174 (s), 1126 (s), 1007 (w), 842 (s), 828 (s), 708 (s)
14) $C_3F_7COMo(CO)_3C_5H_5$	2050 (s), 1966 (s, br)	1655 (m, br)	3080 (w)	1425 (m), 1336 (m), 1270 (m), 1220 (s), 1200 (s), 1180 (s), 1136 (m), 1110 (s), 1008 (w), 945 (w), 860 (w), 825 (m), 765 (m), 730 (w), 713 (m), 696 (s)
15) $(CF_2)_3(CO)_2[Mo(CO)_3C_5H_5]_2$	2042 (s), 1961 (s), $\left\{\begin{matrix}1938\ (s)\\1924\ (s)\end{matrix}\right\}$	1657 (m), 1637 (m)	3100 (w)	1425 (m), 1420 (m), 1260 (w), 1249 (w), 1150 (s), 1134 (s) 1060 (w), 1007 (m), 915 (m), 848 (m), 823 (s), 680 (m)

(*continued on p. 21*).

TABLE 2 (*continued*)

Compound	*Metal Carbonyl Bands*[a]	*Acyl Carbonyl Bands*[a]	*C–H Bands*[b]	*Other Bands*[b]
16) $CF_3Mo(CO)_3C_5H_5$	2054 (s), 1976 (vs)	none	3100 (w)	1425 (m), 1417 (m), 1405 (w), 1350 (vw), 1044 (vs), 1004 (vs), 976 (vs), 935 (m), 907 (w), 860 (m), 825 (s), 693 (m)
17) $C_3F_7Mo(CO)_3C_5H_5$	2055 (s), 1977 (vs), 1926 (w)	none	3100 (w)	1425 (m), 1355 (vw), 1321 (s), 1220 (s), 1180 (vs), 1166 (s), 1156 (sh), 1075 (s), 1020 (s), 1017 (s), 986 (s), 982 (s), 935 (w), 888 (vw), 863 (vw), 852 (w), 832 (s), 793 (s), 713 (s)
18) $(CF_2)_3[Mo(CO)_3C_5H_5]_2$	2048 (s), { 1978 (s) 1963 (s) 1956 (s) }, { 1942 (s) 1931 (s) }	none	3100 (vw)	1424 (w), 1134 (w), 1069 (w), 1065 (w), 1040 (w), 1010 (m), 892 (vw), 850 (br, sh), 825 (m)
C. Tungsten Compounds				
19) $CF_3COW(CO)_3C_5H_5$	2043 (s), 1960 (vs), { 1900 (w) 1911 (w) }	1616 (s)	3100 (w) 3070 (w)	1420 (m), 1228 (s), 1175 (s), 1126 (s), 1008 (m), 925 (vw), 875 (m), 853 (vs), 848 (vs), 840 (vs), 713 (s)
20) $C_3F_7COW(CO)_3C_5H_5$	2043 (s), 1957 (vs)	1627 (s)	3080 (w)	1420 (m), 1335 (m), 1270 (w), 1220 (s), 1202 (s, sh), 1175 (m), 1133 (m), 1110 (s), 1007 (w), 945 (w), 865 (w), 855 (vw), 834 (m), 765 (m), 703 (m)
21) $CH_2{=}CHCOW(CO)_3C_5H_5$	2025 (s), { 1942 (sh) 1933 (vw) } 1892 (s)	{ 1630 (m) 1623 (m) }	3080 (w)	1570 (s)[d], 1420 (m), 1385 (w), 1270 (vs), 1115 (m), 1060 (w), 1012 (m), 980 (w), 950 (w), 907 (m), 898 (s), 835 (s), 713 (w)

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[a] Beckman IR-9 spectrometer, Halocarbon Oil Mull unless otherwise indicated.

[b] Perkin-Elmer Model 21 spectrometer, potassium bromide pellets, unless otherwise indicated.

[c] Perkin-Elmer Model 21 spectrometer used in all regions. Potassium bromide pellets for solid compounds and liquid films for liquid compounds.

[d] Carbon–carbon double bond frequency.

[e] Trace of $[C_5H_5Fe(CO)_2]_2$ as impurity.

TABLE 3

ULTRAVIOLET SPECTRA OF SOME CYCLOPENTADIENYLMETAL CARBONYL DERIVATIVES

Compound	*Maxima in mμ*[a,b]		
	A. Iron Compounds		
$CH_3Fe(CO)_2C_5H_5$[c]			353 (730)
$C_6H_5Fe(CO)_2C_5H_5$	225 (23,900)		354 (1070)
$CF_3Fe(CO)_2C_5H_5$			334 (1130)
$C_2F_5Fe(CO)_2C_5H_5$			341 (1025)
$C_6H_5COFe(CO)_2C_5H_5$	232 (21,600)		332 (4570)
$CF_3COFe(CO)_2C_5H_5$	242 (10,100)		321 (2900)
$C_2F_5COFe(CO)_2C_5H_5$	246 (11,600)		324 (3230)
$C_5H_5Mn(CO)_3$[c]			332 (1010)
$C_6H_5CH{=}CHCOFe(CO)_2C_5H_5$	221 (25,900)		298 (29,600)
	B. Molybdenum and Tungsten Compounds		
$CH_3Mo(CO)_3C_5H_5$[c]			315 (1960)
$C_2H_5Mo(CO)_3C_5H_5$[c]			313 (2120)
$CH_3W(CO)_3C_5H_5$[c]			313 (2430)
$C_2H_5W(CO)_3C_5H_5$[c]			313 (2390)
$CF_3Mo(CO)_3C_5H_5$	220 (22,200)		308 (2940)
$C_3F_7Mo(CO)_3C_5H_5$	218 (23,800)		310 (2490)
$CF_3COMo(CO)_3C_5H_5$		259 (10,900)	
$C_3F_7COMo(CO)_3C_5H_5$		262 (11,600)	
$CF_3COW(CO)_3C_5H_5$	218 (15,700)	253 (14,800)	300 (4300)
$C_3F_7COW(CO)_3C_5H_5$		256 (15,000)	302 (4400)
$CH_2{=}CHCOW(CO)_3C_5H_5$		278 (13,300)	

[a] Extinction coefficient given in parentheses.

[b] In all cases the absorption rose strongly as the wavelength approached 210 mμ, the lower limit of the spectrometer.

[c] Data from ref. 17.

NMR spectra

In order to conserve sample, the NMR spectra of certain compounds were studied in chloroform solution containing a few per cent each of 1,2-difluoro-1,1,2,2-tetrachloroethane (Freon 112) and of hexamethyldisiloxane as internal standards for fluorine (67.8 φ) and hydrogen (9.95 τ) respectively. This permitted observation of both proton and ^{19}F NMR spectra and determination of all chemical shifts on a single sample tube. In other cases, proton spectra were studied in carbon disulfide solution containing hexamethyldisiloxane. The binuclear derivatives obtained from perfluoroglutaryl dichloride were less soluble than the mononuclear derivatives. Therefore, the ^{19}F NMR spectra of these compounds, as in earlier work[1], were obtained in tetrahydrofuran solutions containing CCl_3F (Freon 11) as an internal standard (0.0 φ). The proton NMR spectra were recorded on a Varian A-60 spectrometer. The fluorine NMR spectra (Table 4) were recorded at 56.4 Mc on a Varian DP-60 spectrometer. The fluorine chemical shifts determined by "sidebanding" with known audio frequencies are given in φ values essentially according to Filipovich and Tiers[18]. Since the fluorine chemical shifts were only determined to the nearest 0.1 φ (~5.6 c.p.s.), the difference between the two quantities of Filipovich and Tiers[18] φ (chemical shift at infinite

TABLE 4

^{19}F AND ^{1}H NMR SPECTRA OF SOME FLUOROCARBON–METAL CARBONYL DERIVATIVES

Compound	*^{19}F NMR Spectra, ϕ*			*Proton NMR Spectra, τ*
	α(CF_2 or CF_3)	*β(CF_2 or CF_3)*	*γ(CF_3)*	*C_5H_5*
$CF_3COFe(CO)_2C_5H_5$	+ 80.1	—	—	5.09
$CF_3COMo(CO)_3C_5H_5$	+ 78.3	—	—	4.45
$CF_3COW(CO)_3C_5H_5$	+ 78.9	—	—	4.35
$CF_3Fe(CO)_2C_5H_5$	— 11.6	—	—	5.06
$CF_2Mo(CO)_3C_5H_5$	— 12.3	—	—	4.45
$CF_3Mn(CO)_5$[a]	— 9.3	—	—	—
$CF_3Co(CO)_4$[a]	— 10.5	—	—	—
$CF_3Fe(CO)_4I$[b]	+ 14.7	—	—	—
$C_2F_5COFe(CO)_2C_5H_5$	+ 113.6	+ 80.3	—	5.03
$C_2F_5COMn(CO)_5$[b]	+ 114.5	+ 80.3	—	—
$C_2F_5CORe(CO)_5$	+ 116.7	+ 80.5	—	—
$C_2F_5Fe(CO)_2C_5H_5$	+ 62.4	+ 82.1	—	5.01
$C_2F_5Mn(CO)_5$[b]	+ 68.8	+ 84.0	—	—
$C_2F_5Fe(CO)_4I$[b]	+ 59.0	+ 83.5	—	—
$C_3F_7COFe(CO)_2C_5H_5$	+ 110.7	+ 126.2	+ 81.0	5.02
$C_3F_7COMo(CO)_3C_5H_5$	+ 109.6	+ 126.3	+ 81.2	4.45
$C_3F_7COW(CO)_3C_5H_5$	+ 108.8	+ 126.1	+ 81.1	4.32
$C_3F_7CORe(CO)_5$[b]	+ 113.7	+ 126.7	+ 81.0	—
$C_3F_7Fe(CO)_2C_5H_5$	+ 58.3	+ 114.8	+ 79.1	
$C_3F_7Mo(CO)_3C_5H_5$	+ 56.2	+ 113.3	+ 79.0	4.42
$C_3F_7CoC_5H_5(CO)I$[b]	+ 56.3	+ 114.1	+ 79.1	4.35
$C_3F_7Mn(CO)_5$[b]	+ 65.6	+ 115.3	+ 78.8	—
$C_3F_7Co(CO)_4$[b]	+ 51.0	+ 94.9	+ 78.5	—
$C_3F_7Fe(CO)_4I$	+ 54.9	+ 114.4	+ 78.6	—
$(C_3F_7)_2Fe(CO)_4$	+ 69.1	+ 115.3	+ 78.6	—
$(CF_2)_3(CO)_2[Fe(CO)_2C_5H_5]_2$[c]	+ 109.0	+ 122.0	—	5.04
$(CF_2)_3(CO)_2[Mo(CO)_3C_5H_5]_2$	+ 107.8	+ 120.7	—	4.48
$(CF_2)_3(CO)_2[Mn(CO)_5]_2$[d]	+ 109.0	+ 121.0	—	—
$(CF_2)_3[Fe(CO)_2C_5H_5]_2$	+ 48.5	+ 97.7	—	5.04
$(CF_2)_3[Mo(CO)_3C_5H_5]_2$	+ 46.0	+ 92.9	—	
$(CF_2)_3[Mn(CO)_5]_2$[d]	+ 55.0	+ 99.0	—	—

[a] Data from ref. 7, converted to the ϕ scale.
[b] Data from ref. 29.
[c] Data from ref. 10.
[d] Data from ref. 1.

dilution) and φ^* (actual chemical shift of a given solution) is ignored. In previous papers[1,10] by one of us (R.B.K.) on work done at the Mellon Institute, some ^{19}F chemical shifts including those of $(CF_2)_3(CO)_2[Fe(CO)_2C_5H_5]_2$, $(CF_2)_3(CO)_2[Mn(CO)_5]_2$, and $(CF_2)_3[Mn(CO)_5]_2$ were given in p.p.m. upfield from $CFCl_3$. This scale, of course, is identical to the φ-scale used in this paper and numerical values are directly comparable.

Reagents

Tetrahydrofuran and 1,2-dimethoxyethane were always freshly redistilled over lithium aluminum hydride. Trifluoroacetic anhydride and the acid chlorides were purchased from various sources such as Aldrich Chemical Co., Columbia Organic Chemicals Inc., Borden's Monomer-Polymer Laboratories, Matheson, Coleman and Bell, and Fisher Scientific Co. Iron pentacarbonyl was purchased from the Antara Division of General Aniline and Film and the hexacarbonyls of molybdenum and tungsten from Climax Molybdenum Company.

Preparation of the sodium salts of the cyclopentadienylmetal carbonyls

A. NaFe(CO)$_2$C$_5$H$_5$ (ref. 17). A sample of $[C_5H_5Fe(CO)_2]_2$ was stirred at room temperature with a 30% excess of sodium metal as freshly prepared ~1% amalgam. After stirring for ~1 h, the original red-brown of the $[C_5H_5Fe(CO)_2]_2$ had become an orange-brown. Excess amalgam was then drained off through a stopcock at the bottom of the reaction vessel and the resulting solution generally after cooling in a —78° bath treated with the desired halide.

B. NaW(CO)$_3$C$_5$H$_5$ (ref. 17). Tungsten hexacarbonyl was refluxed 16 h with a 20% excess of sodium cyclopentadienide in 1,2-dimethoxyethane. The resulting yellow solution generally after cooling was treated with the desired halide.

C. NaMo(CO)$_3$C$_5$H$_5$ (refs. 17 and 19). A sample of $[C_5H_5Mo(CO)_3]_2$ (ref. 19) was stirred at room temperature with a 30% excess of sodium metal as freshly prepared ~1% amalgam. The red-violet color of the $[C_5H_5Mo(CO)_3]_2$ soon became the yellow-grey color of the $[C_5H_5Mo(CO)_3]^-$ anion. Excess amalgam was drained off and the resulting solution generally after cooling used for the desired reaction.

In some cases, when the presence of excess sodium cyclopentadienide was not detrimental, the sodium salt $NaMo(CO)_3C_5H_5$ was obtained by refluxing molybdenum hexacarbonyl with a ~20% excess of sodium cyclopentadienide in tetrahydrofuran for ~16 h. This method is especially suitable for larger scale preparations since it avoids the use of large quantities of mercury. Side reactions of some halides with the excess of sodium cyclopentadienide or possible presence of small quantities of unreacted molybdenum hexacarbonyl may make isolation and purification of certain products more difficult if this route to $NaMo(CO)_3C_5H_5$ is used.

These sodium salts were always handled under nitrogen and cooled to —78° before adding the acid chloride or trifluoroacetic anhydride.

Preparation of C$_6$H$_5$COFe(CO)$_2$C$_5$H$_5$

A solution of 100 mmoles of $NaFe(CO)_2C_5H_5$ in 300 ml of tetrahydrofuran was treated at —78° with 14.1 g (100 mmoles) of benzoyl chloride. After stirring 16 h at room temperature, solvent was removed at 30 mm. The resulting brown residue was extracted with 350 ml of chloroform in several portions. These extracts were filtered first by suction through ~30 g of alumina and then by gravity collecting the final filtrate under nitrogen. After removal of solvent at ~30 mm, the remaining crystals were washed with 300 ml of pentane in 5 portions and dried to give 16.7 g of dirty orange $C_6H_5COFe(CO)_2C_5H_5$, m.p. 60–63°. An additional quantity of less pure material was isolated from the pentane washings making the total yield of crude $C_6H_5Fe(CO)_2C_5H_5$ 21.1 g (75%). The analytical sample, m.p. 59–62°, was obtained by sublimation of the crude product at ~90°/0.2 mm.

The proton NMR spectrum of $C_6H_5COFe(CO)_2C_5H_5$ exhibited a resonance at 2.69 τ due to the five phenyl protons and a resonance at 5.21 τ due to the five cyclopentadienyl protons.

Preparation of C$_6$H$_5$CH=CHCOFe(CO)$_2$C$_5$H$_5$

A 24.7 g (80% yield) sample of crude $C_6H_5CH{=}CHCOFe(CO)_2C_5H_5$ was obtained from 100 mmoles of $NaFe(CO)_2C_5H_5$ and 100 mmoles of cinnamyl chloride completely analogous to the preparation of the crude $C_6H_5COFe(CO)_2C_5H_5$. Further purification was accomplished by chromatography on a 5 × 50 cm alumina column in benzene solution. The product formed a very large orange band preceded by a small orange band ($Hg[Fe(CO)_2C_5H_5]_2$?) and a small red-brown band ($[C_5H_5Fe(CO)_2]_2$). After eluting out these impurities with benzene, the orange band of $C_6H_5CH{=}CHCOFe(CO)_2C_5H_5$ was also eluted with benzene. This orange eluate was filtered collecting the filtrate under nitrogen. After removal of solvent from the filtrate at ~30 mm, the resulting orange crystals of $C_6H_5CH{=}CHCOFe(CO)_2C_5H_5$ were purified by crystallization from a mixture of dichloromethane and hexane.

An attempt to purify $C_6H_5CH{=}CHCOFe(CO)_2C_5H_5$ by vacuum sublimation led instead to extensive decomposition to non-volatile materials.

The proton NMR spectrum of $C_6H_5CH{=}CHCOFe(CO)_2C_5H_5$ exhibited a resonance at 2.71 τ due to the five aromatic protons, coupled doublets ($J = 15$ c.p.s.) centered at 3.16 τ and 3.52 τ due to the two non-equivalent olefinic protons, and a sharp peak at 5.16 τ due to the five equivalent cyclopentadienyl protons.

Preparation of $CH_2{=}CHCOFe(CO)_2C_5H_5$

A solution of 100 mmoles of $NaFe(CO)_2C_5H_5$ in 300 ml of tetrahydrofuran was treated at ~ −78° with 9.1 g (100 mmoles) of acrylyl chloride. The reaction mixture was stirred ~ 16 h at room temperature and solvent removed from the reaction mixture at ~ 30 mm leaving an orange-brown residue. After (accidentally!) introducing ~ 50 ml of water, the product was extracted with three 100 ml portions of dichloromethane. Solvent was removed from the filtered (through ~ 30 g of alumina) dichloromethane extracts at ~ 30 mm. A filtered solution of the residue in ~ 300 ml of benzene was chromatographed on a 5 × 30 cm alumina column. After development with benzene, the initial yellow and brown bands of the rather complex chromatogram suggestive of partial decomposition were eluted with benzene and the eluates discarded. The remaining yellow band of the $CH_2{=}CHCOFe(CO)_2C_5H_5$ was then also eluted with benzene. This yellow eluate was filtered by gravity collecting the filtrate under nitrogen. Removal of solvent from the filtrate at ~ 30 mm left behind a dirty yellow liquid. This liquid was dissolved in ~ 45 ml of pentane, filtered, and cooled in a −78° bath. Yellow crystals separated. While still cold, the supernatant liquid was removed with a syringe and the residue then dried in a vigorous stream of nitrogen while warming to room temperature. Before they reached room temperature, the yellow crystals melted to give 1.25 g (5 % yield) of yellow-orange liquid $CH_2{=}CHCOFe(CO)_2C_5H_5$.

Preparation of the perfluoroacyl derivatives $R_fCOFe(CO)_2C_5H_5$

A solution of 100 mmoles of $NaFe(CO)_2C_5H_5$ in ~ 300 ml of tetrahydrofuran was treated at −78° with 100 mmoles of either trifluoroacetic anhydride or the perfluoroacyl chloride. After stirring ~ 16 h at room temperature, solvent was removed at ~ 30 mm. After admitting nitrogen, the residue was extracted with three 100 ml portions of dichloromethane. The extracts were first filtered by suction through ~ 30 g of alumina and then by gravity collecting the final filtrate under nitrogen. Removal of solvent from this filtrate at ~ 30 mm left a brown residue containing $[C_5H_5Fe(CO)_2]_2$, $R_fCOFe(CO)_2C_5H_5$, and tarry by-products. A filtered benzene solution of this residue was chromatographed on a 5 × 30 to 40 cm alumina column. A red-brown band appeared consisting of a mixture of $[C_5H_5Fe(CO)_2]_2$ and the perfluoroacyl derivative $R_fCOFe(CO)_2C_5H_5$. Although a yellow zone containing the perfluoroacyl derivative sometimes was observed adjoining the red-brown band of $[C_5H_5Fe(CO)_2]_2$, the separation of these materials was incomplete. Nevertheless, the chromatography step was important in eliminating tarry by-products impeding crystallization of the rather low-melting $R_fCOFe(CO)_2C_5H_5$ compounds.

The red-brown band containing $[C_5H_5Fe(CO)_2]_2$ and the desired perfluoroacyl derivative and any adjoining yellow zones of partially separated perfluoroacyl derivative were eluted with benzene. After removal of solvent from the filtered eluate at ~ 30 mm, the residue was extracted with 50–100 ml of pentane in several portions to separate the pentane-soluble perfluoroacyl derivatives from the nearly pentane-insoluble $[C_5H_5Fe(CO)_2]_2$. The filtered pentane extracts were cooled in a —78° bath to precipitate yellow to orange crystals of the perfluoroacyl derivative. In the cases of the compounds $CF_3COFe(CO)_2C_5H_5$ and $C_2F_5COFe(CO)_2C_5H_5$ which are solids at room temperature (25–28°), the crystals were filtered in the usual manner and purified further by sublimation at 50–80°/0.1–0.5 mm. If necessary, dry-ice cooling was used to induce crystallization of the sublimate. The compound $C_3F_7COFe(CO)_2C_5H_5$, a liquid at room temperature, was isolated in a manner similar to that described above for $CH_2{=}CHCOFe(CO)_2C_5H_5$.

Photochemical decarbonylation of $CH_3COFe(CO)_2C_5H_5$

A solution of 1.0 g (4.54 mmoles) of $CH_3COFe(CO)_2C_5H_5$ in 25 ml of hexane was irradiated for 16 h. The reddish reaction mixture was poured onto a 2 × 50 cm alumina column and the chromatogram developed with pentane. The single yellow band was eluted with pentane. Solvent was removed from the filtered eluate at ~ 30 mm leaving a yellow-orange solid. This was dissolved in ~ 10 ml of pentane. Cooling the filtered yellow-orange solution in a —78° bath precipitated yellow-orange crystals which were finally purified by a rapid sublimation at 50–70°/0.1 mm to give 0.30 g (34% yield) of waxy yellow-orange $CH_3Fe(CO)_2C_5H_5$ identical with an authentic sample obtained from $NaFe(CO)_2C_5H_5$ and methyl iodide according to the procedure of Piper and Wilkinson[17].

Preparation of $C_6H_5Fe(CO)_2C_5H_5$ from $C_6H_5COFe(CO)_2C_5H_5$

A solution of 3.0 g (10.65 mmoles) of $C_6H_5COFe(CO)_2C_5H_5$ in 25 ml of thiophene-free benzene was irradiated for 14 h. Solvent was removed from the filtered reaction mixture at ~ 30 mm. A yellow-brown solution of the residue in pentane was chromatographed on alumina as described above for the isolation of $CH_3Fe(CO)_2C_5H_5$. A single crystallization of a pentane solution of the product at —78° then gave 0.47 g (17% yield) of yellow crystalline $C_6H_5Fe(CO)_2C_5H_5$, m.p. 35–36° (lit.[17] 26–30°).

The proton NMR spectrum of $C_6H_5Fe(CO)_2C_5H_5$ (not reported by Piper and Wilkinson[17]) exhibited resonances at 2.74 τ (complex multiplet) and 3.22 τ (complex multiplet) of relative intensities 2:3 due to the five phenyl protons and a resonance at 5.27 τ (sharp singlet) of relative intensity 5 due to the five cyclopentadienyl protons.

Preparation of $CH_2{=}CHFe(CO)_2C_5H_5$

A solution of 100 mmoles of $NaFe(CO)_2C_5H_5$ in 250 ml of tetrahydrofuran was treated at —78° with 9.1 g (100 mmoles) of acrylyl chloride. After warming to room temperature the reaction mixture was irradiated 18 h under nitrogen in a quartz tube. Tetrahydrofuran was then removed from the reaction mixture at

~ 30 mm. A filtered benzene extract (~ 150 ml) of the residue was chromatographed on a 5 × 50 cm alumina column. Upon development with benzene, a yellow band of $CH_2{=}CHFe(CO)_2C_5H_5$ appeared turning black like $C_6H_5Fe(CO)_2C_5H_5$ on exposure to light followed by the usual red-brown band of $[C_5H_5Fe(CO)_2]_2$. These bands were eluted with benzene. Evaporation of the yellow benzene eluate of $CH_2{=}CHFe(CO)_2C_5H_5$ left a yellow liquid contaminated with some crystals, probably $Hg[Fe(CO)_2C_5H_5]_2$. This product was extracted with 50 ml of pentane in two portions. Since crystals could not be obtained by cooling the filtered pentane extract several days at —78°, the pentane solution was transferred to a sublimation apparatus and the pentane then removed at ~ 30 mm. The residual liquid was sublimed at 60°/0.1 mm onto a probe cooled to —78°. A yellow-orange crystalline sublimate was obtained melting on warming to room temperature to give 0.3 g (2% yield) of $CH_2{=}CHFe(CO)_2C_5H_5$ containing ~ 5 % of ferrocene as indicated by NMR.

Preparation of the perfluoroalkyl derivatives $R_fFe(CO)_2C_5H_5$

A solution of 1.0 g of the perfluoroacyl derivative $R_fCOFe(CO)_2C_5H_5$ in 25 ml of hexane was irradiated 16 h under nitrogen in a quartz vessel. The product was then precipitated from the filtered hexane solution by cooling to —78°. After removing the product by filtration, it was purified further by sublimation at ~ 50°/0.1 mm in a closed system. During the sublimation of the rather low-melting $C_3F_7Fe(CO)_2C_5H_5$, the probe was cooled to —78°.

Since the trifluoromethyl derivative $CF_3Fe(CO)_2C_5H_5$ is less soluble than the corresponding pentafluoroethyl and heptafluoropropyl derivatives, crystals of the product separated from the hexane solution after the irradiation. These were recovered by filtration and then dissolved in pentane (3 × 20 ml). On cooling the filtered pentane solution to —78°, the product readily crystallized out. It was isolated by filtration and purified further by vacuum sublimation.

Preparation of $(CF_2)_3[Fe(CO)_2C_5H_5]_2$

A solution of 1.0 g (1.79 mmoles) of $(CF_2)_3(CO)_2[Fe(CO)_2C_5H_5]_2$ (ref. 10) in 25 ml of benzene was irradiated 16 h under nitrogen with magnetic stirring. The reaction mixture was then filtered and the residue washed with 20 ml of benzene. Solvent was removed from the benzene filtrate and washings at ~ 30 mm leaving a brownish residue. After washing with two 15 ml portions of pentane and drying, this residue (0.6 g) was sublimed at 140–160°/0.25 mm for ~ 22 h to give 0.4 g (44 % yield) of yellow crystalline $(CF_2)_3[Fe(CO)_2C_5H_5]_2$.

The infrared spectrum of material obtained in this matter indicated the presence of a small amount of acyl derivative as an impurity. In a repeat preparation chromatography was attempted in order to obtain a purer product. However, this proved unsatisfactory, apparently due to decomposition on the column.

Preparation of the perfluoroacyl derivatives $R_fCOMo(CO)_3C_5H_5$

A tetrahydrofuran solution of $NaMo(CO)_3C_5H_5$ was treated at —78° with an equivalent quantity of trifluoroacetic anhydride or C_3F_7COCl. After stirring at least overnight at room temperature, solvent was removed at ~ 30 mm. Nitrogen was admitted and the residue extracted with three 100 ml portions of dichloromethane. The dichloromethane extracts were filtered first by suction and then by gravity. Solvent was removed from the final filtrate at ~ 30 mm leaving a black tarry residue. This residue was extracted with ~ 300 ml of pentane in several portions. The pentane extracts were filtered by gravity collecting the filtrate under nitrogen. Cooling the filtrate in a —78° bath precipitated yellow crystals of the $R_fCOMo(CO)_3C_5H_5$ derivative. These were filtered and dried. Further purification was accomplished by dissolving the crude product in a minimum of pentane and cooling the filtered pentane solution generally to —78°. The yellow crystals of the product were then removed by filtration. This recrystallization procedure could be repeated until product of the desired purity was obtained. Analytical data and physical properties reported on the $R_fCOMo(CO)_3C_5H_5$ derivatives were generally obtained on samples crystallized three times from pentane.

If crystallization of pentane solutions of the trifluoroacetyl derivative $CF_3COMo(CO)_3C_5H_5$ is carried out more slowly in a freezer at —15°, yellow needles up to several millimeters long can be obtained.

Preparation of the derivatives $RCOW(CO)_3C_5H_5$

A solution of ~ 50 mmoles of $NaW(CO)_3C_5H_5$ in 250 ml of 1,2-dimethoxyethane was treated at —78° with 50 mmoles of trifluoroacetic anhydride or heptafluorobutyryl chloride. After stirring ~ 16 h at room temperature, solvent was removed from the reaction mixture at ~ 30 mm. After admitting nitrogen, the residue was extracted with three 100 ml portions of dichloromethane. These extracts were filtered first by suction and then by gravity collecting the final filtrate under nitrogen. Removal of solvent from the filtrate left a black residue. This residue was extracted with 250–300 ml of pentane in several portions and the pentane extracts filtered by gravity. Cooling the filtrate in a —78° bath precipitated yellow crystals of the perfluoroacyl derivative $R_fCOW(CO)_3C_5H_5$. Final purification was accomplished by sublimation at 70–80°/0.1 mm. In contrast to the analogous molybdenum derivatives, no decarbonylation occurred during sublimation.

The trifluoroacetyl derivative $CF_3COW(CO)_3C_5H_5$ was only sparingly soluble in pentane. Therefore, substantial additional quantities could be isolated by sublimation at 80–100°/0.1 mm of the black residue remaining after its pentane extraction.

The acrylyl derivative $CH_2{=}CHCOW(CO)_3C_5H_5$ was prepared in a similar manner except that the final sublimation step was omitted.

Preparation of $(CF_2)_3(CO)_2[Mo(CO)_3C_5H_5]_2$

A solution of 50 mmoles of $NaMo(CO)_3C_5H_5$ in 250 ml of tetrahydrofuran (prepared from $[C_5H_5Mo(CO)_3]_2$ and Na/Hg) was treated at —78° with 6.9 g (25 mmoles) of hexafluoroglutaryl dichloride. After stirring for ~ 16 h at room temperature, solvent was removed from the reaction mixture at ~ 30 mm. Nitrogen was admitted and the residue extracted with three 100 ml portions of dichloromethane. The extracts were filtered first by suction and then by gravity collecting the final yellow-black filtrate under nitrogen. Removal of solvent from this filtrate at ~ 30 mm left behind a yellow-black tarry residue.

The tarry impurities were removed by washing with ~250 ml of 95 % ethanol is several portions. Washing of the now crystalline residue with two 25 ml portions of pentane and drying gave 8.1 g (46.5 % yield) of crude dirty-yellow $(CF_2)_3(CO)_2[Mo(CO)_3C_5H_5]_2$. Washing with pentane omitting the ethanol washings was not effective in removing the tarry impurities.

The resulting crude $(CF_2)_3(CO)_2[Mo(CO)_3C_5H_5]_2$ was purified by recrystallization from a mixture of dichloromethane and hexane. The resulting yellow-gray crystals were washed with two 20 ml portions of 95% ethanol, two 20 ml portions of pentane, and dried to give 5.24 g (30% yield) of yellow-gray crystalline $(CF_2)_3(CO)_2[Mo(CO)_3C_5H_5]_2$.

Preparation of $CF_3Mo(CO)_3C_5H_5$

A 1.0030 g (2.93 mmoles) sample of $CF_3COMo(CO)_3C_5H_5$ was heated at 120° for 2 h at approximately atmospheric pressure in a flask attached to a mercury-filled gas buret. A total of 54.6 ml (742.3 mm, 26°) of gas (2.17 mmoles) was evolved. After cooling to room temperature, the black residue was washed on a filter with four 20 ml portions of pentane and dried. Sublimation of this residue at 60–80°/0.1 mm gave 0.22 g (24% yield) of bright yellow crystalline $CF_3Mo(CO)_3C_5H_5$.

In other experiments with samples of $CF_3COMo(CO)_3C_5H_5$ already partially decarbonylated by sublimation, yields up to ~60% of $CF_3Mo(CO)_3C_5H_5$ were obtained. Several grams of $CF_3Mo(CO)_3C_5H_5$ were also obtained by heating the crude product from the reaction between $NaMo(CO)_3C_5H_5$ and trifluoroacetic anhydride to 120°/~740 mm for several hours without previous isolation of $CF_3COMo(CO)_3C_5H_5$.

Preparation of $C_3F_7Mo(CO)_3C_5H_5$

A 0.9822 g (2.22 mmoles) sample of $C_3F_7COMo(CO)_3C_5H_5$ (already partially decarbonylated by a single vacuum sublimation) was heated at 120°/~700–800 mm for ~2 h. The reaction mixture was then cooled to room temperature and product extracted from the black residue with 50 ml of pentane in four portions. The filtered extracts were cooled to −78° for 2 h to precipitate yellow crystals of $C_3F_7Mo(CO)_3C_5H_5$ (0.4 g) which were filtered and sucked dry. Final purification was accomplished by sublimation at 60°/0.1 mm to give 0.38 g (41.3% yield) of bright yellow crystalline $C_3F_7Mo(CO)_3C_5H_5$.

Preparation of $(CF_2)_3[Mo(CO)_3C_5H_5]_2$

A 1.0080 g (1.45 mmoles) sample of $(CF_2)_3(CO)_2[Mo(CO)_3C_5H_5]_2$ was heated at 115–130° at approximately atmospheric pressure until no further gas evolution appeared to occur (~28 h). During this period, a total of 64.1 ml (26°, 743 mm) of gas (2.56 mmoles) was collected. After cooling to room temperature, the black residue was extracted with 50 ml of dichloromethane in three portions. The extracts were filtered by gravity collecting the yellow filtrate under nitrogen. After addition of ~20 ml of 95% ethanol, the filtrate was concentrated at ~30 mm to ~10 ml depositing yellow crystals. These were filtered, washed with 60 ml of ethanol in several portions followed by two 15 ml portions of pentane, and dried to give 0.257 g (28% yield) of yellow crystalline $(CF_2)_3[Mo(CO)_3C_5H_5]_2$, which gradually blackened without melting on heating above ~200°.

Analytical data on samples of $(CF_2)_3[Mo(CO)_3C_5H_5]_2$ (Table 1) suggested the presence of a persistent impurity apparently not removed by crystallization. Unfortunately, $(CF_2)_3[Mo(CO)_3C_5H_5]_2$ could not be sublimed without decomposition. In view of the unsatisfactory results obtained in the chromatography of the more stable $(CF_2)_3[Fe(CO)_2C_5H_5]_2$ (see above), chromatography of $(CF_2)_3[Mo(CO)_3C_5H_5]_2$ did not appear to be a reasonable method of purification. The infrared and NMR spectra of $(CF_2)_3[Mo(CO)_3C_5H_5]_2$ resembled to the expected extent those of $(CF_2)_2[Fe(CO)_2C_5H_5]_2$ and $(CF_2)_3[Mn(CO)_5]_2$ and the persistent impurity could not be identified from these spectra.

DISCUSSION

A. Preparation of the Acyl Derivatives

The new acyl derivatives $RCOFe(CO)_2C_5H_5$ described in this paper were prepared generally by treatment of $NaFe(CO)_2C_5H_5$ with the corresponding acid chloride as in previous work[3,10,11]. Only in the preparation of the trifluoroacetyl derivative $CF_3COFe(CO)_2C_5H_5$ was the liquid trifluoroacetic anhydride used in place of the less convenient gaseous trifluoroacetyl chloride. Previous workers used trifluoroacetic anhydride in similar manners for preparations of $CF_3COMn(CO)_5$ (ref. 3) and $CF_3COCo(CO)_4$ (ref. 8).

The yields of the perfluoroacyl derivatives $R_fCOFe(CO)_2C_5H_5$ were always much lower ($\sim$10%) than in the corresponding preparations of the non-fluorinated acyl derivatives, much $[C_5H_5Fe(CO)_2]_2$ always being produced. This may arise from displacement not only of the chlorine atom of the perfluoroacyl chloride (or a trifluoroacetate group of trifluoroacetic anhydride) with an $-Fe(CO)_2C_5H_5$ group, but also of fluorine atoms of the perfluoroacyl group with $Fe(CO)_2C_5H_5$ groups. The resulting intermediate containing more than one $Fe(CO)_2C_5H_5$ group may be unstable with respect to decomposition into fluorocarbons and $[C_5H_5Fe(CO)_2]_2$.

The yield of the acrylyl derivative $CH_2=CHCOFe(CO)_2C_5H_5$ was also abnormally low ($\sim$5%). In this case, isolation of the liquid product from the reaction mixture was difficult. Filtration steps during this preparation were very slow, permitting some decomposition to occur. Treatment with alumina and later chromatography on alumina were necessary in order to remove tarry by-products; unfortunately $CH_2=CHCOFe(CO)_2C_5H_5$ possibly because of the unsaturation did not appear to be entirely stable to such treatment. Formation of $[C_5H_5Fe(CO)_2]_2$ in the reaction between $NaFe(CO)_2C_5H_5$ and acrylyl chloride as in other reactions between $NaFe(CO)_2C_5H_5$ and non-fluorinated acid chlorides was relatively insignificant and was not responsible for the low yield of $CH_2=CHCOFe(CO)_2C_5H_5$.

An attempt was made to prepare the acetylenic acyl derivative $C_6H_5C\equiv CCOFe(CO)_2C_5H_5$ from $C_6H_5C\equiv CCOCl$ and $NaFe(CO)_2C_5H_5$ using techniques analogous to those suitable for the preparation of many of the acyl derivatives described in this paper such as $C_6H_5COFe(CO)_2C_5H_5$ and $C_6H_5CH=CHCOFe(CO)_2C_5H_5$. Instead of the expected orange product, a black apparently polymeric solid was obtained, giving viscous and difficultly filtered black solutions in organic solvents. Analyses for all elements, although only approximate, suggested that this material consisted mainly of polymeric species of composition $[C_6H_5C_2COFe(CO)_2C_5H_5]_n$. The infrared spectrum exhibited strong terminal metal carbonyl bands at 2025 and 1960 cm^{-1} and ketonic or acyl carbonyl or carbon–carbon multiple bond absorption at 1762 (s), 1715 (m), and 1580 (w, br) cm^{-1}. This obviously complex material has not been investigated in detail.

The perfluoroacyl molybdenum derivatives $R_fCOMo(CO)_3C_5H_5$ were obtained in an analogous manner from $NaMo(CO)_3C_5H_5$ and the appropriate acid chloride or trifluoroacetic anhydride. Only in the preparation of $CF_3COMo(CO)_3C_5H_5$ was the formation of any $[C_5H_5Mo(CO)_3]_2$ observed in contrast to the preparations of the iron analogues. However, $NaMo(CO)_3C_5H_5$ is significantly less reactive than $NaFe(CO)_2C_5H_5$* and thus is probably not capable of replacing fluorine atoms in perfluoroacyl groups. Work carried out in this laboratory and described elsewhere[21] on reactions between metal carbonyl anions and certain aromatic fluorocarbons demonstrates the lower reactivity of $NaMo(CO)_3C_5H_5$ than of $NaFe(CO)_2C_5H_5$ in displacement of fluorine atoms thus supporting this hypothesis.

These new perfluoroacyl derivatives $R_fCOMo(CO)_3C_5H_5$ are yellow crystalline solids which, especially when impure, turn blue on exposure to air for several hours. Although they are appreciably volatile, they cannot be purified by vacuum sublimation due to partial thermal decarbonylation. The yellow to orange sublimates obtained from sublimation of the $R_fCOMo(CO)_3C_5H_5$ compounds thus consists of mixtures of $R_fCOMo(CO)_3C_5H_5$ and the corresponding $R_fMo(CO)_3C_5H_5$ compounds. For example, analysis by ^{19}F NMR of the material obtained from a single sublimation of $CF_3COMo(CO)_3C_5H_5$ indicated it to be a mixture of ~50% $CF_3Mo(CO)_3C_5H_5$ and only ~50% $CF_3COMo(CO)_3C_5H_5$. Similarly, material obtained from a single sublimation of $C_3F_7COMo(CO)_3C_5H_5$ consisted of ~20% $C_3F_7COMo(CO)_3C_5H_5$ and ~80% $C_3F_7Mo(CO)_3C_5H_5$.

Several years ago, the preparation of $C_3F_7COMo(CO)_3C_5H_5$ was briefly described[6]. However, this material was purified by vacuum sublimation. The instability of $C_3F_7COMo(CO)_3C_5H_5$ to vacuum sublimation and the infrared spectrum of the material from this older preparation[12] indicate that the compound then under investigation was mainly $C_3F_7Mo(CO)_3C_5H_5$ containing only sufficient $C_3F_7COMo(CO)_3C_5H_5$ to exhibit a medium intensity acyl carbonyl band in the infrared spectrum.

In agreement with previous observations on the instability of $RCOMo(CO)_3C_5H_5$ derivatives where R is a non-fluorinated acyl group[3,11], we were unable to obtain the acrylyl and benzoyl derivatives by treatment of $NaMo(CO)_3C_5H_5$ with acrylyl and benzoyl chlorides, respectively. The only identifiable product of these reactions was $[C_5H_5Mo(CO)_3]_2$. In an attempt to prepare the chromium derivative $CF_3COCr(CO)_3C_5H_5$, the green derivative $[C_5H_5Cr(CO)_3]_2$ (ref. 22) was reduced in tetrahydrofuran with dilute sodium amalgam to give a yellow solution apparently containing the sodium salt $NaCr(CO)_3C_5H_5$. Treatment of this solution at —78° with trifluoroacetic anhydride gave a yellow solution which turned red on warming to room temperature. Neither vacuum sublimation nor pentane crystallization after initially removing the product by dichloromethane extraction gave significant amounts of $CF_3COCr(CO)_3C_5H_5$ or its decarbonylation product $CF_3Cr(CO)_3C_5H_5$.

The analogous tungsten derivatives $RCOW(CO)_3C_5H_5$ were obtained in a manner completely analogous to the molybdenum derivatives. They were more stable than the molybdenum derivatives and could be purified by vacuum sublimation without danger of partial decarbonylation to produce the corresponding alkyl derivatives. Even the acrylyl derivative $CH_2{=}CHCOW(CO)_3C_5H_5$ could be obtained as a stable yellow-orange solid in contrast to the molybdenum derivative too unstable for preparation at least by techniques used in this work. Formation of $[C_5H_5W(CO)_3]_2$ was never observed in the preparation of any of these acyl derivatives.

The absence of the two pentafluoropropionyl derivatives $C_2F_5COM(CO)_3C_5H_5$

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* For a general discussion on the reactivity of metal carbonyl anions see ref. 20.

(M = Mo and W) among the compounds described in this paper reflects the unexpected failures in several attempts at their preparation from the corresponding sodium salts and either pentafluoropropionyl chloride or pentafluoropropionic anhydride. It is presently not clear why the preparation of these pentafluoropropionyl derivatives should present more difficulties than the preparation of the analogous trifluoroacetyl and heptafluorobutyryl derivatives.

B. Decarbonylation of the Acyl Derivatives

Piper and Wilkinson[17] describe the preparation of the phenyl derivative $C_6H_5Fe(CO)_2C_5H_5$ in 3 % yield by treatment of $NaFe(CO)_2C_5H_5$ with iodobenzene and in 2 % yield by treatment of $C_5H_5Fe(CO)_2I$ with phenylmagnesium bromide. The preparation of $C_6H_5Fe(CO)_2C_5H_5$ by photochemical decarbonylation of the benzoyl derivative $C_6H_5COFe(CO)_2C_5H_5$ appears to be far superior to either of their preparations. The benzoyl derivative $C_6H_5COFe(CO)_2C_5H_5$ may be readily obtained in 75 % yield from $NaFe(CO)_2C_5H_5$ and benzoyl chloride. Its photochemical decarbonylation to the phenyl derivative $C_6H_5Fe(CO)_2C_5H_5$ proceeds in 17 % yield. The overall yield of $C_6H_5Fe(CO)_2C_5H_5$ from $[C_5H_5Fe(CO)_2]_2$ is thus ~12 %. Moreover, $C_6H_5Fe(CO)_2C_5H_5$ obtained from the benzoyl derivative was found to melt sharply at 35–36° whereas Piper and Wilkinson report their $C_6H_5Fe(CO)_2C_5H_5$ to melt at 26–30°. The lower melting point and greater melting range of the material reported by Piper and Wilkinson suggest that neither of their syntheses of $C_6H_5Fe(CO)_2C_5H_5$ produces material as pure as that obtained by photochemical decarbonylation of the benzoyl derivative as described in this paper.

As described above, the isolation of the $CH_2{=}CHCOFe(CO)_2C_5H_5$ from the reaction mixture obtained from $NaFe(CO)_2C_5H_5$ and acrylyl chloride was difficult and the yield of pure acrylyl derivative was low. Therefore, the vinyl derivative $CH_2{=}CHFe(CO)_2C_5H_5$ was obtained by direct irradiation of the reaction mixture obtained from $NaFe(CO)_2C_5H_5$ and acrylyl chloride avoiding the difficult and inefficient intermediate isolation of the acrylyl derivative. The yield of the vinyl derivative was also low and its isolation difficult. Even the best sample was contaminated by amounts of ferrocene detectable in the NMR spectrum, but not sufficient to noticeably affect the elemental analyses. Although the preparation of this vinyl derivative described in this paper is inconvenient and inefficient and does not lead to an entirely pure product, it is very significant in representing the first preparation of a compound with an unsubstituted uncomplexed vinyl group directly bonded to a transition metal.

Initial attempts to decarbonylate the molybdenum derivatives $R_fCOMo(CO)_3C_5H_5$ were carried out photochemically analogous to the successful decarbonylation of the iron derivatives $RCOFe(CO)_2C_5H_5$. These experiments led to extensive decomposition into black insoluble and non-volatile material. Small quantities of the corresponding perfluoroalkyl derivatives $R_fMo(CO)_3C_5H_5$ (~15 % yield at best) were isolated from some of these reactions but were often contaminated with unchanged perfluoroacyl derivative.

The decarbonylation of $R_fCOMo(CO)_3C_5H_5$ derivatives on sublimation suggested thermal rather than photochemical decarbonylation for the preparation of $R_fMo(CO)_3C_5H_5$ derivatives. It was found possible to convert these perfluoroacyl derivatives to the corresponding perfluoroalkyl derivatives by heating at 120° at atmospheric pressure until no further gas evolution occurred. Some decomposition also occurred to produce black insoluble material.

The trifluoromethyl derivative $CF_3Mo(CO)_3C_5H_5$ is a bright-yellow solid which darkens on exposure to light. Like $CF_3Fe(CO)_2C_5H_5$, it possesses a higher melting point (~ 150°) and lower solubility than most other $RMo(CO)_3C_5H_5$ derivatives. In an attempt to prepare a fluorocarbon transition metal derivative containing two different transition metals, the reaction between $NaFe(CO)_2C_5H_5$ and $CF_3Mo(CO)_3C_5H_5$ was investigated. An exothermic reaction occurred but the only products isolated from the reaction mixture after chromatography were $[C_5H_5Fe(CO)_2]_2$ and unchanged $CF_3Mo(CO)_3C_5H_5$.

C. *Infrared Spectra*

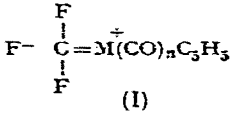
In general, the infrared spectra (Table 2) of the new compounds described in this paper correspond to those previously reported for related compounds. All of these cyclopentadienyl derivatives exhibit a weak, but definite carbon–hydrogen stretching frequency at 3070–3100 cm^{-1} arising from the carbon–hydrogen bonds of the cyclopentadienyl ring. In most cases, the $RFe(CO)_2C_5H_5$ derivatives exhibit two strong bands in the range 2050–1950 cm^{-1} due to the metal carbonyl groups; the $RM(CO)_3C_5H_5$ ($M = Mo$ or W) derivatives may exhibit two or three frequencies. In addition, the acyl derivatives exhibit a medium to strong band in the range 1600–1660 cm^{-1} as in previously reported acyl derivatives[10,23] due to the acyl carbonyl group. The cyclopentadienyl group is responsible for medium to strong absorptions generally in the range 800–850 cm^{-1} and some weaker absorptions around 1000 cm^{-1} as indicated by comparison of the spectra of other similar cyclopentadienyl derivatives.

In addition to these absorptions, the infrared spectra of the fluorocarbon derivatives exhibit strong absorptions in the range 950–1300 cm^{-1} due to the carbon–fluorine stretching frequencies[23]. The presence of more than one kind of fluorine in the pentafluoroethyl, heptafluoropropyl, hexafluorotrimethylene, and corresponding acyl derivatives complicates interpretation of this region of their spectra. However, the presence of only one type of carbon–fluorine bond in the trifluoromethyl and corresponding trifluoroacetyl derivatives simplifies the interpretation of this region of their infrared spectra.

The three trifluoroacetyl derivatives $CF_3COFe(CO)_2C_5H_5$ and $CF_3COM(CO)_3C_5H_5$ ($M = Mo$ and W) exhibit three strong carbon–fluorine bands in their infrared spectra at 1224 ± 4, 1175 ± 1, and 1126 ± 1 cm^{-1}. The two trifluoromethyl derivatives $CF_3Fe(CO)_2C_5H_5$ and $CF_3Mo(CO)_3C_5H_5$ exhibit three or four strong carbon–fluorine bands in their infrared spectra but at the much lower frequencies of 1068, 1042, 1015, and 985 cm^{-1} for the iron complex and at 1044, 1004, and 976 cm^{-1} for the molybdenum complex. The much lower carbon–fluorine stretching frequencies of the trifluoromethyl derivatives indicates a lower carbon–fluorine bond order in these compounds. This could arise from significant contributions of ionic "no-bond" resonance structures such as (I) with a double bond between the metal atom and the carbon atom of the CF_3 group and no bond between this carbon atom and one of the fluorine atoms.

Resonance structures related to (I) of perfluoroalkyl–transition metal derivatives permits explanation of much of their chemistry and prediction of new chemistry.

Contribution of such structures would be expected to *strengthen the metal–carbon bond but to weaken the carbon–fluorine bond.* This is in excellent agreement with the well-



$$F^{-}\quad \overset{F}{\underset{F}{C}}=\overset{+}{M}(CO)_nC_5H_5$$

(I)

known stability of fluorocarbon–transition metal derivatives to cleavage of the metal–carbon bond[*] but their susceptibility to removal of fluorine by basic reagents[25].

D. *NMR spectra*

The close similarities between the ^{19}F NMR spectra of the new fluorocarbon derivatives described in this paper and previously reported fluorocarbon derivatives (Table 4) demonstrate the similarities between fluorocarbon derivatives of cyclopentadienyl metal carbonyls and pure metal carbonyls. The fluorine atoms of the α-CF_2 or CF_3 groups of the perfluoroalkyl derivatives $R_fFe(CO)_2C_5H_5$ and $R_fMo(CO)_3C_5H_5$ like those of the perfluoroalkyl derivatives $R_fM(CO)_5$ ($M =$ Mn and Re) and $R_fFe(CO)_4I$ exhibit unusually low chemical shifts. The chemical shifts of the fluorine atoms of the α-CF_2 or α-CF_3 groups consistently decrease in the series $R_fMn(CO)_5 > R_fFe(CO)_2C_5H_5 > R_fMo(CO)_3C_5H_5$.

The chemical shifts of the resonance due to the five cyclopentadienyl protons of the cyclopentadienyl ring of the $R_fFe(CO)_2C_5H_5$ and $R_fMo(CO)_3C_5H_5$ derivatives are almost identical to the chemical shifts of the cyclopentadienyl protons in the corresponding $R_fCOFe(CO)_2C_5H_5$ and $R_fCOMo(CO)_3C_5H_5$ derivatives. As an approximation, the chemical shifts of the cyclopentadienyl protons in $C_5H_5Fe(CO)_2R$ derivatives appear to be inversely related to the electronegativity of the R group[10], but influenced not only by the effects of the σ-bond between the iron atom and the R group, but also by any back-donation of the lone electron pairs on the iron atom to the R group[**]. The similarity of the chemical shifts of the cyclopentadienyl resonances in $R_fFe(CO)_2C_5H_5$ and the corresponding $R_fCOFe(CO)_2C_5H_5$ derivatives suggests similar electronegativities for perfluoroalkyl and the corresponding perfluoroacyl groups taking into account any effects of back-donation. Partially decarbonylated mixtures of perfluoroacyl derivatives could not be analyzed from their cyclopentadienyl NMR resonances due to this chemical shift similarity.

The preparation of the first transition metal derivative of an unsubstituted, uncomplexed vinyl group, $CH_2{=}CHFe(CO)_2C_5H_5$, made of particular interest a comparison of the NMR spectrum due to its vinyl group with that due to the vinyl groups in the acrylyl-transition metal derivatives and in $CH_2{=}CHCCo_3(CO)_9$ (II) (ref. 26), where a vinyl group in a transition metal complex is likewise bonded to a carbon atom rather than directly to a transition metal (Table 5).

A vinyl group contains three different types of single protons. If the chemical

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[*] For example, the stability of the iron–carbon bonds in $(CF_2)_4Fe(CO)_4$ to bromine at 50° (ref. 24).

[**] Thus the chemical shifts of the cyclopentadienyl protons in the halides $C_5H_5Fe(CO)_2X$ in chloroform solution are 4.96 τ ($X =$ Cl), 4.97 τ ($X =$ Br), and 4.93 τ ($X =$ I). The effect of electronegativity increasing in the series I < Br < Cl is almost completely balanced by the effect of increasing back-donation in the series Cl < Br < I.

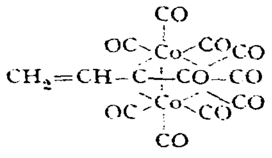
TABLE 5

PROTON NMR SPECTRA OF VINYL AND ACRYLYL TRANSITION METAL DERIVATIVES

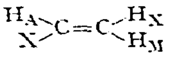
Compound	*Chemical Shifts of Vinyl Protons, τ*			*Coupling Constants c.p.s.*			*C_5H_5 Protons*
	A	*M*	*X*	$\lvert J\rvert_{AM}$	$\lvert J\rvert_{AX}$	$\lvert J\rvert_{MX}$	τ
$CH_2{=}CHCOFe(CO)_2C_5H_5$	3.55	4.80	5.22	17	10	2	5.16
$CH_2{=}CHCOW(CO)_3C_5H_5$	3.62	4.65	4.92	17	10	2	4.42
$CH_2{=}CHFe(CO)_2C_5H_5$	3.07	4.68	4.18	17	8	not observed	5.25
$CH_2{=}CHCCo_3(CO)_9$[a]	2.27	4.54	4.71	17	11	2	—

[a] Ref. 26.

shifts of these protons are large in comparison with the coupling constants between them as is the case with the vinyl and acrylyl transition metal derivatives, the NMR spectrum of a vinyl group may be analyzed as an AMX system for which a twelve-line spectrum is expected. In this particular case, it is convenient to designate as A the proton bonded to the carbon atom to which no other proton is bonded; as M the proton in a *trans*-position relative to the proton designated as A; and as X the proton in a *cis*-position relative to A (III). Analyses[27] of the spectra of other vinyl derivatives demonstrate that $\lvert J_{AM}\rvert > \lvert J_{AX}\rvert > \lvert J_{MX}\rvert$*, *i.e.*, the coupling constant between the protons in *trans*-positions on neighboring olefinic carbon atoms is greater than the coupling constant between the protons in *cis*-positions on neighboring olefinic carbon atoms which in turn is greater than the coupling constant between protons bonded to the same olefinic carbon atom. If we assume that in the vinyl and acrylyl derivatives of which the spectra are given in Table 5, a similar relationship of coupling constants holds, then in the two acrylyl derivatives $CH_2{=}CHCOFe(CO)_2C_5H_5$ and $CH_2{=}CHCOW(CO)_3C_5H_5$ the chemical shifts increase in the series $A < M < X$, whereas the chemical shifts of the vinylic protons in $CH_2{=}CHFe(CO)_2C_5H_5$ where the vinyl group is directly bonded to an iron atom increase in the series $A < X < M$. Thus, the sequence of chemical shifts of two of the three protons of a vinyl group directly bonded to a transition metal appears to be inverted relative to the sequence of two of the three protons of a vinyl group bonded to a main group element such as carbon. It is of interest that in $CH_2{=}CHCCo_3(CO)_9$ where the vinyl group is bonded to a carbon atom rather than to the cobalt atom, the chemical shifts like those of the acrylyl derivatives increase in the series $A < M < X$, although the chemical shift



(II)



(III)

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* In this paper, the question of the signs of the coupling constants is ignored.

of the proton designated as A is greatly different from the corresponding proton in either the acrylyl derivatives or $CH_2{=}CHFe(CO)_2C_5H_5$.

An alternative, although less likely, interpretation of the spectrum of $CH_2{=}CHFe(CO)_2C_5H_5$ is that the chemical shifts increase in the series $A < M < X$ as in the acrylyl derivatives but that two of the coupling constants are reversed such that they decrease in the series $|J_{AX}| > |J_{AM}| > |J_{MX}|$. In any case, the NMR spectrum of $CH_2{=}CHFe(CO)_2C_5H_5$ suggests that vinyl groups bonded directly to transition metals may be distinguished by NMR from those bonded to carbon atoms just as similar distinctions can be made by NMR concerning the atom to which a hydrogen atom, perfluoroalkyl group, or methyl group is bonded.

E. Ultraviolet spectra

It is of interest to compare the ultraviolet spectra of the new compounds described in this paper with those of the $RFe(CO)_2C_5H_5$ and $RM(CO)_3C_5H_5$ (M = Mo and W) derivatives of Piper and Wilkinson[17] and with the spectra reported by Lundquist and Cais (Table 3)[23]. In all of these compounds, a maximum was noted at 300 to 360 mμ with extinction coefficients of ~700 to ~5000 except where the presence of an adjacent much stronger maximum obscured this band [*e.g.*, $C_6H_5CH{=}CHCOFe(CO)_2C_5H_5$ and the perfluoroacyl derivatives $R_fCOMo(CO)_3C_5H_5$]. This maximum corresponds to the "MC-band" of Lundquist and Cais[23]. In addition, the ultraviolet spectrum of the acyl derivatives exhibited a much stronger maximum (ε = 10,000 to 15,000)* at ~240 to ~280 mμ, apparently characteristic of the bond between the metal and the acyl carbonyl group. In the case of the acyl derivatives $R_fMo(CO)_3C_5H_5$ and $CH_2{=}CHCOW(CO)_3C_5H_5$, this relatively strong maximum due to the acyl carbonyl group apparently overlaps sufficiently with the much weaker "MC-band" so as to prevent observation of the latter.

SUMMARY

Ultraviolet irradiation of the acyl derivatives $RCOFe(CO)_2C_5H_5$ ($R = CF_3$, C_2F_5, C_3F_7, CH_3, C_6H_5, and $CH_2{=}CH$) in benzene, hexane or tetrahydrofuran solution produces the corresponding alkyl derivatives $RFe(CO)_2C_5H_5$. Heating the acyl derivatives $RCOMo(CO)_3C_5H_5$ ($R = CF_3$ or C_3F_7) to ~120° produces the corresponding alkyl derivatives $RMo(CO)_3C_5H_5$. The new compounds $(CF_2)_3[Mo(CO)_3C_5H_5]_2$, $(CF_2)_3[Fe(CO)_2C_5H_5]_2$ and $RCOW(CO)_3C_5H_5$ ($R = CF_3$, C_3F_7, and $CH_2{=}CH$) are also described.

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* In the derivatives $C_6H_5Fe(CO)_2C_5H_5$, $C_6H_5COFe(CO)_2C_5H_5$, and $C_6H_5CH{=}CHCOFe(CO)_2C_5H_5$ absorption due to the benzene ring obscures the absorption due to the acyl carbonyl group.

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