ORGANOMETALLIC TRANSITION METAL DERIVATIVES CONTAINING FLUORINE
I. PERFLUOROCARBOXYLATE DERIVATIVES

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SUMMARY

Reactions of various π-cyclopentadienyl and carbonyl halides with silver perfluorocarboxylates in dichloromethane solution yield new organometallic transition metal perfluorocarboxylates by metathetical reactions. The following types of compounds have been prepared: (a) red-orange $R_fCO_2Fe(CO)_2C_5H_5$; (b) red-brown $R_fCO_2Mo(CO)_3C_5H_5$; (c) yellow $R_fCO_2Mn(CO)_5$; (d) white $R_fCO_2Re(CO)_5$; (e) yellow-orange $[C_5H_5Mo(NO)(CO_2R_f)_2]_2$; (f) yellow $R_fCO_2Fe(CO)_3(\pi\text{-}C_3H_5)$; (g) red-brown $R_fCO_2Co(CO)(C_3F_7)(C_5H_5)$; (h) red-orange $(C_5H_5)_2Ti(CO_2R_f)_2$; (i) white $(C_5H_5)_2Zr(CO_2R_f)_2$. In most cases the trifluoroacetates $(R_f=CF_3)$, pentafluoropropionates $(R_f=C_2F_5)$, and heptafluorobutyrates $(R_f=n\text{-}C_3F_7)$ were prepared. In these compounds the perfluorocarboxylate groups appear to be bonded to the transition metal thru the oxygen atom. They exhibit a characteristic $v(CO)$ frequency in the range 1680–1730 cm^{-1} arising from the carbonyl group of the perfluorocarboxylate ligand. The force constants k_1, k_2, and k_i calculated from the $v(CO)$ frequencies in the $R_fCO_2M(CO)_5$ (M=Mn or Re) compounds by the Cotton–Kraihanzel procedure were found to be similar to those in the metal carbonyl halides $M(CO)_5X$ (M=Mn or Re) indicating similar bonding properties of the perfluorocarboxylate and halide ligands.

INTRODUCTION

Relatively few metal carbonyl derivatives with metal–oxygen bonds are known. Some substituted octahedral metal carbonyls with ether ligands [*e.g.* (diglyme)-Mo(CO)$_3$, ref. 1] have been described. Metal carbonyl anions of chromium[2], molybdenum[3], tungsten[4], and rhenium[5] containing hydroxide and/or aquo ligands have been prepared but not studied in much detail. The known osmium carbonyl oxide Os$_4$O$_4$(CO)$_{12}$ (ref. 6) contains osmium–oxygen bonds but not involving the same osmium atom as the osmium–carbonyl bonds.

Recently Green *et al.*[7] described the reaction between the σ-allylmanganese derivative C$_3$H$_5$Mn(CO)$_5$ and trifluoroacetic acid with propene evolution to give the

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TABLE 1

NEW COMPOUNDS PREPARED

Compound[a]	Color	M.p. (°C)	Subl. temp. (°C) at 0.1 mm	Yield[b] (%)	Analyses, found (calcd.) (%)				Mol.wt., found[f] (calcd.)
					C	H	F	Metal	
$CF_3CO_2Fe(CO)_2C_5H_5$	Red-brown	72–73	70–80	93[c]	37.1 (37.3)	1.8 (1.7)	19.5 (19.7)	18.9 (Fe) (19.3)(Fe)	
$C_3F_7CO_2Fe(CO)_2C_5H_5$	Red-orange	59–60	50	60[c]	33.7 (33.9)	1.3 (1.3)	34.5 (34.1)		424 (390)
$CF_3CO_2Mo(CO)_3C_5H_5$	Red-brown	68	70–80	40[d]	34.2 (33.5)	1.7 (1.4)			
$C_2F_5CO_2Mo(CO)_3C_5H_5$	Red-brown	58–59	70–80	40[d]	33.1 (32.4)	1.4 (1.2)	23.0 (23.3)		
$CF_3CO_2Mn(CO)_5$	Yellow	70		83[c]	27.0 (27.3)		19.4 (18.5)		
$C_2F_5CO_2Mn(CO)_5$	Yellow	58–59		62[c]	27.0 (26.8)		27.0 (26.5)	15.5 (Mn) (15.3)(Mn)	
$C_3F_7CO_2Mn(CO)_5$	Yellow	38–39	40	60[c]	26.8 (26.5)		33.4 (32.6)	13.9 (Mn) (13.5)(Mn)	
$CF_3CO_2Re(CO)_5$	White	94	40	100[c,d]	19.2 (19.1)		13.0 (13.0)		
$C_2F_5CO_2Re(CO)_5$	White	78–79	50	80[c,d]	19.8 (19.6)		19.5 (19.4)		
$C_3F_7CO_2Re(CO)_5$	White	75–76	50	90[c,d]	20.2 (20.0)		25.2 (24.7)		
$[C_5H_5Mo(NO)(CO_2CF_3)_2]_2$	Yellow	140–141		98[c]	26.0 (25.9)	1.4 (1.2)	26.8 (27.3)	23.3 (Mo) (23.0)(Mo)[g]	
$[C_5H_5Mo(NO)(CO_2C_2F_5)_2]_2$	Yellow	107 (dec.)		82[c]	25.9 (25.5)	1.3 (1.0)	32.9 (36.7)[h]		1021 (1034)
$[C_5H_5Mo(NO)(CO_2C_3F_7)_2]_2$	Yellow	130 (dec.)		72[c]	25.3 (25.3)	1.2 (0.8)[f]			1203 (1234)
$CF_3CO_2Fe(CO)_3(C_3H_5)$	Yellow	60	40	85[c,d]	32.9 (32.7)	1.8 (1.7)	19.4 (19.4)	18.8 (Fe) (19.0)(Fe)	312 (294)
$C_2F_5CO_2Fe(CO)_3(C_3H_5)$	Yellow-brown	40	50–60	80[d]	31.4 (31.4)	1.4 (1.5)	28.1 (27.6)		

Compound	Color	m.p.		Yield	C	H	F	Metal	Mol. wt.
$CF_3CO_2Co(CO)(C_3F_7)(C_5H_5)$	Red-brown	102–103		84[c]	30.4 (30.4)	1.2 (1.2)	43.8 (43.8)	14.1 (Co) (13.6)(Co)	481 (434)
$C_2F_5CO_2Co(CO)(C_3F_7)(C_5H_5)$	Brown	64–66	60	80[d]	29.9 (29.8)	0.9 (1.0)	47.0 (47.1)		
$C_3F_7CO_2Co(CO)(C_3F_7)(C_5H_5)$	Brown	51–53	60	85[d]	29.3 (29.2)	0.9 (0.9)	50.0 (49.8)		
$(C_5H_5)_2Ti(CO_2CF_3)_2$	Red-orange	130 (dec.)	110–120	70[c,d]	41.6 (41.4)	2.9 (2.5)	28.6 (28.1)	11.9 (Ti) (12.3)(Ti)	
$(C_5H_5)_2Ti(CO_2C_2F_5)_2$	Orange	112–113	90–100	82[d]	38.3 (38.0)	1.7 (2.0)	37.2 (37.5)		
$(C_5H_5)_2Ti(CO_2C_3F_7)_2$	Orange	141–142	90–100	90[d]	35.7 (35.7)	1.4 (1.7)	44.0 (43.9)		
$(C_5H_5)_2Zr(CO_2CF_3)_2$	White	93–94	80–90	70[d]	38.3 (37.6)	2.4 (2.2)		20.3 (Zr) (20.4)(Zr)	
$(C_5H_5)_2Zr(CO_2C_3F_7)_2$	White	35–36	100–110	82[d]	33.6 (33.4)	1.5 (1.6)		12.8 (Zr) (14.1)(Zr)	597 (604)

[a] In all cases C_3F_7 refers to the n-heptafluoropropyl group $CF_3CF_2CF_2$. [b] Purification processes used for product isolation indicated by footnotes in the sequence performed. The reported yields are those obtained after the first purification step. [c] Recrystallized from a mixture of dichloromethane and hexane. [d] Sublimed at 0.1 mm. [e] Recrystallized from hexane. [f] Vapor pressure osmometer in benzene solution. [g] Found: N, 3.2. Calcd.: N, 3.4%. [h] Found: N, 3.1. Calcd.: N, 2.7%. [i] Found: N, 2.7. Calcd.: N, 2.3%.

TABLE 2

IR SPECTRA OF COMPOUNDS PREPARED (cm^{-1})

Compound[a]	ν(CO) Metal carbonyl groups[b]	Carboxylate[b]	ν(CH)[c]	Other bands
$CF_3CO_2Fe(CO)_2C_5H_5$	2059 s, 2019 s	1680 m	3120 w	1430 w, 1414 (sh), 1406 m, 1332 vw, 1195 s, 1158 m, 1132 m, 1024 w, 1007 w, 898 vw, 850 m, 838 w(sh), 788 w, 730 m
$C_3F_7CO_2Fe(CO)_2C_5H_5$	2071 s, 2020 s	1696 m	3080 vw	1425 vw, 1380 vw, 1328 m, 1270 w, 1222 s, 1210 s(sh), 1185 w, 1150 w, 1110 m, 1074 vw, 1050 vw, 1010 vw, 994 vw, 960 vw, 925 w, 835 vw, 806 w, 736 vw, 712 w

TABLE 2 (*continued*)

Compound[a]	ν(CO)[b] Metal carbonyl groups	Carboxylate	ν(CH)[c]	Other bands[c]
CF$_3$CO$_2$Mo(CO)$_3$C$_5$H$_5$	2052 s, 1992 s, 1970 s	1712 m	3100 vw	1427 w, 1142 m, 844 w(sh), 1417 m, 1058 vw, 815 m, 1394 m, 1010 m, 779 w, 1357 vw, 995 vw, 717 m, 1182 s, 862 vw,
C$_2$F$_5$CO$_2$Mo(CO)$_3$C$_5$H$_5$	2050 s, 1991 s, 1970 s	1711 m	3100 w	1350 w, 1155 s, 865 vw, 1427 w, 1315 m, 1055 vw, 822 m, 1418 w, 1220 m, 1017 m, 810 m, 1395 vw, 1198 w, 1005 w(sh), 723 m, 1373 w, 1190 w, 870 vw,
CF$_3$CO$_2$Mn(CO)$_5$	*a*	1686 m		1587 w, 883 vw, 1455 vw, 844 m, 1411 m, 836 w(sh), 530 w, 1190 vs, 785 m, 1150 vs, 722 m,
C$_2$F$_5$CO$_2$Mn(CO)$_5$	*a*	1686 m		1386 m, 1126 w(sh), 616 s, 1322 m, 1020 m, 576 vw, 1216 m, 816 m, 1193 m, 760 vw, 1160 s, 724 m,
C$_3$F$_7$CO$_2$Mn(CO)$_5$	*a*	1687 m		1388 m, 1114 m, 736 w, 1328 m, 1076 w, 714 w, 1258 m(sh), 961 m, 1216 vs, 926 m, 1160 m(sh), 810 m,
CF$_3$CO$_2$Re(CO)$_5$	*a*	1692 m		1582 w, 990 vw, 1412 m, 905 vw, 1182 vs, 844 m, 1150 s, 782 w, 1035 vw, 722 m,
C$_2$F$_5$CO$_2$Re(CO)$_5$	*a*	1693 m		1402 w(sh), 1160 vw, 762 vw, 1390 m, 1028 s, 728 m, 1328 s, 996 w, 1220 s, 910 vw, 1200 s, 820 m,
C$_3$F$_7$CO$_2$Re(CO)$_5$	*a*	1694 m		1387 m, 1181 m, 957 vw, 713 m, 1330 m, 1145 m, 925 m, 1277 w, 1132 w, 902 vw, 1220 w, 1111 s, 810 m, 1203 s, 1077 w(sh), 737 w(sh),
[C$_5$H$_5$Mo(NO)(CO$_2$CF$_3$)$_2$]$_2$	1695–1665 m(br)[d,e]	1730 m[e]	3110 vw	1417 m, 1020 vw, 718 m, 1360 vw, 996 vw, 1186 s, 840 w, 1144 s, 814 w, 1056 vw, 779 w,
[C$_5$H$_5$Mo(NO)(CO$_2$C$_2$F$_5$)$_2$]$_2$	1682–1665 m(br)[d,e]	1726 m[e]	3080 vvw	1392 m, 1022 m, 1320 m, 810 w, 1212 m, 725 w, 1162 s, 1138 (sh),
[C$_5$H$_5$Mo(NO)(CO$_2$C$_3$F$_7$)$_2$]$_2$	1705–1680 m(br)[d,e]	1725 m[e]	*f*	1395 m, 1160 m, 810 m, 1330 m, 1116 m, 752 vw, 1270 w, 1080 w, 735 w, 1220 s, 1016 m, 712 w, 1180 m, 962 w,

Compound	ν(CO)			ν(CH)					
$CF_3CO_2Fe(CO)_3C_3H_5$	2103 s, 2057 s, 2015 s	1698 m	3100 vw, 3090 vvw, 3080 vvw,	1580 w, 1222 w(sh), 955 w,	1502 vw, 1190 s, 922 w,	1462 w, 1138 s, 842 m,	1404 m, 1067 vw, 780 m,	1395 m(sh), 1010 vw, 722 m
$C_2F_5CO_2Fe(CO)_3C_3H_5$	2102 s, 2055 s, 2013 s	1700 m	3070 vw, 3050 vw	1505 vw, 1160 s, 818 m,	1465 w, 1065 w, 775 w,	1380 m, 1021 s, 765 vw,	1320 m, 935 vw(sh), 726 m	1211 s, 920 vw,
$CF_3CO_2Co(CO)(C_3F_7)(C_5H_5)$	2103 sᵉ	1691 mᵉ	3100 vw	1443 w, 1198 s, 1065 w, 801 m,	1404 m, 1180 s, 1038 m, 780 w,	1320 m, 1158 s, 992 vw, 716 s,	1236 m, 1138 m, 953 m, 657 m	1213 s, 1086 m, 823 vw,
$C_2F_5CO_2Co(CO)(C_3F_7)(C_5H_5)$	2104 sᵉ	1690 mᵉ	3030 w	1441 vw, 1200 s(sh), 991 vw, 716 m	1414 w, 1160 s, 846 w,	1400 w, 1088 m, 816 w,	1318 s, 1063 w, 800 w,	1214 s, 1024 s, 726 w(sh),
$C_3F_7CO_2Co(CO)(C_3F_7)(C_5H_5)$	2105 sᵉ	1693 mᵉ	3100 vw(br)	1447 w, 1280 w(sh), 1090 m, 991 vw(sh), 810 m(sh),	1415 w, 1217 s, 1065 w(sh), 960 w, 800 m,	1386 w, 1200 s(sh), 1042 w(sh), 927 w, 752 vw,	1332 m(sh), 1163 s, 1032 m, 847 w, 736 w,	1320 s, 1115 m, 1017 w, 827 vw, 717 s,
$(C_5H_5)_2Ti(CO_2CF_3)_2$		1710 m	3110 w	1561 w, 1140 s, 755 m	1446 w, 1016 w, 710 m	1404 s, 1006 w,	1318 w, 832 m(sh),	1186 vs, 822 m,
$(C_5H_5)_2Ti(CO_2C_2F_5)_2$		1710 m	3100 vw	1523 vw, 1207 s, 803 m(sh),	1442 w, 1160 s, 756 vw,	1388 m(sh), 1066 vw, 716 m	1370 m, 1020 s,	1314 s, 820 m,
$(C_5H_5)_2Ti(CO_2C_3F_7)_2$		1710 m	3100 vw	1440 w, 1213 vs, 1022 w, 861 w, 705 m	1384 m, 1162 s, 1017 w, 824 m,	1357 m, 1156 m(sh), 960 m, 800 m,	1324 s, 1110 s, 926 m, 750 w,	1271 m(sh), 1077 m, 730 m,
$(C_5H_5)_2Zr(CO_2CF_3)_2$		1685 m	3100 vvw	1480 w, 1016 w,	1448 w, 848 w,	1400 w, 816 m,	1204 s, 786 w,	1152 m, 720 m
$(C_5H_5)_2Zr(CO_2C_3F_7)_2$		1686 m	∫	1443 vw(sh), 1168 vs, 928 m,	1403 s, 1116 s, 810 s,	1330 s, 1080 m, 753 vw,	1268 m(sh), 1031 m, 703 m	1206 vs, 963 m,

ᵃ In all cases C_3F_7 refers to the n-heptafluoropropyl group $CF_3CF_2CF_2$. ᵇ The ν(CO) frequencies were obtained in cyclohexane solution unless otherwise indicated. ᶜ These frequencies were obtained in KBr pellets. ᵈ ν(NO) frequency. ᵉ These ν(CO) frequencies were obtained in dichloromethane solutions. ∫ ν(CH) frequencies too weak to be unequivocally observed. ᵍ See Table 4.

trifluoroacetate $CF_3CO_2Mn(CO)_5$, a derivative with a metal–oxygen bond. Similarly Davison, McFarlane, Pratt, and Wilkinson[8] have reported the preparations of the trifluoroacetates $CF_3CO_2M(CO)_3$ C_5H_5 (M = Mo and W) and $CF_3CO_2Re(CO)_5$ by treatment of the corresponding methyl derivatives with trifluoroacetic acid. Lawson and Wilkinson[9] have described the reaction between $[Rh(CO)_2Cl]_2$ and various silver carboxylates in non-coordinating solvents to give the rhodium carbonyl carboxylates $[Rh(CO)_2CO_2R]_2$. This paper reports the synthesis of a wide range of new metal carbonyl perfluorocarboxylates by metathetical reactions with the corresponding silver perfluorocarboxylates and metal carbonyl halide in a non-coordinating solvent. A few related metal perfluorocarboxylates also containing π-cyclopentadienyl and/or nitrosyl ligands are also described.

EXPERIMENTAL

Microanalyses (Table 1) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Molecular weight determinations (Table 1) were performed by Schwarzkopf Microanalytical Laboratories, Woodside, New York, using a Mechrolab vapor pressure osmometer in benzene solution. IR spectra (Tables 2 and 4) were run in potassium bromide pellets or cyclohexane or dichloromethane solutions using a Perkin–Elmer Model 621 spectrometer with grating optics and calibrated against the known 1601.4 cm^{-1} band of polystyrene. Proton NMR spectra (Table 3) were run in chloroform-d or acetone solutions at 100 Mc using a Varian A-60 Spectrometer at 60 Mc or a Varian HA-100 spectrometer at 100 Mc with acetone or tetramethylsilane as an internal standard. Fluorine-19 NMR spectra (Table 3) were run in dichloromethane or acetone solutions at 94.1 Mc using a Varian HA-100 spectrometer with 1,2-difluoro-1,1,2,2-tetrachloroethane (ϕ 67.8) as an internal standard. Melting point determinations were obtained of samples in capillaries and are uncorrected.

The $C_5H_5Fe(CO)_2I$ was prepared from $[C_5H_5Fe(CO)_2]_2$ and iodine[10]. The $C_5H_5Mo(CO)_3Cl$ was prepared by treatment of a tetrahydrofuran solution of $NaMo(CO)_3C_5H_5$ at 0° with an excess of a mixture of glacial acetic acid and carbon tetrachloride[11]. The metal pentacarbonyl bromides $M(CO)_5Br$ (M = Mn or Re) were prepared by reaction of the corresponding $M_2(CO)_{10}$ (M = Mn or Re) derivatives with bromine in dichloromethane solution at room temperature[12]. The $[C_5H_5-Mo(NO)I_2]_2$ was prepared from $C_5H_5Mo(CO)_2NO$ and iodine[13]. The π-C_3H_5-$Fe(CO)_3I$ was prepared from $Fe(CO)_5$ and allyl iodide[14]. The $C_5H_5Co(CO)(C_3F_7)I$ was prepared from $C_5H_5Co(CO)_2$ and 1-iodoheptafluoropropane[15]. The biscyclopentadienylmetal dichlorides $(C_5H_5)_2MCl_2$ (M = Ti and Zr) were purchased from Arapahoe Chemical Corp., Boulder, Colorado. The silver perfluorocarboxylates were purchased from Columbia Organic Chemicals, Inc., Columbia, South Carolina.

General preparative procedure

A mixture of the metal halide derivative (1 to 5 g) and the silver perfluorocarboxylate (5% excess over the calculated amount) was stirred for at least 4 h at room temperature in dichloromethane solution (50–100 ml)*. Precipitation of silver

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* In the case of the reaction between $C_5H_5Fe(CO)_2I$ and silver trifluoroacetate to give $CF_3CO_2Fe(CO)_2$-C_5H_5, benzene could be used in place of dichloromethane as a solvent. However, when tetrahydrofuran was used as a solvent for this reaction, no product was obtained.

TABLE 3

PROTON AND FLUORINE NMR SPECTRA OF PERFLUOROCARBOXYLATE DERIVATIVES[a,b]

Compound	^{19}F NMR spectra[d]				Proton NMR
	Solvent	$\alpha(CF_2$ or $CF_3)$	$\beta(CF_2$ or $CF_3)$	$\gamma(CF_3)$	spectra $\tau(C_5H_5)$[c]
Trifluoroacetates					
$CF_3CO_2Fe(CO)_2C_5H_5$	$CDCl_3$	74.2 (S)			4.92 (S)
$CF_3CO_2Mo(CO)_3C_5H_5$	Me_2CO	74.6 (S)			4.12 (S)
$CF_3CO_2Mn(CO)_5$	CH_2Cl_2	NO			
$CF_3CO_2Re(CO)_5$	CH_2Cl_2	74.0 (S)			
$[C_5H_5Mo(NO)(CO_2CF_3)_2]_2$	Me_2CO	75.4 (S)			3.62 (S)
$CF_3CO_2Fe(CO)_3C_3H_5$	$CDCl_3$	75.3 (S)			CH: 4.63(TT,8,14)
					CH_2: 5.32(D,8)
					CH_2: 7.32(D,14)
$CF_3CO_2Co(CO)(C_3F_7)(C_5H_5)$	Me_2CO				
CF_3CO_2:		74.0 (S)			3.90 (S)
C_3F_7Co:		?	$\begin{cases}115.6\\116.8\end{cases}$	79.8	
$(C_5H_5)_2Ti(CO_2CF_3)_2$	$CDCl_3$	75.8 (S)			3.35 (S)
$(C_5H_5)_2Zr(CO_2CF_3)_2$	Me_2CO	76.6 (S)			3.42 (S)
Pentafluoropropionates					
$C_2F_5CO_2Mo(CO)_3C_5H_5$	Me_2CO	119.5(Q, 1.5 br.)	83.6 (T, 1.5)		4.13 (S)
$C_2F_5CO_2Mn(CO)_5$	CH_2Cl_2	NO	83.7		
$C_2F_5CO_2Re(CO)_5$	CH_2Cl_2	119.5(Q, 1.5)	83.8(T, 1.5)		
$[C_5H_5Mo(NO)(CO_2C_2F_5)_2]_2$	Me_2CO	120.7 (br)	83.3 (br)		
$C_2F_5CO_2Fe(CO)_3C_3H_5$	$CDCl_3$	120.0(Q, 1.5)	83.4(T, 1.5)		CH: 4.60(TT,9,14)
					CH_2: 5.31(D,8)
					CH_2: 7.34(D,14)
$C_2F_5CO_2Co(CO)(C_3F_7)(C_5H_5)$	Me_2CO				3.92 (S)
$C_2F_5CO_2$:		118.8	83.6		
C_3F_7Co:		?	$\begin{cases}115.6\\116.8\end{cases}$	79.8	
$(C_5H_5)_2Ti(CO_2C_2F_5)_2$	$CDCl_3$	120.9	83.3		3.34 (S)
Heptafluorobutyrates					
$C_3F_7CO_2Fe(CO)_2C_5H_5$	$CDCl_3$	116.7(Q,8)	127.7	81.6(T,8)	4.98 (S)
$C_3F_7CO_2Mn(CO)_5$	CH_2Cl_2	NO	127.4 (br)	81.5 (br)	
$C_3F_7CO_2Re(CO)_5$	CH_2Cl_2	117.4(T, 1; Q,8)	127.8	81.5(T,8)	
$[C_5H_5Mo(NO)(CO_2C_3F_7)_2]_2$	Me_2CO	118.2	127.2	81.4(T,8)	3.63 (S)
$C_3F_7CO_2Co(CO)(C_3F_7)(C_5H_5)$	$CDCl_3$				4.30 (S)
$C_3F_7CO_2$:		116.2(T,9)	127.4	81.5(T,9)	
C_3F_7Co:		59.5(Q,11)	$\begin{cases}116.8\\115.6\end{cases}$	79.8(T,11)	
$(C_5H_5)_2Ti(CO_2C_3F_7)_2$	$CDCl_3$	118.2(Q,9)	127.1	81.5(T,9)	3.30 (S)
$(C_5H_5)_2Zr(CO_2C_3F_7)_2$	$CDCl_3$	119.5(Q,9, br)	127.0	81.4(T,9)	3.58 (S)

[a] These spectra were taken on a Varian HA-100 NMR spectrometer at 94.1 Mc (^{19}F) or 100 Mc (^1H) in the indicated solvents. [b] S=singlet; D=doublet; T=triplet; Q=quartet; TT=triplet of triplets; br=broad; NO=not observed under conditions comparable to those under which the resonances cited in this table were observed. [c] In the cases of the two π-allyl derivatives, the resonances cited in this column correspond to the three different protons of the π-allyl ligand. [d] The ϕ scale used here is the one proposed by G. Filipovich and G. V. D. Tiers[31]. On this scale ϕ (CFCl$_3$) = 0.0 and ϕ (CFCl$_2$CFCl$_2$) = 67.8. A separation of 1 ϕ corresponds to 1 ppm.

TABLE 4

IR $v(CO)$ FREQUENCIES AND FORCE CONSTANTS IN $R_fCO_2M(CO)_5$ COMPOUNDS

Compound	$v(CO)$ frequencies (cm^{-1})				Force constants (Mdyne/Å)			Graham's parameters	
	A_1	B_1	E	A_1	k_1	k_2	k_i	$\Delta\sigma$	$\Delta\pi$
$CF_3CO_2Mn(CO)_5$	2136 w	2088 vw	2054 vs	1997 s	16.18	17.47	0.22	1.23	−0.58
$C_2F_5CO_2Mn(CO)_5$	2137 w	2089 vw	2056 vs	1998 s	16.10	17.50	0.21	1.37	−0.69
$C_3F_7CO_2Mn(CO)_5$	2138 w	2090 w	2057 vs	2000 s	16.25	17.51	0.21	1.24	−0.55
$CF_3CO_2Re(CO)_5$	2150 w	2084 w	2040 vs	1995 m	16.20	17.38	0.29		
$C_2F_5CO_2Re(CO)_5$	2151 w	2084 w	2042 vs	1995 m	16.20	17.41	0.29		
$C_3F_7CO_2Re(CO)_5$	2150 w	2085 w	2039 vs	1995 m	16.32	17.33	0.27		

halide occurred. A noticeable color change of the dichloromethane solution also occurred as the reaction proceeded particularly when the starting material was a metal iodide derivative. After the reaction period was over, the reaction mixture was filtered collecting the filtrate under nitrogen. Solvent was removed from the filtrate at ~25°/40 mm leaving a residue (generally crystalline) of the crude metal perfluoro-carboxylate complex. This was purified as indicated in Table 1 using vacuum sublimation or recrystallization from hexane often mixed with dichloromethane.

DISCUSSION

The synthesis of the metal perfluorocarboxylate derivatives from corresponding metal halide derivatives and silver perfluorocarboxylates by a metathetical reaction is an extension of the method used by Lawson and Wilkinson[9] for the preparation of the rhodium carbonyl carboxylates $[Rh(CO)_2CO_2R]_2$. The use of a non-coordinating solvent was found to be necessary for the synthesis of CF_3CO_2-$Fe(CO)_2C_5H_5$ from $C_5H_5Fe(CO)_2I$ and silver trifluoroacetate. Thus no CF_3CO_2-$Fe(CO)_2C_5H_5$ could be isolated from the mixture obtained by reaction between $C_5H_5Fe(CO)_2I$ and silver trifluoroacetate in the coordinating solvent *tetrahydrofuran*. There were also limits to which this metathetical reaction between metal halide derivatives and silver salts could be extended even using the favorable solvent dichloromethane. Thus $C_5H_5Fe(CO)_2I$ failed to react with AgF, $AgCO_2CH_3$, $AgCO_2CF_2Cl$, and $AgCO_2(CF_2)_3CF_3$ at room temperature apparently owing to insufficient solubility of the silver salt in the dichloromethane solvent*. Furthermore, the halide derivatives n-$C_3F_7Fe(CO)_4I$ and $C_5H_5Co(CO)I_2$ reacted very readily with silver trifluoroacetate in dichloromethane solution but with extensive decomposition, since the products obtained after evaporating the solvent from the filtered solution no longer contained $v(CO)$ metal carbonyl frequencies in the IR spectrum.

The metal perfluorocarboxylate complexes described in this paper are crystalline solids of similar solubility, volatility, and air-stability to the corresponding metal halide complexes. However, the colors of the metal perfluorocarboxylate complexes are appreciably lighter than those of the corresponding metal halide complexes (particularly the iodides) owing to the lower polarizability of the perfluorocarboxylate

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* Silver perfluorocarboxylates have been reported[16] to be soluble in benzene and their hydrogen analogues to be insoluble in benzene.

groups than the halogen atoms*. All of the perfluorocarboxylate complexes exhibit a medium intensity infrared band in the range 1680–1730 cm^{-1} arising from the $v(C=O)$ stretching frequency of the perfluorocarboxylate ligand. The $v(C-O)$ frequency in the perfluorocarboxylate complexes is expected[17] to fall in the range 1160–1260 cm^{-1}, but could not be clearly identified owing to the appearance of $v(C-F)$ and π-cyclopentadienyl frequencies in this region. The perfluorocarboxylate complexes with carbonyl or nitrosyl ligands also exhibit in their IR spectra appropriate $v(CO)$ or $v(NO)$ frequencies arising from these ligands.

The iron complexes $R_fCO_2Fe(CO)_2C_5H_5$ (I) resemble most closely the thiolbenzoate $C_6H_5COSFe(CO)_2C_5H_5$ believed to have structure (II) with an iron–sulfur bond[18]. The complexes $R_fCO_2Fe(CO)_2C_5H_5$ exhibited the expected two $v(CO)$ metal carbonyl frequencies for a $C_5H_5Fe(CO)_2Y$ compound. Several attempts to prepare $C_2F_5CO_2Fe(CO)_2C_5H_5$ from silver pentafluoropropionate and C_5H_5-$Fe(CO)_2X$ (X=Cl or I) led to brown tars which could not be crystallized.

(I) (II) (III)
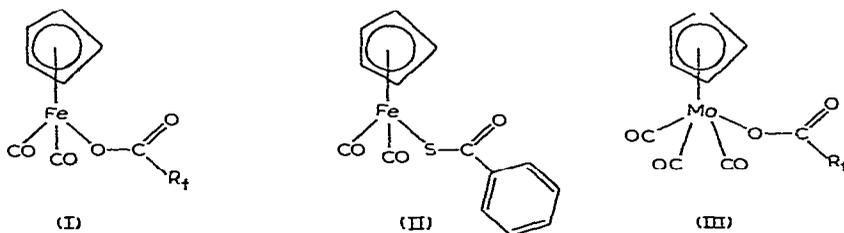
The preparation of the molybdenum complexes $R_fCO_2Mo(CO)_3C_5H_5$ (III) from $C_5H_5Mo(CO)_3Cl$ and silver perfluorocarboxylates did not proceed as readily as in the other cases. Fractional crystallization and/or sublimation were sometimes necessary to free the products from unreacted $C_5H_5Mo(CO)_3Cl$. The heptafluorobutyrate $C_3F_7CO_2Mo(CO)_3C_5H_5$ was not obtained completely pure. The m.p. 68° found for the trifluoroacetate $CF_3CO_2Mo(CO)_3C_5H_5$ was appreciably lower than the value of 84° found in the previous work[8] for material prepared from CH_3-$Mo(CO)_3C_5H_5$ and trifluoroacetic acid; however, this value was approximately reproduced with material from two independent preparations. The IR spectra of the $R_fCO_2Mo(CO)_3C_5H_5$ compounds (III) exhibited the expected three $v(CO)$ metal carbonyl frequencies for $C_5H_5Mo(CO)_3Y$ derivatives with electronegative Y substituents**.

The π-allyl derivatives $R_fCO_2Fe(CO)_3C_3H_5$ (IV) form volatile yellow solids exhibiting the expected three $v(CO)$ metal carbonyl frequencies for $C_3H_5Fe(CO)_3Y$ derivatives. The proton NMR spectra of the $R_fCO_2Fe(CO)_3C_3H_5$ derivatives (IV) (Table 3) were unusually well-resolved compared with the spectra of other π-allyl derivatives. Thus these spectra clearly exhibited the nine-line triple triplet pattern centered at $\tau 4.61 \pm 0.02$ for the central CH proton split unequally $(J_1 = 8$ cps; $J_2 = 14$ cps) by two pairs of protons from the end CH_2 groups.

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* In this discussion only chlorine, bromine, and iodine are considered. Few metal carbonyl fluorides are known.

** The $C_5H_5Mo(CO)_3Y$ derivatives (Y = Cl, Br, I, $(CH_3)_3Sn$, and C_3F_7) exhibit the expected three $v(CO)$ frequencies whereas $CH_3Mo(CO)_3C_5H_5$ and many other $C_5H_5Mo(CO)_3Y$ derivatives with the Y group bonded to the molybdenum atom thru a carbon atom exhibit but two $v(CO)$ frequencies. Further details of the $v(CO)$ frequencies in these compounds are currently under investigation[19].

The brown derivatives $R_fCO_2Co(CO)(C_3F_7)(C_5H_5)$ (V) are the first perfluoro-alkyl derivatives of cobalt to be isolated which also contain cobalt–oxygen bonds. Their formation from $C_5H_5Co(CO)(C_3F_7)I$ and the silver perfluorocarboxylate however has a precedent the reported[20] reaction of $C_5H_5Co(CO)(C_3F_7)I$ with silver

(IV)   (V)

(VI)
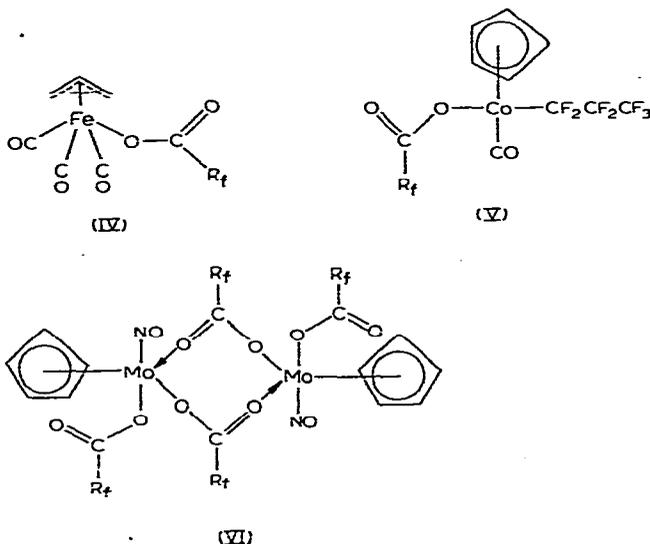
perchlorate in benzene solution to give a moisture-sensitive red solution containing the unstable perchlorate $C_5H_5Co(CO)(C_3F_7)(OClO_3)$, a related compound containing a cobalt–oxygen bond*,**.

The yellow molybdenum derivatives $[C_5H_5Mo(NO)(CO_2R_f)_2]_2$ were the only binuclear derivatives studied in this work. The binuclear formulations of the pentafluoropropionate and heptafluorobutyrate were confirmed by molecular weight determinations in solution. A further indication of a binuclear rather than a mono-nuclear formula for the $[C_5H_5Mo(NO)(CO_2R_f)_2]_2$ derivatives was the failure for the pentafluoropropionate to sublime upon heating to 120° at 0.1 mm. The most likely structure for the $[C_5H_5Mo(NO)(CO_2R_f)_2]_2$ derivatives is (VI) with equal numbers of bridging and terminal perfluorocarboxylate groups. However, in all three cases the ^{19}F NMR spectra of the $[C_5H_5Mo(NO)(CO_2R_f)_2]_2$ derivatives showed only one type of perfluorocarboxylate group suggesting a rapid interchange between bridging and terminal perfluorocarboxylate groups. The IR spectra of the $[C_5H_5Mo(NO)(CO_2R_f)_2]_2$ compounds exhibited broad absorptions in the range ~ 1660–$1730\ cm^{-1}$. By comparison with the IR spectra of other perfluorocarboxylate

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* The presence of the σ-perchlorate $C_5H_5Co(CO)(C_3F_7)(OClO_3)$ with a cobalt–oxygen bond in the red solution obtained by Treichel and Werber[20] from $C_5H_5Co(CO)(C_3F_7)I$ and silver perchlorate in benzene solution is indicated by the following two observations: (a) the precipitation of silver iodide from the reaction between $C_5H_5Co(CO)(C_3F_7)I$ and silver perchlorate to form the red solution; (b) the reaction of the red solution with various nucleophiles Y^- ($Y = Br$ and Cl) to form $C_5H_5Co(CO)(C_3F_7)Y$ compounds.

** In some of the ^{19}F NMR spectra the resonance of the α-CF_2 fluorine atoms of the C_3F_7Co group was not observed. Treichel and Werber[20] report the α-CF_2 resonances of the halides $C_5H_5Co(CO)(C_3F_7)X$ ($X = Cl$ or Br) to be broad singlets. Possibly the breadth of these α-CF_2 resonances is preventing their observation in certain cases. Broad α-CF_2 resonances in a C_3F_7Co group could result in coupling of these fluorine atoms with the ^{59}Co nucleus which has a quadrupole moment ($I = 7/2$).

and $C_5H_5Mo(NO)I_2L$ complexes[13] a maximum in this band at 1725 cm^{-1} could be assigned to a $\nu(CO)$ perfluorocarboxylate frequency and at least a portion of the broad absorption in the range 1660–1700 cm^{-1} to the $\nu(NO)$ frequency. The breadth of this IR absorption in the $\sim$1660–1730 cm^{-1} region may arise partially from closely overlapping $\nu(CO)$ and $\nu(NO)$ frequencies lending further support to structure (VI) with two different types of perfluorocarboxylate ligands and hence at least two $\nu(CO)$ frequencies.

The titanium and zirconium derivatives $(C_5H_5)_2M(CO_2R_f)_2$ are somewhat less unusual than the other compounds in this paper since titanium–oxygen and zirconium–oxygen bonds are known in other π-cyclopentadienyl derivatives such as $[(C_5H_5)_2MCl]_2O$ (M = Ti[21] and Zr[22]). Furthermore, a variety of other metathesis reactions of the dichlorides $(C_5H_5)_2MCl_2$ (M = Ti and Zr) to give other $(C_5H_5)_2MY_2$

(VII)   (VIII)   (IX)
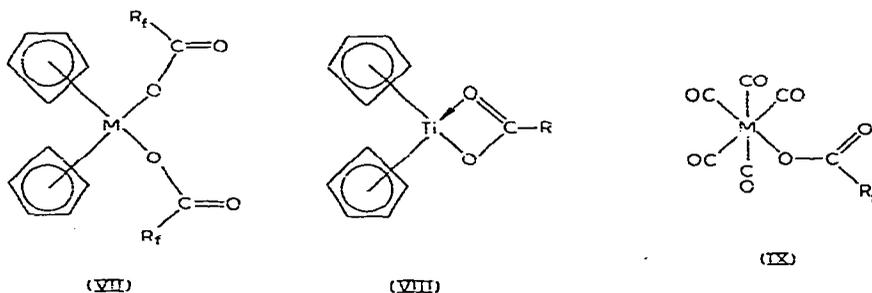
compounds are known[23]. The medium intensity IR band at 1710 cm^{-1} in the $(C_5H_5)_2Ti(CO_2R_f)_2$ derivatives and at 1685 cm^{-1} in the $(C_5H_5)_2Zr(CO_2R_f)_2$ derivatives suggests structure (VII) (M = Ti or Zr) with monodentate perfluorocarboxyalate groups as found in the other complexes discussed in this paper. By contrast the dicyclopentadienyltitanium(III) derivatives $(C_5H_5)_2TiCO_2R$ with structure (VIII) containing symmetrical bidentate carboxylate groups are reported[24] to exhibit $\nu(CO)$ carboxylate frequencies in the range 1420–1550 cm^{-1}.

The manganese[7] and rhenium[8] carbonyl trifluoroacetates $CF_3CO_2M(CO)_5$ [(IX), $R_f = CF_3$] have been previously prepared from trifluoroacetic acid and $CH_2=$ $CHCH_2Mn(CO)_5$ or $CH_3Re(CO)_5$, respectively. The melting points of the trifluoroacetates prepared in this work from silver trifluoroacetate and $M(CO)_5Br$ agreed with their previously reported melting points $CF_3CO_2Mn(CO)_5$: this work m.p. 70°, lit.[9] m.p. 76–78°; $CF_3CO_2Re(CO)_5$: this work m.p. 94°, lit.[8] m.p. 93–94°). The ^{19}F NMR spectra of the rhenium compounds $R_fCO_2Re(CO)_5$ [(IX), M = Re)] exhibited not only the expected resonances from the perfluorocarboxylate group but also fine structure arising from both 1,2 coupling ($J \sim 1$ cps) and 1,3 coupling ($J \sim 8$ cps). The greater value for the apparently more distant 1,3 coupling than the 1,2 coupling agrees with prior ^{19}F NMR studies on fluorocarbon derivatives[25] including those of transition metals[26]. In the cases of all three manganese compounds R_fCO_2-$Mn(CO)_5$ [(IX), M = Mn, $R_f = CF_3$, C_2F_5, or n-C_3F_7] the ^{19}F resonances for the CF_2 or CF_3 group directly bonded to the carboxyl group could not be found even under conditions where the other ^{19}F resonances were observed. The coupling of the ^{55}Mn nucleus with a quadrupole moment ($I = \frac{5}{2}$) to these fluorine atoms may be sufficient to obliterate their resonances.

Kaesz, Bau, Hendrickson, and Smith[27] have recently investigated in detail the

$v(CO)$ frequencies of the metal pentacarbonyl halides $M(CO)_5X$ ($M = Mn$ or Re, $X = Cl$, Br, or I). With this work as a guide it is possible to assign the observed $v(CO)$ metal carbonyl frequencies in the perfluorocarboxylates $R_fCO_2M(CO)_5$ (Table 4). The strongest frequency which occurs at 2055 ± 2 ($M = Mn$) or 2040 ± 2 ($M = Re$) cm^{-1} may be assigned to the E mode (band e in ref. 27). The second strongest frequency which occurs at 1998 ± 2 ($M = Mn$) or 1995 ($M = Re$) cm^{-1} may be assigned to the lower frequency A_1 mode (band g in ref. 27). The second higher frequency A_1 mode (band a in ref. 27) appears as a weak band at 2137 ± 1 ($M = Mn$) or 2150 ± 1 ($M = Re$) cm^{-1}. A weak band appearing at 2089 ± 1 ($M = Mn$) or 2084 ± 1 ($M = Re$) cm^{-1} may be assigned to the B_1 mode (band c in ref. 27). The B_1 mode is normally IR inactive in $YM(CO)_5$ complexes. However, previous work[28] has shown that the normally IR-inactive B_1 mode can become slightly IR active in $YM(CO)_5$ derivatives where the Y group no longer has cylindrical symmetry. This would be the case with perfluorocarboxylate groups where the presence of lone pairs on the oxygen atom would cause the carbon–oxygen–metal line of the bonded perfluorocarboxylate group to be bent and hence the R_fCO portion of the perfluorocarboxylate group to lean preferentially to one side at least on a time scale relative to that of the IR measurement. This deviation of the $R_fCO_2M(CO)_5$ compounds from ideal octahedral local symmetry is sufficient to make the B_1 mode slightly IR active but not sufficient to cause a definite splitting of the E mode* such as occurs with other $YM(CO)_5$ derivatives with apparently even more assymmetrical Y groups[28].

Two weak $v(CO)$ frequencies in the $R_fCO_2M(CO)_5$ compounds (IX) not listed in Table 4 have also been observed. The first of these weak frequencies occurs at 2026 ± 1 ($M = Mn$) or 2014 ± 1 ($M = Re$) cm^{-1}. This frequency appears to correspond to band f in ref. 27 which has been assigned to the A' mode of the radial mono-^{13}CO molecule. The other weak frequency in the $R_fCO_2M(CO)_5$ compounds (IX) occurs at 1968 ± 2 ($M = Mn$) or 1958 ± 1 ($M = Re$) cm^{-1}. This frequency appears to correspond to band h in ref. 27 which has been assigned to the A_1 mode of the axial mono-^{13}CO molecule.

In order to gain a greater insight into the bonding in the $R_fCO_2M(CO)_5$ derivatives the approximate force constants (Table 4) were calculated from the A_1, E, and A_1 frequencies by the Cotton–Kraihanzel method[29] with the usual approximations ($k_t = 2k_c = 2k_{c'}$). These force constants were very similar to the corresponding force constants in the metal pentacarbonyl halides $M(CO)_5X$ particularly the chlorides[27]. The $\Delta\sigma$ and $\Delta\pi$ parameters of Graham[30] (Table 4) relative to CH_3-$Mn(CO)_5$ were also calculated for the manganese derivatives $R_fCO_2Mn(CO)_5$. The similarity of the $\Delta\sigma$ and $\Delta\pi$ parameters of the perfluorocarboxylates R_fCO_2-$Mn(CO)_5$ [(IX), $M = Mn$)] to those of $Mn(CO)_5Cl$ ($\Delta\sigma = 1.25$, $\Delta\pi = -0.57$) indicate that the bonding properties of the perfluorocarboxylate and chloride ligands are similar both being π donors and σ acceptors. The π donor and σ acceptor character of the perfluorocarboxylate ligands is in accord with the presence of lone electron pairs on the oxygen atom for π donation and with the electronegativity of the oxygen atom for σ withdrawal.

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* Wilford and Stone[28] cite cases [e.g. $HCFClCF_2Re(CO)_5$] where the B_1 mode but not the splitting of the E mode are observed in the IR spectrum.

REFERENCES

1 R. P. M. WERNER AND T. H. COFFIELD, *Chem. Ind. (London),* (1960) 936.
2 W. HIEBER, K. ENGLERT AND K. RIEGER, *Z. Anorg. Allg. Chem.,* 300 (1959) 288.
3 W. HIEBER, K. ENGLERT AND K. RIEGER, *Z. Anorg. Allg. Chem.,* 300 (1959) 295.
4 W. HIEBER AND K. ENGLERT, *Z. Anorg. Allg. Chem.,* 300 (1959) 304, 311.
5 W. HIEBER AND L. SCHUSTER, *Z. Anorg. Allg. Chem.,* 285 (1956) 205.
6 B. F. G. JOHNSON, J. LEWIS, L. G. WILLIAMS AND J. WILSON, *Chem. Commun.,* (1966) 391.
7 M. L. H. GREEN, A. G. MASSEY, J. T. MOELWYN-HUGHES AND P. L. I. NAGY, *J. Organometal. Chem.,* 8 (1967) 511.
8 A. DAVISON, W. MCFARLANE, L. PRATT AND G. WILKINSON, *J. Chem. Soc.,* (1962) 3653.
9 P. N. LAWSON AND G. WILKINSON, *J. Chem. Soc.,* (1965) 1900.
10 T. S. PIPER AND G. WILKINSON, *J. Inorg. Nucl. Chem.,* 2 (1956) 38; R. B. KING, *Organometal. Syn.,* 1 (1965) 175.
11 T. S. PIPER AND G. WILKINSON, *J. Inorg. Nucl. Chem.,* 3 (1956) 104.
12 E. W. ABEL AND G. WILKINSON, *J. Chem. Soc.,* (1959) 1501; R. B. KING, *Organometal. Syn.,* 1 (1965) 174.
13 R. B. KING, *Inorg. Chem.,* 6 (1967) 30.
14 R. A. PLOWMAN AND F. G. A. STONE, *Z. Naturforsch., B,* 17 (1962) 575; R. B. KING, *Organometal. Syn.,* 1 (1965) 176.
15 R. B. KING, P. M. TREICHEL AND F. G. A. STONE, *J. Amer. Chem. Soc.,* 83 (1961) 3593.
16 J. G. TRAYNHAM AND J. S. DEHN, *J. Org. Chem.,* 23 (1958) 1545.
17 H. W. THOMPSON AND P. TORKINGTON, *J. Chem. Soc.,* (1945) 640.
18 R. B. KING, *J. Amer. Chem. Soc.,* 85 (1963) 1918.
19 R. B. KING AND L. W. HOUK, unpublished results.
20 P. M. TREICHEL AND G. P. WERBER, *J. Organometal. Chem.,* 7 (1967) 157.
21 P. CORRADINI AND G. ALLEGRA, *J. Amer. Chem. Soc.,* 81 (1959) 5510; G. ALLEGRA, P. GANISO, L. PORRI AND P. CORRADINI, *Atti Accad. Naz. Lincei,* 30 (1961) 44; S. A. GIDDINGS, *Inorg. Chem.,* 3 (1964) 684.
22 E. M. BRAININA, R. KH. FREIDLINA AND A. N. NESMEYANOV, *Dokl. Akad. Nauk SSSR,* 154 (1964) 1113; A. F. REID, J. S. SHANNON, J. M. SWAN AND P. C. WAILES, *Austr. J. Chem.,* 18 (1965) 173.
23 L. SUMMERS, R. H. ULOTH AND A. HOLMES, *J. Amer. Chem. Soc.,* 77 (1955) 3604; H. KÖPF AND M. SCHMIDT, *Angew. Chem.,* 77 (1965) 965; J. LOCKE AND J. A. MCCLEVERTY, *Inorg. Chem.,* 5 (1966) 1157; R. S. P. COUTTS, J. R. SURTEES, J. M. SWAN AND P. C. WAILES, *Austr. J. Chem.,* 19 (1966) 1377; R. S. P. COUTTS AND P. C. WAILES, *Austr. J. Chem.,* 19 (1966) 2069; R. B. KING AND C. A. EGGERS, *Inorg. Chem.,* 7 (1968) 340.
24 R. S. P. COUTTS AND P. C. WAILES, *Austr. J. Chem.,* 20 (1967) 1579.
25 L. M. CRAPO AND C. H. SEDERHOLM, *J. Chem. Phys.,* 33 (1960) 1583.
26 P. M. TREICHEL AND F. G. A. STONE, *Advan. Organometal. Chem.,* 1 (1964) 143; E. PITCHER, A. D. BUCKINGHAM AND F. G. A. STONE, *J. Chem. Phys.,* 36 (1962) 124.
27 H. D. KAESZ, R. BAU, D. HENDRICKSON AND J. M. SMITH, *J. Amer. Chem. Soc.,* 89 (1967) 2844.
28 J. B. WILFORD AND F. G. A. STONE, *Inorg. Chem.,* 4 (1965) 389.
29 F. A. COTTON AND C. S. KRAIHANZEL, *J. Amer. Chem. Soc.,* 84 (1962) 4432.
30 W. A. G. GRAHAM, *Inorg. Chem.,* 7 (1968) 315.
31 G. FILIPOVICH AND G. V. D. TIERS, *J. Phys. Chem.,* 63 (1959) 761.