that of the five-coordinate cobalt(I) *tert*-butyl isocyanide complex [(*t*-BuNC)$_5$Co][PF$_6$] discussed above. Unchanged [(*t*-BuNC)$_6$Mn][PF$_6$] was the only manganese(I) complex recovered from its reactions with several of the trivalent phosphorus and arsenic ligands in boiling ethanol. Even in boiling diglyme the [(*t*-BuNC)$_6$Mn][PF$_6$] was recovered unchanged from its attempted reactions with all of the trivalent phosphorus ligands tried except for triphenylphosphine. This lower reactivity of [(*t*-BuNC)$_6$Mn][PF$_6$] relative to [(*t*-BuNC)$_5$Co][PF$_6$] is the expected trend for an octahedral complex relative to a trigonal–bipyramidal complex and is similar to the lower reactivity of Cr(CO)$_6$ relative to Fe(CO)$_5$.[19]

The reaction between [(*t*-BuNC)$_6$Mn][PF$_6$] and triphenylphosphine in boiling diglyme gave a low yield of the yellow crystalline monosubstituted derivative [(*t*-BuNC)$_5$MnP(C$_6$H$_5$)$_3$][PF$_6$] (IX) which had to be separated from unchanged [(*t*-BuNC)$_6$Mn][PF$_6$] by hand picking the crystals. The infrared spectrum of [(*t*-BuNC)$_5$MnP(C$_6$H$_5$)$_3$][PF$_6$] (IX) exhibited three ν(CN) frequencies in accord with the C_{4v} symmetry of the complex cation. The weak ν(CN) band at 2166 cm^{-1} may be assigned to the A$_1$ mode of the C_{4v} system. The remaining ν(CN) bands at 2093 and 2059 cm^{-1} are strong and may be assigned to the other A$_1$ mode and the E mode. The proton nmr spectrum of [(*t*-BuNC)$_5$MnP(C$_6$H$_5$)$_3$][PF$_6$] exhibited two methyl resonances with a 1:4 relative intensity ratio. The less intense resonance can be assigned to the nine methyl protons of the single axial *tert*-butyl isocyanide ligand and the more intense resonance can be assigned to the 36 methyl protons of the four equivalent equatorial *tert*-butyl isocyanide ligands.

(19) R. B. King, "Transition Metal Organometallic Chemistry: An Introduction," Academic Press, New York, N. Y., 1969.

Acknowledgment.—We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-71-2000. We also acknowledge the collaboration of Miss Melanie J. Loots and Miss Susan J. Redding as students in the Secondary Science Training Program sponsored by the National Science Foundation for the summers 1970 and 1971, respectively.

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Organometallic Transition Metal Derivatives Containing Fluorine. V. Some Perfluoro-1-methylpropenyl Derivatives of Metal Carbonyls and Metal Cyclopentadienyls[1,2]

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Received November 24, 1971

Reactions of various transition metal halide derivatives with perfluoro-1-methylpropenylsilver, C$_4$F$_7$Ag, in dichloromethane solution at room temperature give the corresponding perfluoro-1-methylpropenyl transition metal derivatives. Thus reactions of the metal pentacarbonyl bromides M(CO)$_5$Br (M = Mn and Re) with C$_4$F$_7$Ag give the volatile white crystalline C$_4$F$_7$M(CO)$_5$ (M = Mn and Re). Similarly, treatment of C$_5$H$_5$Fe(CO)$_2$I with C$_4$F$_7$Ag gives the volatile yellow crystalline C$_4$F$_7$Fe(CO)$_2$C$_5$H$_5$. Reaction of C$_5$H$_5$Cr(NO)$_2$Cl with C$_4$F$_7$Ag gives the volatile green crystalline C$_4$F$_7$Cr(NO)$_2$C$_5$H$_5$. Reactions of the fluorocarbon transition metal halides R$_f$Fe(CO)$_4$I (R$_f$ = C$_2$F$_5$, CF$_3$CF$_2$CF$_2$, and (CF$_3$)$_2$CF) and C$_5$H$_5$Co(CO)(R$_f$)I (R$_f$ = C$_2$F$_5$ and CF$_3$CF$_2$CF$_2$) with C$_4$F$_7$Ag give volatile pale yellow R$_f$Fe(CO)$_4$C$_4$F$_7$ (R$_f$ = C$_2$F$_5$, CF$_3$CF$_2$CF$_2$, and (CF$_3$)$_2$CF) and volatile yellow C$_5$H$_5$Co(CO)(R$_f$)(C$_4$F$_7$) (R$_f$ = C$_2$F$_5$ and CF$_3$CF$_2$CF$_2$), respectively. The infrared, fluorine nmr, and mass spectra of these new compounds are discussed.

Introduction

Within the last decade fluorocarbon transition metal derivatives have received considerable attention largely because of their stability relative to their hydrocarbon analogs.[3] Such compounds are prepared by the following general methods: (1) reactions of metal carbonyl anions with perfluoroacyl derivatives followed by decarbonylation; (2) nucleophilic substitution of fluoride with metal carbonyl groups by reactions of fluorinated olefins or aromatic compounds with metal carbonyl anions;[4] (3) addition of fluoroolefins, fluorinated alkynes, or perfluoroalkyl iodides to appropriate transition metal systems, particularly those in lower oxidation states; (4) reactions of metal halide derivatives with fluoroalkyl or fluoroaryl derivatives of electropositive metals such as lithium or magnesium. This repertoire of preparative methods in fluorocarbon transition metal chemistry has the following limitations: (1) the need of a sufficiently nucleophilic metal carbonyl anion for the reactions with perfluoroacyl derivatives, fluoroolefins, and fluorinated aromatic compounds (methods 1 and 2 above) or the need of an appropriately reactive low-oxidation-state derivative for the reactions with fluoroolefins, fluorinated alkynes, or perfluoroalkyl iodides (method 3 above); (2) the instability of many fluorocarbon derivatives of electropositive metals such as lithium or magnesium coupled with the high reactivity of organometallic derivatives of such electropositive metals which makes them able to effect undesirable side reactions (method 4). For these

(1) For part IV of this series see R. B. King, R. N. Kapoor, and K. H. Pannell, *J. Organometal. Chem.*, **20**, 187 (1969).

(2) Portions of this work were presented to the Division of Fluorine Chemistry at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971; see Abstract FLUO-7.

(3) For a review article discussing fluorocarbon transition metal derivatives, see P. M. Treichel and F. G. A. Stone, *Advan. Organometal. Chem.*, **1**, 143 (1964).

(4) For a review of nucleophilic reactions of metal carbonyl anions with fluorocarbons, see M. I. Bruce and F. G. A. Stone, *Angew. Chem., Int. Ed. Engl.*, **7**, 747 (1968).

TABLE I

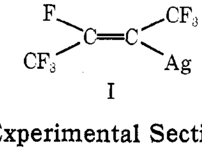
REACTIONS OF PERFLUORO-1-METHYLPROPENYLSILVER WITH VARIOUS TRANSITION METAL HALIDE DERIVATIVES

Halide (g, mmol)	Quantity of C_4F_7Ag, g (mmol)	Solvent (ml)	Time, hr	Product	Yield, g (%)
$Mn(CO)_5Br$ (1.0, 3.9)	1.42 (4.9)	CH_2Cl_2 (50)	4	$C_4F_7Mn(CO)_5$	0.67 (46)
$Re(CO)_5Br$ (1.1, 2.8)	1.0 (3.5)	CH_2Cl_2 (50)	5	$C_4F_7Re(CO)_5$	1.02 (73)
$C_5H_5Fe(CO)_2I$ (0.84, 2.8)	1.0 (3.5)	CH_2Cl_2 (50)	5	$C_4F_7Fe(CO)_2C_5H_5$	0.7 (71)
$C_5H_5Fe(CO)_2I$ (0.84, 2.8)	1.0 (3.5)	THF (50)	1	$C_4F_7Fe(CO)_2C_5H_5$	0.11 (11)
$C_5H_5Cr(NO)_2Cl$ (0.58, 2.8)	1.0 (3.5)	CH_2Cl_2 (50)	3	$C_4F_7Cr(NO)_2C_5H_5$	0.68 (68)
$C_2F_5Fe(CO)_4I$ (4.60, 9.9)	4.0 (13.8)	CH_2Cl_2 (100)	3	$(C_2F_5)(C_4F_7)Fe(CO)_4$	1.23 (27)
$(n\text{-}C_3F_7)Fe(CO)_4I$ (1.81, 4.9)	1.42 (4.9)	CH_2Cl_2 (50)	10	$(n\text{-}C_3F_7)(C_4F_7)Fe(CO)_4$	0.89 (44)
$(i\text{-}C_3F_7)Fe(CO)_4I$ (1.29, 2.8)	1.0 (3.5)	CH_2Cl_2 (50)	6	$(i\text{-}C_3F_7)(C_4F_7)Fe(CO)_4$	0.44 (29)
$C_5H_5Co(CO)(C_2F_5)I$ (0.9, 2.3)	0.82 (2.8)	CH_2Cl_2 (40)	6	$C_5H_5Co(CO)(C_2F_5)(C_4F_7)$	0.25 (20)
$C_5H_5Co(CO)(n\text{-}C_3F_7)I$ (0.4, 0.9)	0.34 (1.2)	CH_2Cl_2 (50)	6	$C_5H_5Co(CO)(n\text{-}C_3F_7)(C_4F_7)$	0.07 (16)
$(C_5H_5)_2TiCl_2$ (0.69, 2.8)	2.0 (6.9)	CH_2Cl_2 (50)	23	$(C_5H_5)_2TiF_2$	0.06 (8)
$(C_5H_5)_2ZrCl_2$ (0.8, 2.8)	2.0 (6.9)	CH_2Cl_2 (50)	14	$(C_5H_5)_2ZrF_2$	0.09 (12)

reasons the development of new and distinctly different methods for the synthesis of fluorocarbon transition metal derivatives would allow a considerable extension of the range of fluorocarbon transition metal derivatives that can be prepared.

A significant recent development in fluorocarbon chemistry has been the discovery of stable fluorocarbon derivatives of the coinage metals. Stable compounds of this type include pentafluorophenylcopper (C_6F_5Cu),[5] perfluoro-*tert*-butylcopper [$(CF_3)_3CCu$],[5] perfluoro-1-methylpropenylsilver (C_4F_7Ag),[6] and pentafluorophenylsilver (C_6F_5Ag).[7] Reactions of such fluorocarbon derivatives of coinage metals with transition metal halide derivatives appeared to provide a method for the preparation of fluorocarbon transition metal derivatives not obtainable by previous methods. Fluorocarbon derivatives of coinage metals would have a high tendency to react with transition metal halide derivatives because of the insolubility of the coinage metal halide but would have a much lower tendency to effect undesirable side reactions than similar fluorocarbon derivatives of relatively electropositive metals such as lithium or magnesium.

These considerations led us to investigate reactions of coinage metal fluorocarbon derivatives with transition metal halide derivatives as possible routes to new fluorocarbon transition metal derivatives. We selected perfluoro-1-methylpropenylsilver (I) as the coinage metal fluorocarbon derivative for our studies for the following reasons: (1) its relatively facile preparation[6] from silver(I) fluoride and the commercially available hexafluorobutyne-2; (2) its stability which allows purification by vacuum sublimation. This paper reports the details of our work in this area. Of particular interest is the preparation of the first known derivatives with two different fluorocarbon groups bonded to the same transition metal atom.



I

Experimental Section

A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions, (b) handling all filtered solutions of organometallic compounds, and (c) admitting to evacuated vessels containing organometallic compounds.

Materials.—Perfluoro-1-methylpropenylsilver (I) was prepared by the published procedure[6] which employs the reaction of silver(I) fluoride with hexafluorobutyne-2 in acetonitrile at room temperature. We purified the acetonitrile used in this preparation by distillation over phosphorus pentoxide. The perfluoro-1-methylpropenylsilver (I) was always vacuum sublimed (~100° (0.1 mm)) before use.

The following transition metal derivatives were purchased from the indicated commercial sources: $Fe(CO)_5$ (GAF Corp., New York, N. Y.), $Co_2(CO)_8$ (Strem Chemical Co., Danvers, Mass.), $CH_3C_5H_4Mn(CO)_3$ (Ethyl Corp., New York, N. Y.), $Mo(CO)_6$ and $Re_2(CO)_{10}$ (Pressure Chemical Corp., Pittsburgh, Pa.), and $(C_5H_5)_2MCl_2$ (M = Ti and Zr) (Arapahoe Chemical Corp., Boulder, Colo.). The compounds $Mn_2(CO)_{10}$,[8] $Mn(CO)_5Br$,[9a] $C_5H_5Fe(CO)_2I$,[9b] $C_5H_5Cr(NO)_2Cl$,[9c] $R_fFe(CO)_4I$ (R_f = C_2F_5,[10] $CF_3CF_2CF_2$,[9d] and $(CF_3)_2CF$[11]), $C_5H_5Co(CO)_2$[9e] $C_5H_5Co(CO)(R_f)I$ (R_f = C_2F_5 and $CF_3CF_2CF_2$),[12] $[C_5H_5Mo(NO)I_2]_2$,[13] and $Fe(CO)_4I_2$[14] were prepared by the cited published procedures.

Reactions of Transition Metal Halide Derivatives with Perfluoro-1-methylpropenylsilver (Table I).—The indicated quantities of the transition metal halide derivative and perfluoro-1-methylpropenylsilver were stirred in the indicated quantity of dichloromethane (redistilled over phosphorus pentoxide) for the indicated period of time (see Table I). After the reaction period was over, the precipitated silver(I) halide was removed by filtration. Solvent was removed from the dichloromethane filtrate at 25° (25 mm). The product was isolated from the residue in the indicated yield (Table I) by vacuum sublimation (or distillation in the case of $(C_2F_5)(C_4F_7)Fe(CO)_4$).

Analytical data and other properties of the new perfluoro-1-methylpropenyl transition metal derivatives are given in Table II.

The product $(C_5H_5)_2TiF_2$ from the reaction of $(C_5H_5)_2TiCl_2$ and C_4F_7Ag was identified by comparison of its infrared and mass spectra with those reported for an authentic sample.[15] The white crystalline $(C_5H_5)_2ZrF_2$ was identified by its mass spectrum (see below) and by elemental analyses. *Anal.* Calcd for $C_{10}H_{10}F_2Zr$: C, 46.4; H, 3.9; F, 14.7; Zr, 35.1. Found: C, 46.4; H, 3.7; F, 14.6; Zr, 34.9. The fluorine nmr spectrum of $(C_5H_5)_2ZrF_2$ exhibited a single resonance at ϕ −177.4.

Infrared Spectra (Table III).—The infrared spectra of the solid compounds listed in Table III were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 621 spectrometer. The infrared spectrum of the liquid $(C_2F_5)(C_4F_7)Fe(CO)_4$ was measured as a liquid film. The ν(CO) regions of the metal carbonyl derivatives and the ν(NO) region of $C_4F_7Cr(NO)_2C_5H_5$ (Table III) were also measured in cyclo-

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TABLE II

PROPERTIES OF THE TRANSITION METAL PERFLUORO-1-METHYLPROPENYL DERIVATIVES

Compound[a]	Color	Mp,[b] °C	Sublimation conditions, °C (mm)	Analyses, %[c] C	H	F	Metal	Other
$C_4F_7Mn(CO)_5$	White	38	25 (0.1)	28.8 (28.8)		35.3 (35.4)	14.7 (14.6) (Mn)	
$C_4F_7Re(CO)_5$	White	63	25 (0.05)	21.3 (21.4)	0.2 (0.0)	26.0 (26.2)	36.6 (36.7) (Re)	16.0 (15.8) (O)
$C_4F_7Fe(CO)_2C_5H_5$	Yellow	75	40 (0.05)	36.6 (36.9)	1.4 (1.4)	37.0 (37.2)	15.4 (15.6) (Fe)	
$C_4F_7Cr(NO)_2C_5H_5$	Green	80	50 (10)	30.1 (30.2)	1.5 (1.4)	37.2 (37.2)	14.6 (14.6) (Cr)	
$(C_2F_5)(C_4F_7)Fe(CO)_4$	Pale yellow	Liquid	40 (0.1)	24.9 (25.1)	0.2 (0.0)	48.6 (48.8)	11.9 (12.0) (Fe)	
$(n\text{-}C_3F_7)(C_4F_7)Fe(CO)_4$	Pale yellow	51–53	44 (0.1)	23.8 (25.4)	0.4 (0.0)	50.2 (51.4)	11.2 (10.8) (Fe)	12.7 (12.4) (O)
$(i\text{-}C_3F_7)(C_4F_7)Fe(CO)_4$	Pale yellow	55	25 (0.1)	25.4 (25.4)	0.1 (0.0)	51.3 (51.4)	10.9 (10.8) (Fe)	12.4 (12.4) (O)
$C_5H_5Co(CO)(C_2F_5)(C_4F_7)$	Yellow	75	35 (0.05)	31.7 (31.9)	1.1 (1.1)	50.6 (50.7)	13.1 (13.1) (Co)	
$C_5H_5Co(CO)(n\text{-}C_3F_7)(C_4F_7)$	Yellow	94	25 (0.05)	31.2 (31.1)	1.1 (1.0)	52.7 (53.0)	11.7 (11.8) (Co)	

[a] The following abbreviations were used: C_4F_7 = perfluoro-1-methylpropenyl; $n\text{-}C_3F_7$ = $CF_3CF_2CF_2$; $i\text{-}C_3F_7$ = $(CF_3)_2CF$. [b] Melting points were taken in capillaries and are uncorrected. [c] Analyses were performed by Meade Microanalytical Laboratory, Amherst, Mass. Calculated values in parentheses.

TABLE III

INFRARED SPECTRA OF THE TRANSITION METAL PERFLUORO-1-METHYLPROPENYL DERIVATIVES

Compound	Infrared spectrum, cm⁻¹ ν(CH)[a]	ν(CO)[b]	ν(C=C)[a]	ν(CF)[a]	Other bands[a]
$C_4F_7Mn(CO)_5$		2142 (w, A_1), 2056 (vs, E), 2025 (s, A_1)	1618 (m)	1311 (s), 1224 (vs), 1190 (vs), 1153 (vs), 1126 (vs), 1052 (m)	889 (s), 846 (s), 740 (s), 698 (s), 659 (vs), 641 (vs), 619 (s)
$C_4F_7Re(CO)_5$		2155 (w, A_1), 2048 (vs, E), 2015 (s, A_1)	1620 (m)	1320 (s), 1227 (vs), 1205 (vs), 1137 (vvs), 1055 (m)	961 (m), 900 (s), 847 (s), 741 (s), 698 (w), 667 (s), 610 (s), 590 (s)
$C_4F_7Fe(CO)_2C_5H_5$	3150 (vw)	2054 (s), 2012 (s)	1630 (w)	1320 (m), 1228 (s), 1194 (s), 1148 (m), 1134 (s), 1113 (m, sh), 1054 (w)	1432 (w), 1401 (w), 1020 (w), 1010 (vw), 897 (m), 854 (w), 844 (w), 734 (w), 654 (w)
$C_4F_7Cr(NO)_2C_5H_5$	3135 (w)	1820 (s),[c] 1720 (s)[c]	1636 (w)	1323 (s), 1235 (s), 1192 (s), 1138 (s), 1112 (m), 1054 (w)	1439 (w), 1434 (w), 1400 (w), 1024 (w), 1015 (vw) 936 (vw), 905 (m), 848 (m), 842 (m), 748 (w), 664 (m), 645 (w), 613 (w)
$(C_2F_5)(C_4F_7)Fe(CO)_4$[d]		2167 (vw), 2131 (w), 2103 (s), 2071 (w)	1621 (m)	1324 (s), 1310 (s), 1227 (vs), 1200 (vs), 1163 (vs), 1052 (s), 919 (s)	902 (s), 849 (s), 742 (s), 733 (s), 670 (s), 638 (s)
$(n\text{-}C_3F_7)(C_4F_7)Fe(CO)_4$		2166 (vw), 2129 (vw, sh), 2102 (s), 2072 (w)	1620 (w)	1320 (s), 1226 (s), 1204 (s), 1162 (s), 1098 (s), 1066 (w), 1028 (s)	897 (m), 858 (m), 813 (s), 738 (m), 728 (m), 667 (m), 636 (s)
$(i\text{-}C_3F_7)(C_4F_7)Fe(CO)_4$		2135 (vw), 2107 (s), 2077 (vw), 2067 (vw)	1615 (w)	1328 (s), 1292 (m), 1266 (s), 1220–1194 (vs, br), 1167 (vs), 1130 (m), 1079 (w), 1023 (s), 943 (s)	900 (m), 878 (s), 849 (m), 742 (s), 710 (s), 668 (s)
$C_5H_5Co(CO)(C_2F_5)(C_4F_7)$	3131 (w)	2108 (m), 2100 (m)	1614 (w)	1314 (s), 1285 (s), 1229 (s), 1203 (s, sh), 1191 (s), 1153 (s, sh), 1140 (s), 1059 (m), 1045 (m), 1037 (m), 892 (s)	1437 (w), 1422 (w), 962 (w), 908 (m), 862 (s), 848 (m), 837 (w), 741 (m), 732 (s), 663 (s)
$C_5H_5Co(CO)(n\text{-}C_3F_7)(C_4F_7)$	3146 (w)	2105 (s)	1624 (w)	1321 (s), 1252 (m, sh), 1231 (s), 1201 (s), 1181 (m), 1158 (s), 1129 (m), 1093 (m), 1077 (w), 1060 (w), 1044 (w), 1030 (m), 1011 (w)	1448 (w), 1431 (w), 964 (vw), 907 (m), 867 (s), 850 (m), 841 (w), 807 (m), 743 (w), 725 (s), 668 (m), 663 (m)

[a] These frequencies were determined in potassium bromide pellets. [b] These frequencies were determined in cyclohexane solution. Assignments of the ν(CO) frequencies for the $C_4F_7M(CO)_5$ (M = Mn or Re) derivatives are given in parentheses. [c] ν(NO) frequency. [d] A liquid film rather than a KBr pellet was used for the infrared spectrum of this liquid compound.

TABLE IV

FLUORINE NMR SPECTRA OF THE TRANSITION METAL PERFLUORO-1-METHYLPROPENYL DERIVATIVES[a]

Compound	Fluorine nmr spectrum, φ: Perfluoro-1-methylpropenyl fluorines β-CF₃	γ-CF₃	β-CF	³J(FF)	⁴J(FF)	⁵J(FF)	Other fluorines[b] Group	α(CF or CF₂)	β(CF₂ or CF₃)	γ(CF₃)
C_4F_7Ag	50.7	70.0	95.1	12.5	15.1	1.7				
$C_4F_7Mn(CO)_5$[c]	48.8	65.0	71.9	7	20.7					
$C_4F_7Re(CO)_5$	48.4	63.3	80.5	∼6	19.0					
$C_4F_7Fe(CO)_2C_5H_5$	47.8	63.3	71.8	∼6	27.3					
$C_4F_7Cr(NO)_2C_5H_5$	50.8	65.3	79.7	∼6	23.0					
$(C_2F_5)(C_4F_7)Fe(CO)_4$[d]	47.1	64.2	68.9				C_2F_5	∼64?	83.6	
$(n\text{-}C_3F_7)(C_4F_7)Fe(CO)_4$[c]	49.0	65.4	69.2	7	22.3	1.7	$n\text{-}C_3F_7$	61.3 q (10.5)	115.5	80.2 t (10.5)
$(i\text{-}C_3F_7)(C_4F_7)Fe(CO)_4$	46.6	63.7	66?		25.9		$i\text{-}C_3F_7$	68.6 d (∼4)		
$C_5H_5Co(CO)(C_2F_5)(C_4F_7)$	50.1	62.6	68.3 d (103)[e]				C_2F_5	?	80.9	
$C_5H_5Co(CO)(n\text{-}C_3F_7)(C_4F_7)$[c]	50.0	63.8	69.8 d (186)[e]		25.0		$n\text{-}C_3F_7$	53.4 br	115	80.9 t (8.5)

[a] These spectra were obtained at 56.456 MHz on a Perkin-Elmer Model R-20 spectrometer unless otherwise indicated. [b] The following abbreviations are used: d = doublet, t = triplet, q = quartet, br = broad. Separations in Hz are given in parentheses. [c] This spectrum was obtained at 94.1 MHz on a Varian HA-100 spectrometer. [d] The nmr spectrum of this compound exhibited broad resonances apparently because of the presence of paramagnetic impurities. [e] This "doublet" appears to arise from a chemical shift difference rather than spin–spin coupling since in the fluorine nmr spectrum of $C_5H_5Co(CO)(n\text{-}C_3F_7)(C_4F_7)$ the separation was ∼120 Hz at 56.456 MHz and ∼185 Hz at 94.1 MHz. This must arise from the presence of some type of isomerism.

hexane solution. All spectra were calibrated against the 1601.4-cm^{-1} band of polystyrene film.

Fluorine Nmr Spectra (Table IV).—The fluorine nmr spectra listed in Table IV were taken in dichloromethane solution with either fluorotrichloromethane (ϕ 0.0) or 1,2-difluoro-1,1,2,2-tetrachloroethane (ϕ 67.8) as an internal standard and recorded either at 56.456 MHz on a Perkin-Elmer Hitachi Model R-20 spectrometer or at 94.1 MHz on a Varian HA-100 spectrometer. All fluorine nmr chemical shift data are given in the ϕ scale of Filipovich and Tiers.[16]

Mass Spectra.—The mass spectra listed below were taken at the indicated temperatures at 70 eV on a Perkin-Elmer Hitachi RMU-6 mass spectrometer. Relative intensities are given in parentheses.

A. $C_4F_7Re(CO)_5$ (Chamber Temperature 100°; Sample Temperature ~70°).—$C_4F_7Re(CO)_5^+$ (37), $C_4F_7Re(CO)_4^+$ (14), $C_4F_7Re(CO)_3^+$ (11), $C_4F_7Re(CO)_2^+$ (13), $C_4F_7ReCO^+$ (35), $C_4F_6ReCO^+$ (4), $C_4F_7Re^+$ (69), $C_4F_6Re^+$ (6), $Re(CO)_5^+$ (44), $Re(CO)_4F^+$ (58), $Re(CO)_4^+$ (60), $Re(CO)_3F^+$ (100), $C_3F_3Re^+$ (13), CF_4Re^+ (2), $Re(CO)_3^+$ (12), $C_2F_3Re^+$ (10), $Re(CO)_2F^+$ (17), $C_3F_2Re^+$ (6), CF_3Re^+ (4), $C_2F_2Re^+$ (11), ReF_3^+ (14), $Re(CO)_2^+$ (4), CF_2Re^+ (3), $ReCOF^+$ (8), ReC_2F^+ (7), ReF_2^+ (7), $CFRe^+$ (3), $C_4F_6Re(CO)_3^{2+}$ (1), $ReCO^+$ (2), ReC_2^+ (3), ReF^+ (5), ReC^+ (3), $C_4F_6ReCO^{2+}$ (1), Re^+ (6), $C_4F_7H^+$ (89), $C_4F_6Re^{2+}$ (3), $C_4F_6H^+$ (190), $Re(CO)_4^{2+}$ (2), $C_4F_5^+$ (190), $C_3F_5H^+$ (19), $C_4F_4^+$ (42), $C_3F_4H^+$ (440), $C_4F_3^+$ (8), $C_2F_4^+$ (3), $C_3F_3^+$ (360), $C_2F_3H^+$ (20), $C_3F_2H^+$ (43), $C_3F_2^+$ (48), and CF_3^+ (270).

B. $C_4F_7Fe(CO)_2C_5H_5$ (Chamber Temperature 100°; Sample Temperature 100°).—$C_4F_7Fe(CO)_2C_5H_5^+$ (53), $C_4F_7FeCOC_5H_5^+$ (88), $C_4F_7FeC_5H_5^+$ (100), $C_4F_6FeC_5H_4^+$ (4), *m/e* 207 (7), $C_4F_7H^+$ (7), $C_5H_5Fe(CO)_2^+$ (79), *m/e* 169 (10), $C_5H_5FeCOF^+$ (7), $C_4F_6H^+$ (13), $C_4F_6^+$ (12), $C_5H_5FeCO^+$ (24), $C_4F_5^+$ (125), $C_5H_5FeF^+$ (>1000), $C_4F_4^+$ (26), $C_5H_4Fe^+$ (44), $C_3F_4H_2^+$? (22), $C_3F_4H^+$ (28), $C_3F_3^+$ (145), FeF^+ (180), $C_5H_5^+$ (125), Fe^+ (62), and $C_3H_3^+$ (130). Metastable ions at *m/e* 304 s [$C_4F_7Fe(CO)_2C_5H_5^+ \rightarrow C_4F_7FeCOC_5H_5^+ + CO$], *m/e* 276 s [$C_4F_7FeCOC_5H_5^+ \rightarrow C_4F_7FeC_5H_5^+ + CO$], *m/e* 102.9 m [$C_5H_5FeF^+ \rightarrow C_5H_4Fe^+ + HF$], *m/e* 65.0 [$C_4F_7FeC_5H_5^+ \rightarrow C_5H_5FeF^+ + C_4F_6$], *m/e* 60.5 w [$C_4F_5^+ \rightarrow C_3F_3^+ + CF_2$], and *m/e* 23.5 w [$C_5H_5^+ \rightarrow C_3H_3^+ + C_2H_2$].

C. $C_4F_7Cr(NO)_2C_5H_5$ (Chamber Temperature 220°; Sample Temperature 80°).—$C_4F_7Cr(NO)_2C_5H_5^+$ (8), $C_4F_7CrNOC_5H_5^+$ (45), $C_4F_7CrC_5H_5^+$ (4), $C_4F_7H^+$ (33), $C_5H_5Cr(NO)_2^+$ (27), $C_5H_5CrNOF^+$ (14), $C_4F_6H^+$ (72), $C_4F_6^+$ (~400), $C_5H_5CrF_2^+$ (4), $C_3F_6^+$ (3), $C_5H_5CrNO^+$ (5), $C_4F_5^+$ (170), $C_5H_5CrF^+$ (100), $C_4F_4^+$ (29), $C_3F_4H^+$ (48), $C_3F_3^+$ (124), $C_2F_3H^+$ (12), $C_3F_2H^+$ (33), $C_3F_2^+$ (46), CrF^+ (53), CF_3^+ (~50), $C_5H_6^+$ (66), C_5H_5 (25), Cr^+ (23), and $C_3H_3^+$ (29). Metastable ions at *m/e* 300.5 w [$C_4F_7Cr(NO)_2C_5H_5^+ \rightarrow C_4F_7CrNOC_5H_5^+ + NO$], *m/e* 60.5 w [$C_4F_5 \rightarrow C_3F_3^+ + CF_2$], and *m/e* 53.5 w [$C_4F_6^+ \rightarrow C_3F_3^+ + CF_3$].

D. $C_5H_5Co(CO)(C_2F_5)(C_4F_7)$ (Chamber Temperature 80°).—$C_5H_5Co(CO)(C_2F_5)(C_4F_7)^+$ (3.2), $C_5H_5Co(C_2F_5)(C_4F_7)^+$ (3.5), $C_5H_5CoC_6F_{11}^+$ (1.9), $C_5H_5CoC_6F_{10}^+$ (9), $C_5H_5CoC_6F_9^+$ (1.6), $C_5H_4CoC_6F_9^+$ (1.9), $C_5H_5Co(CO)(C_4F_7)^+$ (51), $C_5H_5CoF(C_4F_7)^+$ (1.4), $C_5H_4CoF(C_4F_7)^+$ (0.5), $C_5H_5CoC_4F_7^+$ (100), $C_5H_5Co(CO)(C_2F_5)^+$ (20), $C_5H_5CoF(C_2F_5)^+$ (1.9), $C_5H_5CoC_2F_5^+$ (9), $C_5H_5Co(CO)CF_3^+$ (1.1), $C_4F_8H^+$ (2.2), $C_4F_9^+$ (2.2), *m/e* 207 (15), $C_4F_8^+$ (2.2), $C_5H_5CoCF_3^+$ (3.2), $C_4F_7H^+$ (4), $C_5H_5CoCF_2^+$ (3.2), $C_3F_7^+$ (3.2), $C_4F_6H^+$ (7), $C_4F_6^+$ (3.5), $C_5H_5CoCF^+$ (4), $C_5H_5CoCO^+$ (14), $C_5H_5CoF^+$ and/or $C_4F_5^+$ (320), *m/e* 127 (9), $C_5H_5Co^+$ and/or $C_4F_4^+$ (110), $C_5H_4Co^+$ (95), $C_3F_4H^+$ (16), $C_2F_4^+$ (7), $C_3H_3Co^+$ (14), $C_3H_2Co^+$ (17), C_3HCo^+ (7), $C_3F_3^+$ (46), CoF^+ (15), $C_3F_2H^+$ (5), $C_3F_2^+$ (6), CF_3^+ (23), $C_5H_5^+$ (72), $C_5H_3^+$ (14), Co^+ (55), $C_4H_3^+$ (5), $C_4H_2^+$ (2.7), and $C_3H_3^+$ (~54). Metastable ions at *m/e* 347 w [$C_5H_5CoC_6F_{10}^+ \rightarrow C_5H_4CoC_6F_9^+ + HF$], *m/e* 279 s [$C_5H_5Co(CO)C_4F_7^+ \rightarrow C_5H_5CoC_4F_7^+ + CO$], *m/e* 217.5 w [$C_5H_5Co(CO)C_2F_5^+ \rightarrow C_5H_5CoC_2F_5^+ + CO$], *m/e* 105.9 vs [$C_5H_5CoF^+ \rightarrow C_5H_4Co^+ + HF$], *m/e* 67.0 vw [$C_5H_5CoC_4F_7^+ \rightarrow C_5H_5CoF^+ + C_4F_6$], and *m/e* 23.5 w [$C_5H_5^+ \rightarrow C_3H_3^+ + C_2H_2$].

E. $C_5H_5Co(CO)(CF_2CF_2CF_3)(C_4F_7)$ (Chamber Temperature 80°).—$C_5H_5Co(CO)(C_3F_7)(C_4F_7)^+$ (1.8), $C_5H_5Co(C_3F_7)(C_4F_7)^+$ (4.4), $C_5H_5CoC_7F_{13}^+$ (2.1), $C_5H_5CoC_7F_{12}^+$ (7), $C_5H_5CoC_7F_{11}^+$ (0.6), $C_5H_4CoC_7F_{11}^+$ (0.3), $C_5H_5Co(CO)C_5F_9^+$ (1.2), $C_5H_5CoC_5F_9^+$ (1.8), $C_5H_5Co(CO)(C_4F_7)^+$ (42), $C_5H_5Co(CO)(C_3F_7)^+$ (15), $C_5H_5CoC_4F_7^+$ (100), $C_5H_5CoC_3F_7^+$ (12), $C_5H_5CoC_2F_5^+$ (2.9), $C_4F_9H^+$ (1.2), $C_4F_9^+$ (1.2), *m/e* 207 (14), *m/e* 195 (5.3), $C_4F_7^+$ (4.4), $C_5H_5CoCF_2^+$ (4.4), $C_5H_5Co(CO)F^+$ (1.2), $C_3F_7^+$ (3.5), $C_4F_6H^+$ (7), $C_4F_6^+$ (4.7), $C_5H_5CoCF^+$ (3.8), $C_5H_5CoCO^+$ (17), $C_5H_5CoF^+$ and/or $C_4F_5^+$ (~1050), $C_3F_5^+$ (9), *m/e* 127 (15), $C_5H_5Co^+$ and/or $C_4F_4^+$ (105), $C_4H_4Co^+$ (91), $C_3F_4H^+$ (17), $C_2F_4^+$ (6), $C_3H_3Co^+$ (14), $C_3H_2Co^+$ (18), C_3HCo^+ (7), $C_3F_3^+$ (39), CoF^+ (12), $C_3F_2H^+$ (4.7), $C_3F_2^+$ (5.3), CF_3^+ (38), $C_5H_5^+$ (~38), $C_5H_3^+$ (13), Co^+ (~38), $C_4H_3^+$ (6), $C_4H_2^+$ (2.6), and $C_3H_3^+$ (~38). Metastable ions at *m/e* 279 s [$C_5H_5Co(CO)(C_4F_7)^+ \rightarrow C_5H_5CoC_4F_7^+ + CO$], *m/e* 267.5 m [$C_5H_5Co(CO)(C_3F_7)^+ \rightarrow C_5H_5CoC_3F_7^+ + CO$], *m/e* 105.9 s [$C_5H_5CoF^+ \rightarrow C_5H_4Co^+ + HF$], 67.0 w [$C_5H_5CoC_4F_7^+ \rightarrow C_5H_5CoF^+ + C_4F_6$], and *m/e* 23.5 w [$C_5H_5^+ \rightarrow C_3H_3^+ + C_2H_2$].

F. $(C_5H_5)_2ZrF_2$ (Chamber Temperature 220°; Sample Temperature ~140°).—$(C_5H_5)_2ZrF_2^+$ (24), $(C_5H_5)_2ZrF^+$ (5), $C_5H_5ZrF_2^+$ (100), $C_3H_3ZrF_2^+$ (16), $C_5H_5ZrF^+$ (2), $C_{10}H_{10}^+$ (38), $C_{10}H_9^+$ (42), $C_{10}H_8^+$ (28), $C_9H_7^+$ (27), $C_5H_6^+$ (145), $C_5H_5^+$ (98), $C_5H_3^+$ (24), and $C_3H_3^+$ (54).

Discussion

The syntheses of perfluoro-1-methylpropenyl transition metal derivatives from corresponding metal halide derivatives and perfluoro-1-methylpropenylsilver by metathetical reactions resemble previously reported metathetical syntheses of perfluorocarboxylate[17] and trifluoromethylthio[15] transition metal derivatives using the silver perfluorocarboxylates and trifluoromethylthiosilver, respectively. However, the metathetical reactions of perfluoro-1-methylpropenylsilver with transition metal halide derivatives reported in this paper are the first reported examples of the formation of a metal–carbon bond from a metathetical reaction involving a silver derivative. The only previous examples of the use of an organosilver compound to form a metal–carbon bond are the very recently reported[18] preparations of the perfluoro-1-methylpropenylmetal pentacarbonyl anions $[C_4F_7M(CO)_5]^-$ (M = Cr, Mo, and W) by oxidation of the corresponding decacarbonyldimetalates $[M_2(CO)_{10}]^{2-}$ (M = Cr, Mo, and W) with perfluoro-1-methylpropenylsilver.

The reactions of perfluoro-1-methylpropenylsilver with transition metal halide derivatives to form the corresponding perfluoro-1-methylpropenyl transition metal derivatives appear to be limited to transition metal halide derivatives with only one replaceable halogen atom. Thus attempts to prepare derivatives with two perfluoro-1-methylpropenyl groups attached to a single transition metal atom by reactions of perfluoro-1-methylpropenylsilver with the transition metal dihalide derivatives $Fe(CO)_4I_2$, $C_5H_5Co(CO)I_2$, and $[C_5H_5Mo(NO)I_2]_2$ gave no identifiable fluorocarbon transition metal derivatives. Reactions of the bis(cyclopentadienyl)metal dichlorides of titanium and zirconium, $(C_5H_5)_2MCl_2$ (M = Ti and Zr), with perfluoro-1-methylpropenylsilver gave only the corresponding bis(cyclopentadienyl)metal difluorides $(C_5H_5)_2MF_2$ (M = Ti or Zr). Apparently, the high tendency for fluorine to bond to the relatively electropositive 4+ titanium and zirconium results in a fluoride shift from carbon to the titanium or zirconium possibly with elimination of hexafluorobutyne-2 in a reaction of a reverse type to the formation of perfluoro-1-methylpropenylsilver from silver fluoride and hexafluorobutyne-2. A similar fluoride shift has previously[15] been observed in the reaction of $(C_5H_5)_2TiCl_2$ with trifluoromethylthiosilver to give $(C_5H_5)_2TiF_2$.

The perfluoro-1-methylpropenyl group in all of the new transition metal derivatives prepared in this work

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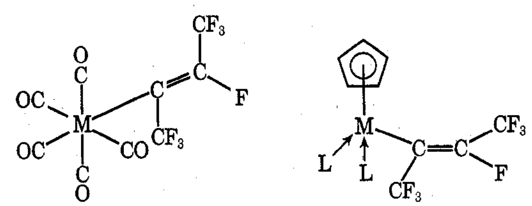
exhibits a characteristic infrared ν(C=C) frequency in the range 1615–1630 cm^{-1} and characteristic ν(CF) frequencies of medium to very strong intensities in the five ranges 1310–1328, 1224–1235, 1190–1205, 1137–1163, and 1052–1055 cm^{-1} (see Table III). The range of ν(C=C) frequencies for the transition metal perfluoro-1-methylpropenyl derivatives falls considerably below the 1675-cm^{-1} ν(C=C) frequency in perfluoro-1-methylpropenylsilver and the 1739-cm^{-1} ν(C=C) frequency in the fluoroolefin *trans*-CF_3CF=$CHCF_3$.[6] The lower ν(C=C) frequencies in the transition metal perfluoro-1-methylpropenyl derivatives can be taken as an indication of the reduction of the carbon–carbon bond order in the perfluoro-1-methylpropenyl group by back-donation of electrons from the filled transition metal d orbitals into the antibonding orbitals of the carbon–carbon double bond of the perfluoro-1-methylpropenyl group. A similar lowering of the ν(C=C) frequency of a polyfluoroalkenyl group upon bonding to a transition metal has been observed in other organometallic derivatives.[19]

The fluorine nmr spectra of the transition metal perfluoro-1-methylpropenyl derivatives (Table IV) exhibit the expected two trifluoromethyl doublets in the ranges ϕ 46.6–50.8 and 62.3–65.4 and a broad resonance (not always readily and unequivocally observed) in the range ϕ 66–80.5 arising from the single olefinic fluorine atom. By analogy with the nmr spectrum of perfluoro-1-methylpropenylsilver[6] the lower field trifluoromethyl doublet is assigned to the trifluoromethyl group bonded to the carbon atom which is also bonded to the transition metal (designated as β-CF_3 in Table IV because the fluorines are bonded to a β carbon atom relative to the transition metal) and the higher field trifluoromethyl doublet is assigned to the trifluoromethyl group bonded to the carbon atom which is also bonded to the single olefinic fluorine atom (designated as γ-CF_3 in Table IV because the fluorines are bonded to a γ carbon atom relative to the transition metal).

The couplings of the single olefinic fluorine atom to the two different trifluoromethyl groups (^3J(FF) and ^4J(FF)) were observed in the fluorine nmr spectra of most of the perfluoro-1-methylpropenyl transition metal derivatives (Table IV). However, the coupling between the fluorine atoms in the two different trifluoromethyl groups (^5J(FF)) was only 1.7 Hz and was thus observed only in a few of the better spectra. Comparison with the published[19–21] ^5J(FF) coupling constants between the fluorine atoms in the two trifluoromethyl groups in the various 1-trifluoromethyl-3,3,3-trifluoropropenyl derivatives obtained by the addition of metal hydrides to hexafluorobutyne-2 indicates that the two trifluoromethyl groups in the perfluoro-1-methylpropenyl transition metal derivatives prepared in this work are in trans positions around the carbon–carbon double bond. Thus in the previous work[19–21] with 1-trifluoromethyl-3,3,3-trifluoropropenyl derivatives, the compounds with a trans configuration of the trifluoromethyl groups around the carbon–carbon double bond exhibited a ^5J(FF) coupling constant between the fluorine atoms of the two trifluoromethyl groups of 1 to 3 Hz, whereas the compounds with a cis configuration of the trifluoromethyl groups around the carbon–carbon double bond exhibited a much larger ^5J(FF) coupling constant between the fluorine atoms of the two trifluoromethyl groups of 12 to 15 Hz. These nmr observations on the small magnitude of the ^5J(FF) coupling constant in the perfluoro-1-methylpropenyl transition metal derivatives thus indicate that the trans configuration of the trifluoromethyl groups around the carbon–carbon bond in perfluoro-1-methylpropenylsilver(I) is retained upon reactions with transition metal halides. A similar retention of the trans configuration of the trifluoromethyl groups around the carbon–carbon double bond has been observed in previously reported[6] reactions of perfluoro-1-methylpropenylsilver with other halogen derivatives such as methyl iodide.

A further feature of interest in the fluorine nmr spectra (Table IV) of the perfluoro-1-methylpropenyl transition metal derivatives is the observation that the ^3J(FF) coupling constant ($\sim$7 Hz) is much less than the more remote (in terms of number of bonds) ^4J(FF) coupling constant (18 to 28 Hz). A similar effect was observed several years ago[22] in the fluorine nmr spectra of transition metal *n*-heptafluoropropyl derivatives where the ^3J(FF) coupling constants (<2 Hz) were found to be much less than the more remote ^4J(FF) coupling constants (11 to 13 Hz).

The work described in this paper resulted in the preparation and characterization of nine new perfluoro-1-methylpropenyl transition metal derivatives. Of these nine derivatives the three compounds $C_4F_7M(CO)_5$ (II, M = Mn and Re) and $C_4F_7Fe(CO)_2C_5H_5$ (III, M = Fe; L = CO) resemble numerous previously reported compounds of the types $R_fM(CO)_5$ (M = Mn and Re)[23] and $R_fFe(CO)_2C_5H_5$,[4,24] respectively, in such respects as color, volatility, and infrared spectra of the metal carbonyl group in the ν(CO) region. The compound $C_4F_7Cr(NO)_2C_5H_5$ (III, M = Cr; L = NO) is apparently the first known neutral fluorocarbon chro-



II III

mium derivative and also apparently the first fluorocarbon derivative of a metal nitrosyl system. However, analogous $RCr(NO)_2C_5H_5$ derivatives, but only with hydrocarbon groups bonded to the chromium atom (*e.g.*, R = methyl, ethyl, chloromethyl, and σ-cyclopentadienyl), have been known for some time[25] being preparable by reactions of the halides $C_5H_5Cr(NO)_2X$ (X = Cl and I) with organomagnesium halides or sodium cyclopentadienide. The compound $C_4F_7Cr(NO)_2C_5H_5$ (III, M = Cr; L = NO), like the previously reported $RCr(NO)_2C_5H_5$ derivatives,[25] is a very

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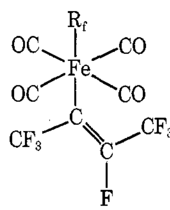
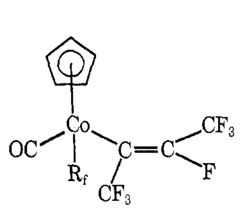
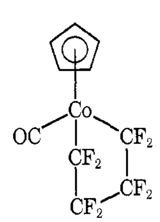
volatile green solid which exhibits two strong ν(NO) frequencies in its infrared spectrum.

The remaining five compounds prepared in this work are of the types $R_fFe(CO)_4C_4F_7$ (IV, R_f = C_2H_5, $CF_3CF_2CF_2$, and $(CF_3)_2CF$) and $C_5H_5Co(CO)(R_f)(C_4F_7)$ (V, R_f = C_2H_5 or $CF_3CF_2CF_2$) and represent the first examples of fluorocarbon transition metal derivatives with two different fluorocarbon groups bonded to a single transition metal atom. The fluorine nmr spectrum (Table IV) of each of these five compounds exhibited resonances with chemical shifts and fine structures corresponding to those expected both for the perfluoro-1-methylpropenyl and the other perfluoroalkyl groups. This provides evidence supporting the proposed structures IV and V and excludes otherwise unlikely possibilities of coupling and/or rearrangement of the two fluorocarbon groups bonded to the transition metal to form a more complex system.


IV


V


VI

The iron compounds of the type $C_4F_7Fe(CO)_4R_f$ (IV, R_f = C_2F_5, $CF_3CF_2CF_2$, and $(CF_3)_2CF$) exhibit a single strong ν(CO) frequency around 2100 cm^{-1} in their infrared spectra in addition to several much weaker ν(CO) frequencies (see Table III). This pattern is tentatively interpreted as suggestive of the indicated isomers IV where the two different fluorocarbon groups occupy trans positions of the iron octahedron. If the two fluorocarbon groups in the iron derivatives IV were equivalent and axially symmetric, these compounds would have D_{4h} symmetry which would give rise to only one infrared-active ν(CO) frequency, a strong E_u mode. Nonequivalence of the fluorocarbon groups in IV reduces the symmetry to C_{4v} which would add a weaker infrared-active A_1 mode to the already very strongly infrared-active E mode. Lack of axial symmetry of the fluorocarbon groups in IV (a possible consequence of restricted rotation around the metal–carbon (C_4F_7) bond in the perfluoro-1-methylpropenyl derivatives arising from retrodative bonding) would further reduce the symmetry of the system which would lead to slight infrared activity of the normally only Raman-active B_1 mode[23] and to splitting of the doubly degenerate E mode. The weak ν(CO) frequencies accompanying the single strong ν(CO) frequency in the $R_fFe(CO)_4C_4F_7$ derivatives most likely arise from these effects associated with deviation of the system from strict D_{4h} symmetry. The alternative explanation of the extra weak ν(CO) frequencies as indicative of the cis isomers of the $R_fFe(CO)_4C_4F_7$ derivatives is less probable because observations on numerous authentic *cis*-$L_2M(CO)_4$ isomers (*e.g.*, (diphos)$M(CO)_4$)[26] indicate similar relative intensities of at least three of the four ν(CO) modes in contrast to the actual observations on the $R_fFe(CO)_4C_4F_7$ derivatives.

The cobalt compounds $C_5H_5Co(CO)(R_f)(C_4F_7)$ (V, R_f = C_2F_5 or $CF_3CF_2CF_2$) are of interest since few compounds of the type $C_5H_5Co(CO)R_2$ are known, even when both alkyl or perfluoroalkyl groups are the same. Previous examples of compounds of the type $C_5H_5Co(CO)(R_f)_2$ in the literature include only the perfluorotetramethylene derivative $C_5H_5Co(CO)(CF_2)_4$ (VI)[27] obtained from $C_5H_5Co(CO)_2$ and tetrafluoroethylene; compounds such as $C_5H_5Co(CO)(C_3F_7)_2$ were briefly mentioned at a meeting several years ago[28] but have not been studied in detail because their preparation was inefficient and inconvenient. Like $C_5H_5Co(CO)(CF_2)_4$ (VI) the compounds $C_5H_5Co(CO)(R_f)(C_4F_7)$ (V, R_f = C_2F_5 or $CF_3CF_2CF_2$) are volatile yellow solids which exhibit the expected single ν(CO) frequency around 2100 cm^{-1}. However, in the *n*-heptafluoropropyl derivative $C_5H_5Co(CO)(C_2F_5)(C_4F_7)$ (V; R_f = C_2F_5) this ν(CO) frequency is split by 8 cm^{-1} possibly because of the presence of conformational isomers arising from restricted rotation around one of the metal–fluorocarbon bonds similar to the splitting of the ν(CO) frequencies in cyclopentadienyliron dicarbonyl compounds such as $CH_3SiCl_2Fe(CO)_2C_5H_5$ arising from restricted rotation around the iron–silicon bond.[29] This type of isomerism could also be responsible for the observation of two β-CF resonances separated by $\sim$2 ppm in the fluorine nmr spectra of both $C_5H_5Co(CO)(R_f)(C_4F_7)$ derivatives (Table IV and ref 3).

The mass spectra of the perfluoro-1-methylpropenyl transition metal derivatives were investigated. The compounds $C_4F_7Mn(CO)_5$ and $R_fFe(CO)_4C_4F_7$ failed to exhibit any metal-containing ions because of decomposition even when the chamber temperature was held to about 100°. Instead, only fluorocarbon ions were observed in these mass spectra.

The mass spectrum of the rhenium compound $C_4F_7Re(CO)_5$ (II, M = Re) exhibited the series of ions $C_4F_7Re(CO)_n^+$ (n = 5, 4, 3, 2, 1, and 0), $C_4F_6Re(CO)_n^+$ (n = 1 and 0), $Re(CO)_nF^+$ (n = 4, 3, 2, 1, and 0), and $Re(CO)_n^+$ (n = 5, 4, 3, 2, 1, and 0) and the dipositive ion series $C_4F_6Re(CO)_n^{2+}$ (n = 3, 1, and 0). The dipositive ions $C_4F_6Re(CO)_n^{2+}$ can arise by loss of fluoride (F^-) from the relatively abundant monopositive ions $C_4F_7Re(CO)_n^+$. In addition, fragments of the types $C_3F_nRe^+$ (n = 3 and 2), $C_2F_nRe^+$ (n = 3, 2, 1, and 0), and CF_nRe^+ (n = 4, 3, 2, 1, and 0) are observed where the rhenium–carbon bond to the perfluoro-1-methylpropenyl group has been maintained but some carbon–carbon bonds of the perfluoro-1-methylpropenyl group have broken.

The mass spectrum of $C_4F_7Fe(CO)_2C_5H_5$ (III, M = Fe; L = CO) exhibited features typical of cyclopentadienyliron dicarbonyl derivatives[30] particularly those with fluorocarbon groups bonded to the iron atom.[31] The observed metastable ions indicate that the molecular ion $C_4F_7Fe(CO)_2C_5H_5^+$ can fragment to the $C_5H_4Fe^+$ ion by the successive losses of its two carbonyl groups followed by elimination of a neutral

(26) For an example of data of this type, see the first three entries of Table I in R. B. King, P. N. Kapoor, and R. N. Kapoor, *Inorg. Chem.*, **10**, 1841 (1971).

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C_4F_6 fragment (presumably hexafluorobutyne-2) from $C_4F_7FeC_5H_5^+$ to give $C_5H_5FeF^+$ which can then undergo loss of a neutral hydrogen fluoride fragment to give $C_5H_4Fe^+$. The mass spectrum of the chromium derivative $C_4F_7Cr(NO)_2C_5H_5$ (III, M = Cr; L = NO), as expected, exhibited many features similar to the mass spectrum of the isostructural and isoelectronic $C_4F_7Fe(CO)_2C_5H_5$ (III, M = Fe; L = CO).

The mass spectra of the cobalt derivatives $C_5H_5Co(CO)(R_f)(C_4F_7)$ (V) provide qualitative comparisons of the relative elimination tendencies of perfluoro-1-methylpropenyl and saturated perfluoroalkyl groups. In both cases (V, $R_f = C_2F_5$ and $CF_3CF_2CF_2$) the ion $C_5H_5Co(CO)(C_4F_7)^+$ is over twice as abundant as the ion $C_5H_5Co(CO)R_f^+$ ($R_f = C_2F_5$ or $CF_3CF_2CF_2$) suggesting that elimination of a saturated perfluoroalkyl group from the molecular ion $C_5H_5Co(CO)(R_f)(C_4F_7)^+$ occurs significantly more readily than elimination of the unsaturated perfluoro-1-methylpropenyl group. This suggests that the bond of the cobalt atom to a saturated perfluoroalkyl group is weaker than the bond of the cobalt atom to the unsaturated perfluoro-1-methylpropenyl group. This effect can be rationalized by the availability of empty antibonding orbitals in the carbon–carbon double bond of the perfluoro-1-methylpropenyl group which can overlap with filled d orbitals of the cobalt atom to provide additional means to strengthen the metal–perfluoro-1-methylpropenyl bond by retrodative bonding. However, arguments of this type based on mass spectra are necessarily imprecise since they rely on the assumption of similar further fragmentation tendencies of the ion $C_5H_5Co(CO)(C_4F_7)^+$ and the saturated perfluoroalkyl ion $C_5H_5Co(CO)R_f^+$.

The mass spectra of the cobalt derivatives $C_5H_5Co(CO)(R_f)(C_4F_7)$ (V, $R_f = C_2F_5$ and $CF_3CF_2CF_2$) also exhibited some features similar to those found in the mass spectra of the iron derivative $C_4F_7Fe(CO)_2C_5H_5$ (III, M = Fe; L = CO) discussed above. Thus metastable ions were observed in the mass spectra of both cobalt compounds which correspond to the elimination of a neutral C_4F_6 fragment from $C_5H_5CoC_4F_7^+$ to give $C_5H_5CoF^+$ and the elimination of a neutral HF fragment from $C_5H_5CoF^+$ to give $C_5H_4Co^+$.

Acknowledgment.—We are indebted to the National Institute of General Medical Sciences for partial support of this work under Grant GM-14664-03. We also acknowledge the assistance of Dr. Alan Bond with some of the fluorine nmr experiments.

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Reactions of Fluorocarbon-Bridged Di(tertiary phosphines and arsines) with Manganese and Rhenium Carbonyls

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Received December 27, 1971

Fluorocarbon-bridged di(tertiary arsines and phosphines) react with $M_2(CO)_{10}$ (M = Mn, Re) under a variety of conditions to give complexes of formula $(L\text{–}L)M_2(CO)_8$ which are ligand bridged. The bridged complexes readily react with iodine with cleavage of the M–M bond and yield $(L\text{–}L)[M(CO)_4I]_2$. In the case where (L–L) is $(CH_3)_2AsC{=}CAs(CH_3)_2CF_2CF_2$ isomers of the bridged complexes can also be prepared. These have the structure $(CO)_4M(CH_3)_2AsM(CO)_4(CH_3)_2AsC{=}CCF_2CF_2$ and are the result of a ligand rearrangement reaction.

Introduction

Reactions of dirhenium and dimanganese decacarbonyls with various monodentate ligands have resulted in the replacement of one to four carbonyl groups with the formation of dinuclear compounds such as $M_2(CO)_9L$,[1–4] $[M(CO)_4L]_2$,[2–11] $M_2(CO)_7L_3$,[3–5] and $[M(CO)_3L_2]_2$ in which the metal–metal bond of the parent carbonyl is preserved. Bidentate ligands are reported to yield some chelated products of the types $M(CO)_3(L\text{–}L)$,[11,12] $M(CO)(L\text{–}L)_2$,[11,12] $M_2(CO)_8(L\text{–}L)$,[1,13] and $[M(CO)_3(L\text{–}L)]_2$[11,14] in which the ligand replaces two or four carbonyl groups on a single metal atom.

In the course of a systematic study of the reactions of the versatile fluorocarbon-bridged ligands f4fars and f4fos $YC{=}CYCF_2CF_2$ (Y = $(CH_3)_2As$ or $(C_6H_5)_2P$) with metal carbonyls,[15,16] we have found that these ligands react with dimanganese and dirhenium decacarbonyls to

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