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ORGANOMETALLIC TRANSITION METAL DERIVATIVES CONTAINING FLUORINE–III

REACTIONS OF PERFLUOROALKYLMETAL CARBONYL IODIDES OF IRON AND COBALT WITH OLIGOTERTIARY PHOSPHINES[1]

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Abstract—Reactions of the $R_fFe(CO)_4I$ ($R_f = n\text{-}C_3F_7$ and $(CF_3)_2CF$) derivatives with chelating ditertiary phosphines give the red to brown non-ionic derivatives $R_fFe(CO)_2I$(diphos). However, reactions of the $C_5H_5Co(CO)R_fI$ ($R_f = n\text{-}C_3F_7$ and $n\text{-}C_7F_{15}$) derivatives with chelating ditertiary phosphines give the yellow iodide salts $[C_5H_5Co(\text{diphos})R_f]I$ which can be converted to the corresponding hexafluorophosphate salts by metathesis with NH_4PF_6. The potentially tridentate ligand $CH_3C[CH_2P(C_6H_5)_2]_3$ behaves as only a bidentate ligand in its reactions with $R_fFe(CO)_4I$ and $C_5H_5Co(CO)R_fI$ derivatives. The new compounds $R_fFe(CO)_4I$ and $C_5H_5Co(CO)R_fI$ ($R_f = (CF_3)_2CF$ and $n\text{-}C_7F_{15}$) are also described.

SEVERAL years ago preparations of perfluoroalkylmetal carbonyl iodides of the types $R_fFe(CO)_4I$[2] and $C_5H_5Co(CO)R_fI$[3] were described. More recently, reactions of both the iron[4] and cobalt[5] compounds with pyridine and with monodentate tertiary phosphines were described. This paper now reports reactions of representative $R_fFe(CO)_4I$ and $C_5H_5Co(CO)R_fI$ derivatives with bidentate and tridentate oligotertiary phosphines. The first perfluoroalkylmetal carbonyl halides with the $n\text{-}C_7F_{15}$ and the secondary $(CF_3)_2CF$ perfluoroalkyl groups are also described.

EXPERIMENTAL

A nitrogen atmosphere was always provided for the following three operations: (a) Carrying out reactions (b) Handling all filtered solutions of metal complexes, and (c) Admitting to evacuated vessels. Pressure reactions were carried out in sealed stainless steel cylinders manufactured by Hoke Inc., Cresskill, New Jersey.

The chelating ditertiary phosphine ligands 1,2-bis(diphenylphosphino)ethane (abbreviated as Pf-Pf), 1,2-bis(dimethylphosphino)ethane (abbreviated as Pm-Pm), and *cis*-bis(diphenylphosphino)-

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1. For part II of this series see R. B. King and R. N. Kapoor, *J. inorg. nucl. Chem.* **31**, 2169 (1969). The term "oligotertiary phosphine" rather than "polytertiary phosphine" is used since none of the ligands under investigation contain more than three phosphorus atoms.
2. R. B. King, S. L. Stafford, P. M. Treichel and F. G. A. Stone, *J. Am. chem. Soc.* **83**, 3604 (1961).
3. R. B. King, P. M. Treichel and F. G. A. Stone, *J. Am. chem. Soc.* **83**, 3593 (1961).
4. R. A. Plowman and F. G. A. Stone, *Inorg. Chem.* **1**, 518 (1962).
5. P. M. Treichel and G. Werber, *Inorg. Chem.* **4**, 1098 (1965).

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ethylene (abbreviated as Pf = Pf) were prepared by various published methods[6] all based on the reaction of 1,2-dichloroethane or *cis*-1,2-dichloroethylene with the appropriate alkali-metal dialkylphosphide, MRP_2, in liquid ammonia ($R = CH_3$; $M = Na$) or tetrahydrofuran ($R = C_6H_5$; $M = Li$). The chelating tritertiary phosphine 1,1,1-tris(diphenylphosphinomethyl)ethane (abbreviated as triphos) was prepared by the published procedure[7a] utilizing the reaction between 1,1,1-tris(chloromethyl)ethane[7b] and sodium diphenylphosphide (from $(C_6H_5)_2PH$ and sodium) first in liquid ammonia and then in boiling tetrahydrofuran. Triphenylphosphine was purchased from Eastern Chemical Co., Pequannock, New Jersey. The various perfluoroalkyl iodides used in this work were purchased from Columbia Organic Chemicals, Inc., Columbia, South Carolina.

Iron carbonyl derivatives

Pentacarbonyliron (Antara Division of General Aniline and Film, New York City) was converted to the known[2] n-$C_3F_7Fe(CO)_4I$ by reaction with 1-iodoheptafluoropropane according to the published procedure[8]. The new compounds $(CF_3)_2CFFe(CO)_4I$ and n-$C_7F_{15}Fe(CO)_4I$ were similarly prepared as described below:

(a) $(CF_3)_2CFFe(CO)_4I$*:* A mixture of 30 g (153 mmoles) of $Fe(CO)_5$ and 22 g (74·5 mmoles) of $(CF_3)_2CFI$ was heated for 17 hr at 70–80° in a 300 ml sealed evacuated stainless steel cylinder. Repeated vacuum distillation of the residue gave 27 g (78% yield) of dark red liquid $(CF_3)_2CFFe(CO)_4I$, b.p. 34°/0·2 mm, m.p. 24°.

(b) n-$C_7F_{15}Fe(CO)_4I$*:* A mixture of 2·1 ml (3·0 g, 15 mmoles) of $Fe(CO)_5$ and 1·8 ml. (4·1 g, 8·3 mmoles) of n-$C_7F_{15}I$ was heated for 18 hr at 85° in a 30 ml sealed evacuated stainless steel cylinder. After the reaction was completed, the contents of the reaction vessel were washed out with repeated 50 ml portions of dichloromethane until the washings were no longer red. Evaporation of the dichloromethane (~25°/40 mm) and sublimation of the residue at 25°/0·1 mm gave 2·7 g (49% yield) of n-$C_7F_{15}Fe(CO)_4I$, m.p. 57–58°.

Preparation of the derivatives $R_fFe(CO)_2(diphos)I$*:* The preparations of all of these compounds followed similar procedures. A mixture of equivalent quantities of the $R_fFe(CO)_4I$ derivative (~0·8–0·9 g) and the ditertiary phosphine was heated at 70° in benzene solution (5–50 ml) for 4–6 hr. The reaction mixture was then filtered and solvent removed from the filtrate at 35°/40 mm. Further purification of the product was accomplished by crystallization from mixtures of dichloromethane and hexane or by chromatography on alumina in dichloromethane solution as indicated by footnotes to Table 1.

The preparations of the complexes $(CF_3)_2CFFe(CO)_3IP(C_6H_5)_3$ and $(CF_3)_2CFFe(CO)_2(triphos)I$ followed a similar procedure but used boiling 30–60° petroleum ether rather than benzene as the solvent. In both of these cases the crude product precipitated from the reaction mixture as a brown solid which could be purified by recrystallization from mixtures of dichloromethane and hexane.

Reaction of $(CF_3)_2CFFe(CO)_4I$ with *o*-phenanthroline in benzene solution by this general procedure gave a red precipitate identified as $[Fe(o\text{-}phen)_3]I_2$ by the absence of $\nu(CO)$ and $\nu(CF)$ frequencies in the infrared spectrum and by conversion to the corresponding hexafluorophosphate by treatment of an aqueous solution of this iodide with NH_4PF_6. Reaction of $(CF_3)_2CFFe(CO)_4I$ with pyridine in 30–60° petroleum ether by this general procedure gave a brown precipitate of ferrous iodide identified by analysis of the brown crystalline tetrahydrate obtained after crystallization from a mixture of ethanol and water. *Anal.* Calcd. for $FeI_2 \cdot 4H_2O$: C, 0·0; H, 2·1; N, 0·0. Found: C, 1·3; H, 2·1; N, 0·0.

[6] For the preparation of the chelating ditertiary phosphines see the following references: (a) $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$: J. Chatt and F. A. Hart. *J. chem. Soc.* 1378 (1960); (b) *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$: A. M. Aguiar and D. Daigle *J. Am. chem. Soc.* **82**, 2299 (1964); (c) $(CH_3)_2PCH_2CH_2P(CH_3)_2$: J. Chatt and R. G. Hayter, *J. chem. Soc.* 896 (1961). However, in this work the $NaP(CH_3)_2$ was obtained by cleavage of $(CH_3)_2P{-}P(CH_3)_2$ with sodium metal in liquid ammonia.

[7] (a) W. Hewertson and H. R. Watson, *J. chem. Soc.* 1490 (1962); (b) W. H. Urry and J. R. Eiszner, *J. Am. chem. Soc.* **74**, 5822 (1952).

[8] R. B. King, *Organomet. Synth.* **1**, 177 (1965).

Cyclopentadienylcobalt derivatives

Cyclopentadienyldicarbonylcobalt, $C_5H_5Co(CO)_2$[9] was reacted with 1-iodoheptafluoropropane in benzene solution to give the known[4] $C_5H_5Co(CO)(n\text{-}C_3F_7)I$. The new compounds $C_5H_5Co(CO)[CF(CF_3)_2]I$ and $C_5H_5Co(CO)(n\text{-}C_7F_{15})I$ were similarly prepared as described below:

(a) $C_5H_5Co(CO)[CF(CF_3)_2]I$. A mixture of 2·0 ml (2·6 g, 14 mmoles) of $C_5H_5Co(CO)_2$, 2·5 ml (5·1 g, 17 mmoles) of $(CF_3)_2CFI$, and 60 ml of C.P. benzene was heated at 50° for 18 hr. Removal of solvent (25°/40 mm, then 25°/0·1 mm) followed by sublimation at 70°/0·1 mm gave 1·4 g (22% yield) of a black crystalline sublimate of $C_5H_5Co(CO)[CF(CF_3)_2]I$, m.p. 108–109°.

(b) $C_5H_5Co(CO)(n\text{-}C_7F_{15})I$: A mixture of 1·5 ml (1·95 g, 10·8 mmoles) of $C_5H_5Co(CO)_2$, 2·2 ml (5·0 g, 10 mmoles) of $n\text{-}C_7F_{15}I$, and 30 ml of C.P. benzene was heated at 50° for 18 hr. Removal of solvent (25°/40 mm, then 25°/0·1 mm) gave 5·6 g (86% yield) of crude $C_5H_5Co(CO)(n\text{-}C_7F_{15})I$. The analytical sample m.p. 115–118°, was purified by sublimation at 80–90°/0·1 mm.

Preparation of the cations $[C_5H_5CoR_f(diphos)]^+$. A mixture of equivalent quantities of $C_5H_5Co(CO)R_fI$ (~0·4–0·5 g) and the chelating ditertiary phosphine in benzene solution (50–150 ml) was stirred at room temperature. A yellow precipitate formed almost immediately. After ~ 15 hr this precipitate was filtered, washed with benzene, diethyl ether, or hexane and then dried to give the yellow solid iodide $[C_5H_5CoR_f(diphos)]I$.

For conversion to the corresponding hexafluorophosphate a small quantity of the iodide was dissolved in acetone and treated with an excess of a concentrated aqueous solution of ammonium hexafluorophosphate. Slow evaporation of the solution at 25°/40 mm precipitated the yellow solid hexafluorophosphate which was purified by recrystallization from a mixture of acetone and benzene.

Preparation of the cation $[C_5H_5Co(n\text{-}C_7F_{15})(triphos)]^+$. Owing to the greater solubility of $[(C_5H_5Co(n\text{-}C_7F_{15})(triphos)]^+$ salts in non-coordinating organic solvents, their isolation and purification were somewhat different. A mixture of 0·74 g (1·14 mmoles) of $C_5H_5Co(CO)(n\text{-}C_7F_{15})I$ and 0·7 g (1·12 mmoles) of 1,1,1-tris(diphenylphosphinomethyl)ethane in 125 ml of benzene was stirred for 10 days at room temperature. No product had precipitated at this point. However, some product was precipitated by adding 100 ml of diethyl ether to the reaction mixture. The remaining product was obtained by evaporating the filtrate at 25°/40 mm. The crude iodide $[C_5H_5Co(n\text{-}C_7F_{15})(triphos)]I$ could be recrystallized with difficulty from a mixture of dichloromethane and hexane or from a mixture of benzene and heptane. It was converted to the corresponding hexafluorophosphate in the usual manner.

I.R. Spectra

The i.r. spectra of all of the new solid compounds were taken in the 4000–600 cm^{-1} region in KBr pellets using a Perkin-Elmer Model 621 spectrometer with grating optics. The spectrum of the liquid $(CF_3)_2CFFe(CO)_4I$ was obtained as a liquid film. The ν(CO) frequencies of the metal carbonyl derivatives were also recorded in dichloromethane solution (Table 1). Representative spectra are described below.

A. $(CF_3)_2CFFe(CO)_4I$. ν(CO) frequencies at 2146 (*w*), 2118 (*w*), 2086 (*s*), and 2052 (*w*), cm^{-1}; other bands at 1286 (*m*), 1260 (*s*), 1200 (*s*), 1130 (*m*), 1022 (*m*), 933 (*m*), 872 (*m*), 732 (*m*), and 699 (*m*) cm^{-1}.

B. $n\text{-}C_7F_{15}Fe(CO)_4I$. ν(CO) frequencies at 2140 (*m*), 2114 (*w*), 2090 (*s*), 2076 (*s*), and 2051 (*w*) cm^{-1}; other bands at 1393 (*w*), 1356 (*w*), 1345 (*vw*), 1239 (*s*), 1204 (*s*), 1139 (*s*), 1128 (*m*), 1082 (*m*), 1024 (*m*), 974 (*vw*), 959 (*w*), 923 (*w*), 854 (*w*), 838 (*vw*), 783 (*vw*), 764 (*w*), 759 (*w*), 734 (*w*), and 712 (*w*), cm^{-1}.

C. $(CF_3)_2CFFe(CO)_2I(Pm\text{-}Pm)$. ν(CH) frequencies too weak to be unequivocally observed; ν(CO) frequencies at 2024 (*s*) and 1940 (*s*) cm^{-1}; other bands at 1420 (*m*), 1306 (*w*), 1303 (*w*), 1290 (*m*), 1285 (*m*), 1265 (*s*), 1242 (*s*), 1195 (*s*), 1156 (*s*), 1135 (*s*), 1093 (*m*), 1003 (*s*), 965 (*vw*), 933 (*s*), 912 (*s*), 895 (*m*), 835 (*s*), 785 (*vw*), 775 (*vw*), 733 (*m*), 725 (*s*), 709 (*w*), 697 (*m*), 691 (*s*), 640 (*w*), and 605 (*m*) cm^{-1}.

D. $(CF_3)_2CFFe(CO)_2I(triphos)$. ν(CH) frequencies at 3047 (*w*), 2950 (*w*), and 2916 (*vw*) cm^{-1}; ν(CO) frequencies at 2029 (*s*) and 1981 (*s*) cm^{-1}; other bands at 1481 (*m*), 1431 (*s*), 1259 (*m*), 1240 (*s*), 1201 (*s*), 1168 (*s*), 1155 (*m*), 1109 (*m*), 1086 (*m*), 1028 (*w*), 1018 (*w*), 991 (*w*), 911 (*m*), 828 (*m*), 789 (*w*), 729 (*s*), 727 (*s*), 703 (*m*), 693 (*s*), and 687 (*s*) cm^{-1}.

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[9] E. O. Fischer and R. Jira, *Z. Naturf.* **10b**, 355 (1955); R. B. King, *Organomet. Synth.* **1**, 116 (1965).

Table 1. New compounds prepared in this work

Compound[a]	Color	M.p. (°C)	Yield[c] (%)		Analyses[d] (%) C	H	F	I	Other	Molar conductance[e]	ν(CO) Infrared Frequencies[f]
$(CF_3)_2CFFe(CO)_4I$	deep red	24°	78	Calcd.	18·1		28·7	27·4	12·0(Fe)		2148 (*w*), 2118 (*w*),
				Found	18·3		28·8	27·0	11·6(Fe)		2091 (*vs*), 2051 (*w*)
$C_7F_{15}Fe(CO)_4I$	red-brown	57–58°	49	Calcd.	19·9		42·9	19·1	8·4(Fe)	0·6	2147 (*w*), 2103 (*m*)
				Found	20·1		43·0	19·3	8·4(Fe)		2087 (*s*), 2052 (*w*)
$C_3F_7Fe(CO)_2I(Pm\text{-}Pm)$	amber	131–133°	22[g,i]	Calcd.	23·7	2·9	23·8	22·7		0·6	2030 1987
				Found	24·2	3·0	23·1	23·8			
$(CF_3)_2CFFe(CO)_2I(Pm\text{-}Pm)$	brown	dec. ~ 200°	66[h,i]	Found	23·8	2·8		23·3		1·2	2026 1988
$C_3F_7Fe(CO)_2I(Pf\text{-}Pf)$	pink	115–119°	58[h,i]	Calcd.	46·1	3·2		15·7			2030 1990
				Found	46·8	3·1		15·7			
$C_3F_7Fe(CO)_2I(Pf{=}Pf)$	red	172–176°	74[h]	Calcd.	46·3	2·8		15·8			2036 1996
				Found	45·6	2·6		16·1			
$(CF_3)_2CFFe(CO)_2I(Pf{=}Pf)$	red–violet	82°	80[h,i]	Found	46·3	2·9				13·0	
$C_3F_7Fe(CO)_2I(triphos)$	amber	163–165°	39[h,i]	Calcd.	53·6	3·8		12·3	5·4(Fe)	16·4	2034 1988
				Found	51·2	3·9		12·3	4·9(Fe)		
$(CF_3)_2CFFe(CO)_2I(triphos)$	brown	122–124° (dec.)	80[j]	Found	54·1	4·2		12·2		14·5	2032 1986 2006 (*m*)
$(CF_3)_2CFFe(CO)_2I(bipy)$	brown	dec. ~ 230°	18[k]	Calcd.	31·9	1·4			4·8(N)	4·9	2043 1998
				Found	31·8	1·4			4·9(N)		
$(CF_3)_2CFFe(CO)_3I(PPh_3)$	amber	163–165°	80	Calcd.	41·3	2·2		19·1		13·4	2095 (*w*), 2043 (*s*),
				Found	43·1	2·5		19·9			2028 (*m*, *sh*)
$C_5H_5Co(CO)ICF(CF_3)_2$	black	108–109°	22	Calcd.	24·1	1·1	29·7	28·3	13·1(Co)	0·5	2103 (*s*)
				Found	24·4	1·0	30·0	27·8	13·1(Co)		
$C_5H_5Co(CO)IC_7F_{15}$	black	116–118°	86	Calcd.	24·1	0·8	44·0	19·6			2098 (*s*)
				Found	24·4	0·7	42·6	20·4			
$[C_5H_5Co(Pm\text{-}Pm)C_3F_7]I$	yellow	dec. 274°	99	Calcd.	29·5	3·7	23·3	22·2			
				Found	29·0	3·6	22·9	22·1			
$[C_5H_5Co(Pm\text{-}Pm)C_3F_7]PF_6$	yellow	dec. 262°	100	Calcd.	28·5	3·6	42·0	—			
				Found	28·7	3·4	42·3	—			
$[C_5H_5Co(Pm\text{-}Pm)C_7F_{15}]I$	yellow	dec. 240°	61	Calcd.	28·1	2·7	37·0	16·5			
				Found	28·1	2·9	37·2	16·4			
$[C_5H_5Co(Pm\text{-}Pm)C_7F_{15}]PF_6$	yellow	dec. 260°	91	Calcd.	27·4	2·7	50·6	—			
				Found	27·3	2·8	51·2	—			
$[C_5H_5Co(Pf\text{-}Pf)C_3F_7]I$	yellow	dec. 196°	90	Calcd.	49·9	3·6	16·2	15·5		118 ± 5	
				Found	50·0	3·6	14·9	16·1			

Table 1. (*Contd.*)

Compound[a]	Color	m.p.[b]	Yield[c] (%)		Analyses, % C	H	F	I	Other	Molar conductance[e]	Infrared ν(CO) Frequencies[f]
$[C_5H_5Co(Pf\text{-}Pf)C_3F_7]PF_6$	yellow	dec. 230°	78	Calcd.	48·8	3·5		—		128 ± 1	
				Found	49·8	3·6		—			
$[C_5H_5Co(Pf\text{-}Pf)C_7F_{15}]I$	yellow	dec. 172°	74	Calcd.	44·8	2·9	28·0	12·5		123 ± 1	
				Found	44·9	2·9	28·0	12·5			
$[C_5H_5Co(Pf\text{-}Pf)C_7F_{15}]PF_6$	yellow	135–138°	98	Calcd.	44·0	2·8	38·5	—		131 ± 6	
		dec.		Found	44·3	2·5	39·7	—			
$[C_5H_5Co(Pf{=}Pf)C_3F_7]I$	yellow	178° (dec.)	81	Calcd.	50·0	3·3	16·3	15·5		127 ± 3	
				Found	50·0	3·3	16·1	15·2			
$[C_5H_5Co(Pf{=}Pf)C_3F_7]PF_6$	yellow	135° (dec.)	98	Calcd.	49·0	3·3	30·0	—		126 ± 2	
				Found	50·0	3·4	30·0	—			
$[C_5H_5Co(Pf{=}Pf)C_7F_{15}]I$	yellow	dec. 135°	97	Calcd.	44·9	2·7	28·1	12·5		129 ± 2	
				Found	44·9	2·6	28·1	12·0			
$[C_5H_5Co(Pf{=}Pf)C_7F_{15}]PF_6$	yellow	dec. 187°	h	Calcd.	44·2	2·6	39·0	—		136 ± 2	
				Found	44·2	2·5	39·0	—			
$[C_5H_5Co(Pf{=}Pf)CF(CF_3)_2]PF_6$	yellow-green	> 270°	81	Calcd.	49·0	3·3	30·0	—			
				Found	48·0	3·6	30·0	—			
$[C_5H_5Co(triphos)C_7F_{15}]I$	yellow	dec. ~ 140°	54	Calcd.	51·0	3·6	22·9	10·2	7·5(P)[g]		
				Found	50·2	3·8	23·1	9·7	8·2(P)[g]		
$[C_5H_5Co(triphos)C_7F_{15}]PF_6$	yellow	dec. ~ 160°	92	Calcd.	50·4	3·5		4·7(Co)	9·8(P)		
				Found	50·7	3·6		4·7(Co)	11·2(P)		

[a] The following abbreviations are used: Ph = phenyl; Pf-Pf = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$; Pf=Pf = *cis*-$(C_6H_5)_2PCH = CHP(C_6H_5)_2$; Pm-Pm = $(CH_3)_2PCH_2CH_2P(CH_3)_2$; triphos = $CH_3C[CH_2P(C_6H_5)_2]_3$; $C_3F_7 = CF_3CF_2CF_2$; and $C_7F_{15} = CF_3(CF_2)_6$.

[b] These melting and decomposition points were determined in capillaries and are uncorrected.

[c] In some cases processes used for product isolation and purification are indicated by footnotes in the sequence performed.

[d] These analyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany.

[e] These measurements were performed on acetone solutions using an Industrial Instruments, Inc., Model RC 16B2 conductivity bridge. Concentrations of the solutions used were around 10^{-3} M. Several measurements at different concentrations were made on the ionic derivatives. The molar conductance values are reported in $ohm^{-1}\ cm^2\ mole^{-1}$.

[f] These ν(CO) frequencies were determined from spectra of CH_2Cl_2 solutions recorded on a Perkin-Elmer Model 621 Spectrometer.

[g] Cobalt: Calcd. 4·7; Found 4·7.

[h] Not determined.

[i] Recrystallized from a mixture of CH_2Cl_2 and hexane.

[j] Chromatographed on alumina in dichloromethane solution.

[k] Product precipitated from benzene by adding petroleum ether.

E. $C_5H_5Co(CO)ICF(CF_3)_2$. ν(CH) frequency at 3120 (*w*) cm^{-1}; ν(CO) frequency at 2081 (*s*) cm^{-1}; other bands at 1433 (*m*), 1418 (*m*), 1356 (*w*), 1271 (*s*), 1248(*s*), 1214 (*s*), 1204 (*s*), 1186 (*s, sh*), 1176 (*s*), 1148 (*m*), 1111 (*m*), 1061 (*w*), 1022 (*s*), 1014 (*m*), 996 (*w*), 923 (*s*), 864 (*s*), 846 (*s*), 824 (*m*), 734 (*s*), and 697 (*s*) cm^{-1}.

F. $C_5H_5Co(CO)I(n\text{-}C_7F_{15})$. ν(CH) frequencies too weak to be unequivocally observed; ν(CO) frequency at 2065 (*s*) cm^{-1}; other bands at 1435 (*vw*), 1415 (*vw*), 1395 (*w*), 1357 (*vw*), 1230 (*s*), 1197 (*s*), 1141 (*m*), 1081 (*w*), 1034 (*w*), 1015 (*w*), 975 (*vw*), 955 (*vw*), 836 (*w*), 825 (*vw*), 756 (*w*), and 713 (*w*) cm^{-1}.

G. $[C_5H_5Co(Pm\text{-}Pm)C_3F_7]I$. ν(CH) frequencies at 3124 (*vw*), 3083 (*w, sh*), 3064 (*w*), 2985 (*vw*), 2962 (*vw*), 2949 (*m*), 2900 (*m*), and 2886 (*w*) cm^{-1}; other bands at 1430 (*s*), 1418 (*m*), 1412 (*m*), 1360 (*w*), 1317 (*s*), 1305 (*m*), 1294 (*m*), 1269 (*w*), 1239 (*m*), 1219 (*s*), 1207 (*s*), 1181 (*s*), 1164 (*s*), 1153 (*m*), 1129 (*w*), 1074 (*s*), 1063 (*m*), 1006 (*s*), 983 (*m*), 974 (*s*), 951 (*s*), 938 (*s*), 921 (*s*), 904 (*m*), 880 (*m*), 873 (*m*), 856 (*s*), 844 (*s*), 826 (*m*), 798 (*s*), 736 (*m*), 733 (*w*), 715 (*s*), 654 (*s*), and 634 (*vw*) cm^{-1}.

H. $C_5H_5Co(Pf{=}Pf)C_3F_7]I$. ν(CH) frequencies at 3042 (*vvw*) and 2925 (*vvw*) cm^{-1}; other bands at 1482 (*w*), 1433 (*m*), 1314 (*m*), 1224 (*m*), 1187 (*m*), 1166 (*w*), 1155 (*w*), 1090 (*w*), 1075 (*w*), 1016 (*m*), 993 (*m*), 846 (*w*), 825 (*w*), 791 (*m*), 727 (*m*), 707 (*s*), and 685 (*s*) cm^{-1}.

DISCUSSION

The chelating ditertiary phosphines were found to displace two carbonyl groups from the iron derivatives $R_fFe(CO)_4I$ to form the red to brown non-ionic derivatives $R_fFe(CO)_2I$(diphos) according to the following equation:

$$R_fFe(CO)_4I + \text{diphos} \rightarrow R_fFe(CO)_2I(\text{diphos}) + 2CO.$$

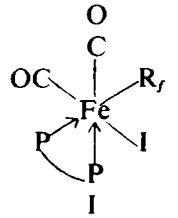
These complexes all exhibited two ν(CO) frequencies in the infrared spectrum in accord with a formulation such as I with the carbonyl groups in *cis*-positions. The molar conductances of the $R_fFe(CO)_2I$(diphos) derivatives fell in the range 1–15 $ohm^{-1}cm^2mole^{-1}$ in accord with formulations as nonelectrolytes.

The chelating ditertiary phosphines were found to displace rapidly at room temperature both the single carbonyl group and the iodide ligand from the cobalt derivatives $C_5H_5Co(CO)R_fI$ to precipitate the yellow ionic iodides $[C_5H_5Co(\text{diphos})R_f]I$ according to the following equation:

$$C_5H_5Co(CO)R_fI + \text{diphos} \rightarrow [C_5H_5Co(\text{diphos})R_f]^+ + I^- + CO.$$

The ionic formulations of these products were supported both by their high conductances in the range 110–140 $ohm^{-1}cm^2mole^{-1}$ and by their conversions to the corresponding hexafluorophosphate salts $[C_5H_5Co(\text{diphos})R_f][PF_6]$ by metathesis with aqueous ammonium hexafluorophosphate. Similar $[C_5H_5CoL_2R_f]^+$ salts but with other L ligands have been reported by Treichel and Werber[6].

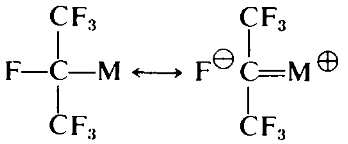
Reactions of both $R_fFe(CO)_4I$ and $C_5H_5Co(CO)R_fI$ with the chelating tritertiary phosphine $CH_3C[CH_2P(C_6H_5)_2]_3$ were also investigated. In all cases the products had similar formulas and physical properties to the corresponding complexes obtained from the



I

chelating ditertiary phosphines. This indicates that in the derivatives of the chelating tritertiary phosphine described in this paper only two of the three phosphorus atoms are coordinated to the metal atom. The i.r. spectrum of $(CF_3)_2CFFe(CO)_2I$(triphos) in the ν(CO) region exhibits not only the expected strong bands at 2032 and 1986 cm^{-1} but also a weaker band at 2006 cm^{-1} which could arise either from the presence of some *trans*-$(CF_3)_2CFFe(CO)_2I$(triphos) or of some monocarbonyl $(CF_3)_2CFFe(CO)I$(triphos) with all three phosphorus atoms of the tritertiary phosphine ligand coordinated to the iron atom. However, attempts to isolate pure monocarbonyl by carrying out the reaction between $(CF_3)_2CFFe(CO)_4I$ and the tritertiary phosphine under more vigorous conditions (e.g. boiling benzene overnight) led instead to decomposition.

This work also resulted in the preparation of the first perfluoroalkylmetal carbonyl iodides containing the $(CF_3)_2CF$ and n-C_7F_{15} groups. The comparable stability and similar ν(CO) frequencies of the $(CF_3)_2CF$ derivatives to those of the n-C_3F_7 derivatives indicates that the presence of only one fluorine atom on the α-carbon atom of a perfluoroalkyl derivative does not appreciably affect the amount of partial metal-carbon (perfluoroalkyl) double bonding. The high chemical shift (~ 160ϕ) of the CF fluorine in the ^{19}FNMR spectra of the $(CF_3)_2CF$ derivatives (Table 2) suggests the presence of a high electron density on this fluorine atom which would be the case if this single CF fluorine atom were heavily involved in no-bond resonance structures[10] such as 11b. The much higher



$$F-\overset{CF_3}{\underset{CF_3}{C}}-M \longleftrightarrow F^{\ominus}\,\overset{CF_3}{\underset{CF_3}{C}}=M^{\oplus}$$

11a 11b

chemical shift of the CF fluorine in $(CF_3)_2CF$ derivatives of transition metals than of the α-CF_2 fluorines in n-C_3F_7 and C_2F_5 derivatives of transition metals may arise from the fact that in the $(CF_3)_2CF$ derivatives there is only one α-fluorine atom to bear all of the negative charge removed from the metal atom by the metal-carbon (perfluoroalkyl) retrodative π-bonding whereas in the n-C_3F_7 and C_2F_5 derivatives there are two α-fluorine atoms to share this negative charge. This explanation is also consistent with the higher chemical shifts of the α-CF_2 fluorines in n-C_3F_7 and C_2F_5 derivatives of transition metals than of the CF_3 fluorines in trifluoromethyl-transition metal derivatives.

Table 2 also gives the ^{19}FNMR spectra for many of the other complexes prepared in this work. Because of their breadth the resonances arising from the fluorine atoms of the α-CF_2 or α-CF groups directly bonded to the metal atom were only observed in the best spectra. The different CF_2 groups of the n-C_7F_{15} derivatives could be clearly separated in the ^{19}FNMR spectra. The ^{19}FNMR spectra of the hexafluorophosphate salts exhibited not only the resonances listed in Table 2 but also a sharp doublet ($J = 712$ c.p.s.), at 72ϕ arising from the PF_6^- anion.

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10. R. B. King and M. B. Bisnette, *J. organomet. Chem.* **2**, 15 (1964); F. A. Cotton and R. M. Wing, *J. Organomet. Chem.* **9**, 511 (1967); H. C. Clark and J. H. Tsai, *J. Organomet. Chem.* **7**, 515 (1967); F. W. B. Einstein, H. Luth and J. Trotter, *J. Chem. Soc.* [A], 89 (1967).

Table 2. ^{19}F NMR Spectra of some perfluoroalkymetal halide derivatives[a]

(A) n-C_3F_7 derivatives

Compound[b]	Solvent	Chemical shifts, ϕ^d α(CF$_2$)	β(CF$_2$)	γ(CF$_3$)	$J_{\alpha\gamma}$, cps	^{1}H NMR $\tau(C_5H_5)^g$
$C_3F_7Fe(CO)_4I^c$	CH_2Cl_2	+54·9	+114·4	+78·6	11·4	—
$C_3F_7Fe(CO)_2I(Pm\text{-}Pm)$	Me_2CO	NO[e]	+115·0	+78·9	12·2	—
$C_3F_7Fe(CO)_2I(Pf\text{-}Pf)$	Me_2CO	NO[e]	+114·5	+79·3	12·6	—
$C_3F_7Fe(CO)_2I(Pf{=}Pf)$	Me_2CO	NO[e]	+114·2	+78·7	12·6	—
$C_5H_5Co(CO)(C_3F_7)I^c$	C_4H_8O	+56·3	+114·1	+79·1		
$[C_5H_5Co(Pm\text{-}Pm)C_3F_7]PF_6$	Me_2CO	NO[e]	+113·2	+78·9	12·4	
$[C_5H_5Co(Pf\text{-}Pf)C_3F_7]PF_6$	Me_2CO	+63·4	+115·2	+79·1	13·0	4·11
$[C_5H_5Co(Pf{=}Pf)C_3F_7]PF_6$	Me_2CO	NO[e]	+113·9	+79·6	11·6	4·17

(B) $(CF_3)_2CF$ derivatives

Compound[b]	Solvent	Chemical shifts, ϕ^d CF	CF$_3$	J(CF–CF$_3$), cps	^{1}H NMR $\tau(C_5H_5)^g$
$(CF_3)_2CFFe(CO)_2I(Pf\text{-}Pf)$	CH_2Cl	NO[e]	+64·2	8·0	—
$(CF_3)_2CFFe(CO)_2I(Pf{=}Pf)$	CH_2Cl_2	NO[e]	+64·4	8·0	—
$C_5H_5Co(CO)[CF(CF_3)_2]I$	CH_2Cl_2	+157·1	+64·1	10·8	4·37
$(CF_3)_2CFMn(CO)_5{}^h$	neat liquid	+163·3	+67·6		

Table 2. (*Contd.*)

		(C) n-C_7F_{15} derivatives Chemical shifts, $\phi^{d,f}$									
Compound[b]	Solvent	$\alpha(CF_2)$	$\beta(CF_2)$	$\gamma(CF_2)$	$\delta(CF)_2$	$\epsilon(CF_2)$	$\zeta(CF_2{}^1)$	$\eta(CF_3)$	$J_{\alpha\gamma}$	$J_{\epsilon\eta}$	^1H NMR $\tau(C_5H_5)$[g]
$C_7F_{15}Fe(CO)_4I$	CH_2Cl_2	53·9	110·6	121·1	122·2	123·0	126·6	81·5	17	11	—
$C_5H_5Co(CO)(C_7F_{15})I$	Me_2CO	54·0	110·7	121·1	122·1	123·1	126·5	81·5	17	10	4·10
$[C_5H_5Co(Pm\text{-}Pm)C_7F_{15}]PF_6$	Me_2CO	NO[e]	108·9	120·7	121·7	122·7	126·2	81·1		10	
$[C_5H_5Co(Pf\text{-}Pf)C_7F_{15}]PF_6$	Me_2CO	NO[e]	110·6	120·3	121·9	122·7	126·1	81·2		10	4·08
$[C_5H_5Co(Pf{=}Pf)C_7F_{15}]PF_6$	Me_2CO	NO[e]	109·5	120·3	122·0	122·8	126·2	81·2		11	4·15

[a] These spectra were taken in the indicated solvents at 94·1 Mc. on a Varian HA-100 spectrometer using 1,2-difluoro-1,1,2,2-tetrachloroethane as an internal standard.

[b] The same abbreviations as in Table 1 are used.

[c] Data from E. Pitcher, A. D. Buckingham and F. G. A. Stone, *J. chem. Phys.* **36**, 124 (1962).

[d] The chemical shifts are reported using the ϕ scale introduced by G. Filipovich and G. V. D. Tiers, *J. phys. Chem.* **63**, 761 (1959). For this scale ϕ ($CFCl_3$) = 0·0 and ϕ ($CFCl_2CFCl_2$) = 67·8. A change of 1 ϕ unit corresponds to 1 ppm.

[e] NO = not observed.

[f] In making the assignments for the CF_2 resonances the chemical shifts are assumed to increase with increasing distance from the metal atom.

[g] In addition resonances from the protons of the chelating ditertiary phosphine ligand were observed. These are not reported here. All of the π-C_5H_5 resonances reported here where apparent singlets.

[h] Data of W. R. McClellan, *J. Am. chem. Soc.* **83**, 1598 (1961), converted to the ϕ scale.

The proton NMR spectra of the π-cyclopentadienyl derivatives exhibited the expected resonance at τ4–5 arising from the five equivalent π-cyclopentadienyl protons. In addition, complex and often ill-defined resonances were exhibited in positions expected for the protons in the chelating polytertiary phosphine ligands. The proton NMR spectra of the two 1,2-bis(dimethylphosphino)ethane complexes $[C_5H_5Co(Pm\text{-}Pm)(C_3F_7)]^+$ and $C_3F_7Fe(CO)_2I(Pm\text{-}Pm)$ exhibited interesting differences. The proton NMR spectrum of the cobalt compound ($(CD_3)_2CO$ solution) exhibited besides the π-C_5H_5 resonance a doublet (J = 12 c.p.s.) at τ7·78 and a triplet (separation 7 c.p.s., broad center resonance) at τ8·19 arising from the four methylene protons and the twelve methyl protons of the 1,2-bis(dimethylphosphino)ethane ligand, respectively. The proton NMR spectrum of the related cobalt cation $[C_5H_5Co(Pm\text{-}Pm)C_7F_{15}]^+$ was likewise very similar. These NMR patterns are the normal patterns expected for a 1,2-bis(dimethylphosphino)ethane complex with the two phosphorus atoms magnetically equivalent. However, the proton NMR spectrum of $C_3F_7Fe(CO)_2I$-(Pm-Pm) exhibits two overlapping doublet methylene resonances at τ7·99 (J = 11 c.p.s.) and τ8·03 (J = 10 c.p.s.) in addition to the triplet methyl resonance of τ8·39 (separation 8 c.p.s.). The two different methylene resonances suggest non-equivalence of the methylene groups in the complexed 1,2-bis(dimethylphosphino)ethane ligand which would be the case if the phosphorus atoms were non-equivalent as in structure 1. The triplet methyl resonances in all of the 1,2-bis(dimethylphosphino)ethane complexes studied as well as in the free ligand indicate strong coupling between the two phosphorus atoms[11]. The higher center peak in the methyl triplet resonance of the octahedral iron complex $C_3F_7Fe(CO)_2I(Pm\text{-}Pm)$ than in the methyl triplet resonance of the cobalt complexes $[C_5H_5Co(Pm\text{-}Pm)R_f]^+$ indicates higher phosphorus-phosphorus coupling in the former complexes.

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[11] R. J. Abraham and H. J. Bernstein, *Can. J. Chem.* **39**, 316 (1961); R. B. King, *Inorg. Chem.* **2**, 936 (1963); R. G. Hayter, *J. Am. chem. Soc.* **85**, 3120 (1963).