Metal Complexes of Fluorophosphines. I. Reactions of Cyclopentadienylmetal Carbonyls with Dialkylaminodifluorophosphines[1]

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Reactions of various cyclopentadienylmetal carbonyl derivatives with the dialkylaminodifluorophosphines $(CH_3)_2NPF_2$, $(C_2H_5)_2NPF_2$, and $C_5H_{10}NPF_2$ ($C_5H_{10}N$ = N-piperidino) are described. Thus $C_5H_5V(CO)_4$ reacts with $C_5H_{10}NPF_2$ in boiling toluene to give the yellow disubstituted derivative $C_5H_5V(CO)_2(PF_2NC_5H_{10})_2$. The methylmolybdenum derivative $CH_3Mo(CO)_3C_5H_5$ reacts with $(CH_3)_2NPF_2$ in acetonitrile at room temperature to give the yellow acetyl derivative $C_5H_5Mo(CO)_2(COCH_3)[PF_2N(CH_3)_2]$. However, the analogous reaction of $CH_3Mo(CO)_3C_5H_5$ with the N-piperidino derivative $C_5H_{10}NPF_2$ results in loss of the methyl and cyclopentadienyl groups to give *cis*-$(C_5H_{10}NPF_2)_4Mo(CO)_2$. Ultraviolet irradiation of $C_3H_5Mo(CO)_2C_5H_5$ with $(C_2H_5)_2NPF_2$ gives yellow $C_5H_5Mo(CO)(C_3H_5)[PF_2N(C_2H_5)_2]$. Reactions of $C_5H_5Mo(CO)_3Cl$ with the three dialkylaminodifluorophosphines R_2NPF_2 in boiling benzene give the orange monosubstituted derivatives $C_5H_5Mo(CO)_2(PF_2NR_2)$ and/or the orange disubstituted derivatives $C_5H_5Mo(CO)(PF_2NR_2)_2Cl$ depending upon the mole ratios of reactants. Reaction of $C_5H_5Mo(CO)[PF_2N(CH_3)_2]_2Cl$ with triphenylphosphine in boiling benzene gives red $C_5H_5Mo(CO)[PF_2N(CH_3)_2][P(C_6H_5)_3]Cl$ with five different groups bonded to the central molybdenum atom. Ultraviolet irradiation of $C_5H_5Mn(CO)_3$ with the dialkylaminodifluorophosphines R_2NPF_2 (R = CH_3 or R_2 = C_5H_{10}) gives the yellow crystalline monocarbonyls $C_5H_5Mn(CO)(PF_2NR_2)_2$. Reaction of $[C_5H_5Fe(CO)_2]_2$ with $(C_2H_5)_2NPF_2$ in boiling benzene gives a mixture of the gray monosubstituted derivative $(C_5H_5)_2Fe_2(CO)_3PF_2N(C_2H_5)_2$ and the green disubstituted derivative $(C_5H_5)_2Fe_2(CO)_2[PF_2N(C_2H_5)_2]_2$. Reactions of the methyliron derivative $CH_3Fe(CO)_2C_5H_5$ with the three dialkylaminodifluorophosphines R_2NPF_2 in boiling methylcyclohexane give the yellow acetyliron derivatives $C_5H_5Fe(CO)(COCH_3)$-(PF_2NR_2). Ultraviolet irradiation of the halides $C_5H_5Fe(CO)_2X$ (X = Br or I) with the dialkylaminodifluorophosphines R_2NPF_2 in benzene solution gives the monosubstituted derivatives $C_5H_5Fe(CO)(PF_2NR_2)X$ and/or the disubstituted derivatives $C_5H_5Fe(PF_2NR_2)_2X$ depending upon the mole ratios of reactants. Reaction of $C_5H_5Fe(CO)_2I$ with $AgBF_4$ in tetrahydrofuran solution followed by addition of $C_5H_{10}NPF_2$ gives the yellow cation $[C_5H_5Fe(CO)_2PF_2NC_5H_{10}]^+$ isolated as its hexafluorophosphate salt. The fluorine nmr spectra of the derivatives $C_5H_5Mo(CO)(C_3H_5)[PF_2N(C_2H_5)_2]$ (0.9 ppm), $C_5H_5Mo(CO)(PF_2NR_2)_2Cl$ (3.2–3.9 ppm), $C_5H_5Fe(CO)(COCH_3)(PF_2NR_2)$ (1.2–1.8 ppm), and $C_5H_5Fe(PF_2NR_2)_2I$ (4.1–4.2 ppm) exhibit patterns corresponding to the indicated chemical shift differences between the two fluorine atoms of each R_2NPF_2 ligand.

Introduction

During the last 15 years the chemistry of the metal carbonyls has been shown to be an area of coordination chemistry of considerable extent and importance.[4] The extent of metal carbonyl chemistry arises at least partially from the high π-acceptor strength of carbon monoxide. The resulting high ability for carbon monoxide to remove electron density from transition metals stabilizes low and negative oxidation states and enables stable zerovalent transition metal derivatives with several carbonyl groups to be prepared. The importance and extent of metal carbonyl chemistry makes of interest a study of the chemistry of transition metal derivatives of other very strong π-acceptor ligands. One such very strong π-acceptor ligand is phosphorus trifluoride (trifluorophosphine). In very recent years the scope and extent of the chemistry of metal trifluorophosphine complexes has been shown to rival that of the metal carbonyls.[5]

Other potential ligands closely related to the strongly π-accepting phosphorus trifluoride are also of considerable interest. Replacement of one of the fluorine atoms of phosphorus trifluoride with a less electronegative group gives a series of potential ligands of the type YPF_2 where the π-acceptor ability can be made to vary within wide limits depending upon the characteristics of the Y group. Of particular interest is the series

PF_3, R_2NPF_2, $(R_2N)_2PF$, and $(R_2N)_3P$ since the first member of the series (PF_3) has a similarly high π-acceptor strength compared to carbon monoxide as discussed above[5] whereas the last member of this series $[(R_2N)_3P]$ at least in the case of tris(dimethylamino)phosphine[6,7] has a similarly low π-acceptor strength compared to tertiary phosphines with three ordinary alkyl or aryl groups. A study of metal complexes of the ligands R_2NPF_2 and $(R_2N)_2PF$ thus provides a useful indication of the chemical properties of transition metal complexes of ligands of intermediate π-acceptor strengths.

This paper discusses the reactions of various cyclopentadienylmetal carbonyl derivatives with the dialkylaminodifluorophosphine, R_2NPF_2 (R = methyl, ethyl, and N-piperidino; in this paper $C_5H_{10}N$ always refers to the N-piperidino group). Reliable preparations of these dialkylaminodifluorophosphines were first developed by Schmutzler in 1964.[8] These dialkylaminodifluorophosphines were shown[8] to form stable zerovalent metal complexes of the types $(R_2NPF_2)_4Ni$ and *cis*-$(R_2NPF_2)_3Mo(CO)_3$ by reactions of the free ligands with $Ni(CO)_4$ and the cycloheptatriene complex C_7H_8-$Mo(CO)_3$, respectively. Furthermore, the dialkylaminodifluorophosphines have been shown to bond to transition metals through the phosphorus atom rather than the nitrogen atom.[8] The relative stability and ease of formation of these coordination complexes of the dialkylaminodifluorophosphines made promising the prospects for the preparation of a wide range of their coordination complexes with other types of transition metal systems.

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(4) For a summary of metal carbonyl chemistry see R. B. King, "Transition Metal Organometallic Chemistry: An Introduction," Academic Press, New York, N. Y., 1969.

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TABLE I

REACTIONS OF CYCLOPENTADIENYLMETAL CARBONYL DERIVATIVES WITH DIALKYLAMINODIFLUOROPHOSPHINES

Metal complex used[a]	Ligand used[c]	Solvent[d]	Temp, °C	Time, hr	Product[a,b]	Yield[e]
CpV(CO)₄ (0.7 g, 3.1 mmol)	C₅H₁₀NPF₂ (1.78 g, 11.6 mmol)	Toluene (25 ml)	110	20	CpV(CO)₂(PF₂NC₅H₁₀)₂	0.087 g (6%)[f,g]
MeMo(CO)₃Cp (1.0 g, 3.85 mmol)	Me₂NPF₂ (2.13 g, 18.8 mmol)	CH₃CN (25 ml)	25	2	CpMo(CO)₂(COMe)(PF₂NMe₂)	0.58 g (40%)[h,g]
MeMo(CO)₃Cp (1.0 g, 3.85 mmol)	C₅H₁₀NPF₂ (1.62 g, 10.6 mmol)	CH₃CN (25 ml)	25	18	cis-(C₅H₁₀PF₂)₄Mo(CO)₂[i]	Low[f,i]
C₃H₅Mo(CO)₂Cp (1.0 g, 3.9 mmol)	Et₂NPF₂ (0.6 g, 4.3 mmol)	MCH (40 ml)	25 (uv)[k]	8	CpMo(CO)(C₃H₅)(PF₂NEt₂)	0.21 g (17%)[g,l]
CpMo(CO)₃Cl (15.0 g, 54 mmol)	Me₂NPF₂ (14.6 g, 129 mmol)	C₆H₆ (150 ml)	80	22	CpMo(CO)(PF₂NMe₂)₂Cl	18.2 g (76%)[m]
CpMo(CO)₃Cl (1.0 g, 3.6 mmol)	C₅H₁₀NPF₂ (1.08 g, 7.0 mmol)	C₆H₆ (50 ml)	80	23	CpMo(CO)(PF₂NC₅H₁₀)₂Cl	0.58 g (31%)[f,j]
CpMo(CO)₃Cl (1.0 g, 3.6 mmol)	Et₂NPF₂ (0.5 g, 3.6 mmol)	C₆H₆ (50 ml)	80	20	{CpMo(CO)(PF₂NEt₂)₂Cl / CpMo(CO)₂(PF₂NEt₂)Cl}	0.10 g (9%)[f,g] / 0.48 g (34%)[f,i]
CpMo(CO)₃Cl (2.0 g, 7.2 mmol)	Et₂NPF₂ (0.75 g, 5.3 mmol)	C₆H₆ (50 ml)	80	19	CpMo(CO)₂(PF₂NEt₂)Cl	0.83 g (29%)[f,i]
CpW(CO)₃I (0.5 g, 1.1 mmol)	C₅H₁₀NPF₂ (1.22 g, 8.0 mmol)	C₆H₆ (50 ml)	80	7	CpW(CO)₂(PF₂NC₅H₁₀)I	0.31 g (48%)[f]
CpMo(CO)(PF₂NMe₂)₂Cl (1.0 g, 2.2 mmol)	Ph₃P (0.57 g, 2.2 mmol)	C₆H₆ (50 ml)	80	29	CpMo(CO)(PF₂NMe₂)(PPh₃)Cl[n]	0.35 g (27%)[m]
CpMn(CO)₃ (1.0 g, 4.9 mmol)	Me₂NPF₂ (2.91 g, 25.7 mmol)	c-C₆H₁₂ (400 ml)	25 (uv)[k]	9	CpMn(CO)(PF₂NMe₂)₂	0.4 g (22%)[f,g]
CpMn(CO)₃ (1.0 g, 4.9 mmol)	C₅H₁₀NPF₂ (3.03 g, 19.8 mmol)	c-C₆H₁₂ (400 ml)	25 (uv)[k]	9	CpMn(CO)(PF₂NC₅H₁₀)₂	0.57 g (26%)[f,g]
CpMn(CO)₃ (14 g, 69 mmol)	C₅H₁₀NPF₂ (21.2 g, 138 mmol)	c-C₆H₁₂ (400 ml)	25 (uv)[k]	93	CpMn(CO)(PF₂NC₅H₁₀)₂	23.9 g (77%)
[CpMn(CO)₂NO][PF₆] (1.1 g, 3.1 mmol)	Et₂NPF₂ (0.6 g, 4.25 mmol)	MeOH (40 ml)	65	4	[CpMn(CO)(NO)P(OMe)₃][PF₆][o]	0.51 g (37%)[p]
[C₅H₅Fe(CO)₂]₂ (1.0 g, 2.9 mmol)	Et₂NPF₂ (0.5 g, 3.5 mmol)	C₆H₆ (50 ml)	80	12	{Cp₂Fe₂(CO)₃(PF₂NEt₂) / Cp₂Fe₂(CO)₂(PF₂NEt₂)₂}	0.10 g (7%)[f,g,q] / 0.21 g (21%)[f,q,r]
MeFe(CO)₂Cp (0.8 g, 4.2 mmol)	Me₂NPF₂ (0.78 g, 6.9 mmol)	MCH (125 ml)	101	23	CpFe(CO)(COMe)(PF₂NMe₂)	0.3 g (23%)[f]
MeFe(CO)₂Cp (1.0 g, 5.2 mmol)	Et₂NPF₂ (0.9 g, 6.4 mmol)	MCH (40 ml)	101	10	CpFe(CO)(COMe)(PF₂NEt₂)	0.8 g (46%)[f]
MeFe(CO)₂Cp (1.0 g, 5.2 mmol)	C₅H₁₀NPF₂ (2.16 g, 14.1 mmol)	MCH (40 ml)	101	18	CpFe(CO)(COMe)(PF₂NC₅H₁₀)	1.0 g (56%)[f,g]
CpFe(CO)₂I (1.0 g, 3.3 mmol)	Et₂NPF₂ (0.6 g, 4 mmol)	c-C₆H₁₂ (30 ml), C₆H₆ (30 ml)	25 (uv)[k]	8	{CpFe(CO)(PF₂NEt₂)I / CpFe(PF₂NEt₂)₂I}	0.86 g (62%)[f,g] / 0.35 g (30%)[f,g]
CpFe(CO)₂Br (1.0 g, 3.9 mmol)	C₅H₁₀NPF₂ (2.16 g, 14.1 mmol)	C₆H₆ (400 ml)	25 (uv)[k]	20	CpFe(PF₂NC₅H₁₀)₂Br	0.24 g (12%)[s]
CpFe(CO)₂I (10.0 g, 32.9 mmol)	C₅H₁₀NPF₂ (17.3 g, 113 mmol)	C₆H₆ (400 ml)	25 (uv)[k]	11	CpFe(PF₂NC₅H₁₀)₂I	12.9 g (70%)[m]
CpFe(CO)₂I (1.0 g, 3.3 mmol), AgBF₄ (0.7 g, 3.6 mmol) [t]	C₅H₁₀NPF₂ (1.1 g, 7.2 mmol)	THF (30 ml)	25	15	[CpFe(CO)₂PF₂NC₅H₁₀][PF₆]	0.31 g (20%)[u]

[a] The following abbreviations are used: Cp, π-cyclopentadienyl; Me, methyl; Et, ethyl. [b] The order of listing two products from a single reaction corresponds to their order of elution from a chromatography column. [c] For the purpose of estimating the quantities of ligands used by volume rather than weight measurements the following specific gravities can be used: Me₂NPF₂, 1.12 g/ml; C₅H₁₀NPF₂, 1.08 g/ml. [d] The following abbreviations are used: MCH, methylcyclohexane; c-C₆H₁₂, cyclohexane; MeOH, methanol; THF, tetrahydrofuran. Acetonitrile was purified by distillation over phosphorus pentoxide and tetrahydrofuran by distillation over lithium aluminum hydride. [e] The isolation and purification procedures for a given product are indicated by the cited footnotes. [f] Chromatography on a 30–60-cm alumina column in pentane or 30–60° petroleum ether solution. Pentane or petroleum ether was used as the developing and eluting solvent with sufficient diethyl ether added to make the bands mobile. [g] The crude product was dissolved in a minimum of pentane at room temperature. The product was crystallized from the filtered pentane solution by cooling to −78°. [h] Chromatography was carried out as in footnote f except Florisil rather than alumina was used. [i] The cis-(C₅H₁₀NPF₂)₄Mo(CO)₂, mp 150–152° (lit.[s] mp 142.0–142.8°), was shown by its infrared spectrum to be identical with that reported by R. Schmutzler, *Inorg. Chem.*, **3**, 415 (1964). [j] The crude product was recrystallized from a mixture of boiling diethyl ether and hexane. [k] Ultraviolet irradiation was used for this reaction. [l] Chromatography on a 30–60-cm alumina column. Pentane was the only solvent used. [m] The crude product was recrystallized from a mixture of dichloromethane and hexane. [n] Attempted chromatography of this product as in footnote f led to decomposition. [o] This product formed yellow crystals, mp 175°. *Anal.* Calcd for C₉H₁₄F₆MnNO₅P₂: C, 24.2; H, 3.1; F, 25.5. Found: C, 24.2; H, 3.1; F, 26.1. An identical product was obtained from the reaction of [C₅H₅Mn(CO)₂NO][PF₆] with trimethyl phosphite in boiling acetone. [p] Crystals of the crude product separated upon concentrating the reaction mixture at 25° (25 mm). These crystals were filtered, washed with diethyl ether, and dried. They were recrystallized from a mixture of methanol and diethyl ether. [q] The residue which remained after evaporating the reaction mixture at 25° (35 mm) was extracted repeatedly with 30–60° petroleum ether. This dissolved the monosubstituted derivative (C₅H₅)₂Fe₂(CO)₃(PF₂NEt₂) but left behind the disubstituted derivative (C₅H₅)₂Fe₂(CO)₂(PF₂NEt₂)₂. [r] The crude product was recrystallized from diethyl ether. [s] Chromatography was carried out as in footnote f except that silica gel rather than alumina was used. [t] The C₅H₅Fe(CO)₂I and AgBF₄ were stirred in the tetrahydrofuran for 20 min and the precipitated silver halide was removed by filtration before addition of the ligand. [u] Solvent was removed from the reaction mixture at 25° (35 mm). The residue was extracted with ∼100 ml of acetone in several portions. The filtered acetone solutions were concentrated at 25° (35 mm) and treated with diethyl ether to give a sticky solid precipitate. This precipitate was dissolved in water and treated with excess aqueous ammonium hexafluorophosphate. The resulting yellow precipitate was filtered, washed with water, and crystallized from a mixture of acetone and diethyl ether.

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. Ultraviolet irradiations were carried out using a jacketed Englehard-Hanovia 450-W mercury ultraviolet lamp

TABLE II
CYCLOPENTADIENYLMETAL COMPLEXES OF DIALKYLAMINODIFLUOROPHOSPHINES

Compd	Color	Mp,^{a} °C	Calcd C Found		Calcd H Found		Calcd F Found		Other Calcd	Found
$C_5H_5V(CO)_2(PF_2NC_5H_{10})_2$	Yellow	113–114	42.6	41.0	5.2	5.4	15.9	15.8	5.8 (N)	5.3 (N)
$C_5H_5Mo(CO)_2(COCH_3)(PF_2NMe_2)$	Yellow	61	35.3	35.2	3.7	3.7	10.0	10.6	3.7 (N)	3.7 (N)
$C_5H_5Mo(CO)(C_3H_5)(PF_2NEt_2)$	Yellow	55	42.1	41.9	5.4	5.6	10.2	10.2		
$C_5H_5Mo(CO)(PF_2NMe_2)_2Cl$	Orange	117–119	26.6	27.0	3.8	3.8	16.9	17.3	21.3 (Mo)	21.7 (Mo)
$C_5H_5Mo(CO)_2(PF_2NEt_2)Cl$	Yellow-orange	138–139	33.5	33.7	3.8	3.7	9.6	9.7		
$C_5H_5Mo(CO)(PF_2NEt_2)_2Cl$	Yellow-orange	111–112	33.2	34.2	4.9	4.9	15.0	15.9		
$C_5H_5Mo(CO)(PF_2NC_5H_{10})_2Cl$	Red-orange	131–133	36.2	36.8	4.7	4.7	14.3	14.2	18.2 (Mo)	18.7 (Mo)
$C_5H_5W(CO)_2(PF_2NC_5H_{10})I$	Orange-brown	159–160	24.6	25.6	2.5	2.8	6.5	5.9		
$C_5H_5Mo(CO)(PF_2NMe_2)(PPh_3)Cl$	Red	234–236	52.0	51.4	4.3	5.2	6.3	6.0	2.3 (N)^c	2.8 (N)^c
$C_5H_5Mn(CO)(PF_2NMe_2)_2$	Yellow	40	32.1	32.4	4.5	4.8	20.3	21.1	14.7 (Mn)	15.4 (Mn)
$C_5H_5Mn(CO)(PF_2NC_5H_{10})_2$	Yellow	70	43.5	42.9	5.5	5.4	16.7	16.7		
$(C_5H_5)_2Fe_2(CO)_2(PF_2NEt_2)$	Gray-green	138–139	43.5	43.6	4.3	4.4			24.0 (Fe)	23.7 (Fe)
$(C_5H_5)_2Fe_2(CO)_2(PF_2NEt_2)_2$	Green	156–157	41.4	41.4	5.2	5.2	13.1	13.3	19.3 (Fe)	19.2 (Fe)
$C_5H_5Fe(CO)(COCH_3)(PF_2NMe_2)$ ·	Yellow-brown	Liquid	39.4	40.3	4.6	4.8	12.4	12.9		
$C_5H_5Fe(CO)(COCH_3)(PF_2NEt_2)$	Yellow	Wax	43.2	43.4	5.4	5.5	11.4	11.3	16.8 (Fe)	16.8 (Fe)
$C_5H_5Fe(CO)(COCH_3)(PF_2NC_5H_{10})$	Yellow	41–42	45.1	45.3	5.2	5.4	11.0	11.0	17.0 (Fe)	16.8 (Fe)
$C_5H_5Fe(CO)(PF_2NEt_2)I$	Gray	90–91	28.8	29.9	3.6	3.8	9.1	9.3	13.4 (Fe)	12.6 (Fe)
$C_5H_5Fe(PF_2NEt_2)_2I$	Dark red	99–100	29.9	29.9	4.7	4.8	14.3	14.5	10.6 (Fe)	10.3 (Fe)
$C_5H_5Fe(PF_2NC_5H_{10})_2Br$	Red	94–96	35.5	35.8	5.0	5.6	15.0	13.7	11.1 (Fe)	9.3 (Fe)
$C_5H_5Fe(PF_2NC_5H_{10})_2I$	Dark red	128–130	30.7	32.4	4.5	4.6	13.7	13.8	5.1 (N)	3.9 (N)
$[C_5H_5Fe(CO)_2(PF_2NC_5H_{10})][PF_6]$	Yellow		30.3	30.3	3.2	3.2	32.0	32.1	11.8 (Fe)	11.8 (Fe)

^{a} Melting points were determined in open capillaries and are uncorrected. ^{b} Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, and Meade Microanalytical Laboratory, Amherst, Mass. ^{c} *Anal.* Calcd: Cl, 5.9; O, 2.7. Found: Cl, 7.7; O, 2.7.

immersed into the reaction mixture. All reactions described in this paper were carried out with magnetic stirring.

Materials.—The dialkylaminodifluorophosphines R_2NPF_2 (R = methyl and ethyl or $R_2 = N$-piperidino) were prepared by fluorination of the corresponding dialkylaminodichlorophosphine R_2NPCl_2 either with antimony trifluoride in the absence of a solvent or with sodium fluoride in tetramethylene sulfone according to published procedures.[8] The following metal carbonyls were purchased from the indicated commercial sources: $M(CO)_6$ (M = Cr, Mo, W) (Pressure Chemical Co., Pittsburgh, Pa.), $[Na(diglyme)_2][V(CO)_6]$ (Strem Chemical Co., Danvers, Mass.), $C_5H_5Mn(CO)_3$ (Ethyl Corp., New York, N. Y.), and $Fe(CO)_5$ (GAF Corp., New York, N. Y.). The organometallic compounds $C_5H_5V(CO)_4$,[9a] $CH_3Mo(CO)_3C_5H_5$,[9b] $[C_5H_5Fe(CO)_2]_2$,[9c] $C_5H_5Fe(CO)_2I$,[9d] $C_3H_5Mo(CO)_2C_5H_5$,[10] C_5H_5-$Mo(CO)_3Cl$,[11] $C_5H_5Fe(CO)_2Br$,[12] and $[C_5H_5Mn(CO)_2NO][PF_6]$[13] were prepared by the cited published procedures. The reaction of $NaW(CO)_3C_5H_5$[11] with iodine was used to prepare C_5H_5W-$(CO)_3I$.

Reactions of Cyclopentadienylmetal Carbonyl Derivatives with Dialkylaminodifluorophosphine (Table I).—The quantities of the cyclopentadienylmetal carbonyl derivative and dialkylaminodifluorophosphine indicated in Table I were stirred, heated, or exposed to ultraviolet irradiation in the indicated solvent at the indicated temperature for the indicated period of time. Solvent was then removed from the reaction mixture under vacuum at room temperature. The product(s) was (were) isolated from the residue by the combinations of chromatography and/or crystallization indicated in Table I.

The properties of the new compounds prepared in this work, including elemental analyses, are given in Table II.

Spectroscopic Studies.—Infrared spectra (Table III) of the new cyclopentadienylmetal complexes of the dialkylaminodifluorophosphines were taken in the $\nu(CO)$ and $\nu(PF)$ regions in the indicated media and were recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. The proton and fluorine nmr spectra of the new compounds prepared in this work are listed in Table IV.

The mass spectra listed below were run at 70 eV on a Perkin-Elmer Hitachi Model RMU-6 mass spectrometer. Unless otherwise specified, the chamber temperature was 220°. Relative intensities are given in parentheses.

A. $C_5H_5Mo(CO)[PF_2N(CH_3)_2]_2Cl$ (sample temperature 110°):

$C_5H_5Mo(CO)[PF_2N(CH_3)_2]_2Cl^+$ (2), $C_5H_5Mo[PF_2N(CH_3)_2]_2Cl^+$ (2), $(C_5H_5)_2Mo_2Cl_2^+$ (4), $(C_5H_5)_2Mo_2Cl^+$ (~2), $C_5H_5Mo(CO)[PF_2$-$N(CH_3)_2]Cl^+$ (12), $C_5H_5Mo[PF_2N(CH_3)_2]Cl^+$ (21), $(C_5H_5)_2Mo$-Cl^+ (5), $(C_5H_5)_2Mo^+$ (9), $C_5H_5MoCl^+$ (100), $C_5H_5MoF^+$ (5), $C_3H_3MoCl^+$ (8), MoF_2^+ (4), $(CH_3)_2NPF_2^+$ (>600), CH_3NCH_2-PF_2^+ (>600), $(CH_3)_2NPF^+$ (>600), CH_2NPF^+ (9), PF_2^+ (>600), $C_5H_5^+$ (12), *m/e* 60 (8), PFH^+ (7), and PF^+ (10).

B. $C_5H_5Mo(CO)[PF_2NC_5H_{10}]_2Cl$ (sample temperature 120°): $C_5H_5Mo(CO)[PF_2NC_5H_{10}]_2Cl^+$ (2), $C_5H_5Mo[PF_2NC_5H_{10}]_2Cl^+$ (2), $(C_5H_5)_2Mo_2Cl_2^+$ (13), $C_5H_5Mo(CO)[PF_2NC_5H_{10}]Cl^+$ (14), $C_5H_5Mo[PF_2NC_5H_{10}]Cl^+$ (30), $(C_5H_5)_2MoCl^+$ (14), $(C_5H_5)_2Mo^+$ (29), $C_5H_5MoCl^+$ (100), $C_5H_5MoF^+$ (6), $C_3H_3MoCl^+$ (12), $C_5H_{10}NPF_2^+$ (off scale), $C_5H_9NPF_2^+$ (off scale), $C_4H_7NPF_2^+$ (42), $C_5H_{10}NPF^+$ (off scale), $C_3H_6NPF_2^+$ (off scale), $C_3H_5NPF_2^+$ (off scale), $C_2H_5NPF_2^+$ (off scale), $CH_2NPF_2^+$ (off scale), $CHNPF_2^+$ (off scale), $C_5H_{10}N^+$ (off scale), CH_2NPF^+ (19), PF_2^+ (off scale), $C_5H_8^+$ (19), $C_5H_7^+$ (25), $C_5H_6^+$ (22), $C_5H_5^+$ (27), $C_4H_9^+$ (52), C_4-H_8^+ (230), $C_4H_7^+$ (off scale), and $C_4H_6^+$ (off scale).

C. $C_5H_5Fe(CO)(COCH_3)(PF_2NC_5H_{10})$ (chamber temperature 80°, sample temperature 59°): $C_5H_5Fe(CO)(COCH_3)(PF_2NC_5$-$H_{10})^+$ (24), $C_5H_5Fe(CO)_2(PF_2NC_5H_{10})^+$ (22), $C_5H_5FeCOCH_3$-$(PF_2NC_5H_{10})^+$ (102), $C_5H_5Fe(CO)(PF_2NC_5H_{10})^+$ (9), C_5H_5Fe-$(CH_3)(PF_2NC_5H_{10})^+$ (110), $C_6H_5FePF_2NC_5H_{10}^+$ (55), C_6H_5Fe-$PF_2NC_5H_{10}^+$ (125), $C_5H_5FePF_2NC_5H_{10}^+$ (100), *m/e* 218 (23), $C_5H_5Fe(CO)_2CH_3^+$ (8), $C_5H_5FeCOCH_3^+$ (64), $C_5H_{10}NPF_2^+$ (9), $C_5H_9NPF_2^+$ (15), $C_6H_3Fe^+$ (86), $C_5H_{10}NPF^+$ and/or $C_6H_6Fe^+$ (~475), $C_5H_5Fe^+$ (62), *m/e* 116 (17), *m/e* 115 (22), $C_6H_6^+$ and/or CH_2NPF^+ (19), and PF_2^+ (26). Metastable ions at *m/e* 291.2 (345→317), *m/e* ~277 (330→302), *m/e* ~264 (317→289), and *m/e* 248.5 (302→274).

Discussion

A. Preparation and Characterization of New Compounds.—Reactions of $C_5H_5V(CO)_4$ with trivalent phosphorus derivatives have been reported to give either monosubstituted derivatives of the type C_5H_5V-$(CO)_3L$ (L = $[(CH_3)_2N]_3P$,[6] $(C_6H_5)_3P$,[14] etc.) or disubstituted derivatives of the type $C_5H_5V(CO)_2L_2$ (L = two trivalent phosphorus atoms of a ditertiary[15] or tritertiary[16] phosphine). The reaction between C_5H_5V-$(CO)_4$ and N-piperidinodifluorophosphine in boiling toluene was found to give a disubstituted derivative

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TABLE III

INFRARED SPECTRA OF CYCLOPENTADIENYLMETAL COMPLEXES OF DIALKYLAMINODIFLUOROPHOSPHINES[a]

	Infrared spectrum, cm^{-1}	
Compound	ν(CO) freq[b]	ν(PF) freq[c]
Me_2NPF_2[d]	. . .	800 vs, 743 vs
Et_2NPF_2[d]	. . .	792 vs, 738 vs
$C_5H_{10}NPF_2$[d]	. . .	793 vs, 737 vs
$C_5H_5V(CO)_2(PF_2NC_5H_{10})_2$	1925 m, 1842 s	781 s, 759 m
$C_5H_5Mo(CO)_2(COCH_3)(PF_2NMe_2)$	1964 s, 1892 vs, 1652 s[e]	778 s, 720 s
$C_5H_5Mo(CO)(C_3H_5)(PF_2NEt_2)$	1883 s	774 s, 733 s
$C_5H_5Mo(CO)(PF_2NMe_2)_2Cl$	1898 s	807 s, 785 m
$C_5H_5Mo(CO)(PF_2NMe_2)(PPh_3)Cl$	1829 s	f
$C_5H_5Mo(CO)_2(PF_2NEt_2)Cl$	1994 s, 1916 s	820 m, 788 m
$C_5H_5Mo(CO)(PF_2NEt_2)_2Cl$	1893 s, ~1872 m, sh	801 s, 780 s
$C_5H_5Mo(CO)(PF_2NC_5H_{10})_2Cl$	1893 s	811 m, 788 s, 776 sh
$C_5H_5W(CO)_2(PF_2NC_5H_{10})I$	1962 s, 1887 s	817 m, 786 m
$C_5H_5Mn(CO)(PF_2NMe_2)_2$	1920 s	805 s, 785 s, 762 s, 747 m
$C_5H_5Mn(CO)(PF_2NC_5H_{10})_2$	1915 s	803 s, 778 s, 760 s, 745 m
$(C_5H_5)_2Fe_2(CO)_3(PF_2NEt_2)$	1974 s, 1954 s, 1800 w, 1763 s, 1732 m	809 s, 780 s
$(C_5H_5)_2Fe_2(CO)_2(PF_2NEt_2)_2$	1742 s	825 m, 805 s, 790 m, 750 s
$C_5H_5Fe(CO)(COCH_3)(PF_2NMe_2)$	1965 s, 1949 s, 1630 m, br[e]	818 s,[d] 790 s[d]
$C_5H_5Fe(CO)(COCH_3)(PF_2NEt_2)$	1962 s, 1948 s, 1626 m, br[e]	810 vs,[d] 785 vs[d]
$C_5H_5Fe(CO)(COCH_3)(PF_2NC_5H_{10})$	1955 s, 1939 m, 1624 m, br[e]	805 m, 780 m
$C_5H_5Fe(CO)(PF_2NEt_2)I$	1999 s, 1980 m	815 s, 794 s
$C_5H_5Fe(PF_2NEt_2)_2I$	. . .	826 s, 796 s
$C_5H_5Fe(PF_2NC_5H_{10})_2Br$	. . .	824 s, 800 s
$C_5H_5Fe(PF_2NC_5H_{10})_2I$	. . .	833 s, 788 s
$[C_5H_5Fe(CO)_2(PF_2NC_5H_{10})][PF_6]$	2090 vs,[g] 2050 vs[g]	~845 vs, br[h]

[a] These infrared spectra were taken in the indicated media and recorded on a Perkin-Elmer Model 621 infrared spectrometer with grating optics. Spectra were calibrated against the 1601.4-cm^{-1} band of polystyrene film. [b] Unless otherwise indicated these ν(CO) frequencies were measured in cyclohexane solution. [c] Unless otherwise indicated these ν(PF) frequencies were measured in potassium bromide pellets. [d] These ν(PF) frequencies were measured as liquid films. [e] Acyl ν(CO) frequency. [f] These ν(PF) frequencies were obscured by some frequencies arising from the benzenoid rings. [g] KBr pellet. [h] The ν(PF) frequencies from the $C_5H_{10}NPF_2$ ligand in $[C_5H_5Fe(CO)_2(PF_2NC_5H_{10})][PF_6]$ were obscured by this ν(PF) frequency of the PF_6 anion.

TABLE IV

NMR SPECTRA OF CYCLOPENTADIENYLMETAL COMPLEXES OF DIALKYLAMINODIFLUOROPHOSPHINES

	Proton nmr spectrum, $\tau^{a,b}$				Fluorine nmr spectrum, $\phi^{b,c}$			
Compound	π-C_5H_5	R_2NPF_2	Other	Solvent	R_2NPF_2	$\Delta\phi^d$	^1J(PF)	^2J(FF')[e]
Me_2NPF_2		7.38 dt (9, 4)		Neat	+65.3	0.0	1196	
Et_2NPF_2				Neat	+64.9	0.0	1195	
$C_5H_{10}NPF_2$		6.95 b, 8.47 s		Neat	+65.2	0.0	1192	
$C_5H_5V(CO)_2(PF_2NC_5H_{10})_2$	5.27 t (2)	6.85 b, 8.47 s		CDCl₃	+28.3	0.0	1154	
$C_5H_5Mo(CO)_2(COCH_3)(PF_2NMe_2)$	4.82 d (2)	7.19 dt (10, 3)	CH₃: 7.50 s	CH₂Cl₂	+26.5	0.0	1131	
$C_5H_5Mo(CO)(C_3H_5)(PF_2NEt_2)$	4.92 s	6.85 b, 8.90 t (7)	C₃H₅: ~6.0 b, ~7.2 b, ~7.75 b	THF	+21.7 +22.6	0.9	1080 1085	~15
$C_5H_5Mo(CO)(PF_2NMe_2)_2Cl$	4.59 s	7.12 dt (10, 3)		CH₂Cl₂	+38.4 +42.0	3.6	1146 1116	~25
$C_5H_5Mo(CO)(PF_2NEt_2)_2Cl$	4.60 s	6.73 b, 8.83 t (7)		CH₂Cl₂	+35.7 +39.6	3.9	1144 1137	~25
$C_5H_5Mo(CO)(PF_2NC_5H_{10})_2Cl$	4.67 s	6.77 b, 8.41 s		CH₂Cl₂	+38.6 +41.8	3.2	1161 1145	~30
$C_5H_5Mo(CO)(PF_2NMe_2)(PPh_3)Cl$	4.92 s	7.44 dt	C₆H₅: ~2.7 m	f				
$C_5H_5Mn(CO)(PF_2NMe_2)_2$	5.58	~7.26 b		CH₂Cl₂	+23.0	~0	1127	
$C_5H_5Mn(CO)(PF_2NC_5H_{10})_2$	5.67 t (2)	6.75 b, 8.43 s		CH₂Cl₂	+22.4	~0.5	~1110	
$(C_5H_5)_2Fe_2(CO)_3(PF_2NEt_2)$	5.32 s 5.46	~6.7 b, 8.86 t (7)		THF	+34.6	<0.5	~1160	
$(C_5H_5)_2Fe_2(CO)_2(PF_2NEt_2)_2$	5.48 s	~6.76, 9.03 t (~7)						
$C_5H_5Fe(CO)(COCH_3)(PF_2NMe_2)$				CH₂Cl₂	+33.2 +34.4	1.2	1132 1152	~20
$C_5H_5Fe(CO)(COCH_3)(PF_2NEt_2)$	5.29 d (1)	~6.7 b, 8.85 t (7)	CH₃: 7.45 s	THF	+30.0 +31.8	1.8	1128 1146	~20
$C_5H_5Fe(CO)(COCH_3)(PF_2NC_5H_{10})$	5.32 s	~6.7 b, 8.42 s	CH₃: 7.48 s	CH₂Cl₂	+32.6 +34.0	1.4	1136 1156	~30
$C_5H_5Fe(CO)(PF_2NEt_2)I$	5.22 s	~6.6 b, 8.80 t (7)		THF	+25.7 +29.8	4.1	1102 1177	
$C_5H_5Fe(PF_2NEt_2)_2I$	5.55 t (1)	~6.6 b, 8.78 t (7)		f				
$C_5H_5Fe(PF_2NC_5H_{10})_2I$	5.58 t (1)	~6.4 b, 8.37 s		CH₂Cl₂	+28.0 +32.2	4.2	1099 1156	

[a] These proton nmr spectra were run in CDCl₃ solution either at 60 Mcps on a Perkin-Elmer Hitachi R-20 spectrometer or at 100 Mcps on a Varian HA-100 spectrometer. [b] The following abbreviations are used: s, singlet; d, doublet; t, triplet; dt, doublet of triplets; m, ill-defined multiplet; b, broad. Coupling constants in cps are given in parentheses. [c] These ^{19}F nmr spectra were run in the indicated solvents at 56.456 Mcps using a Perkin-Elmer Hitachi R-20 spectrometer. Chemical shifts are given in the ϕ scale of G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959). [d] See the text for a definition of $\Delta\phi$. [e] This coupling constant was estimated from the ^{19}F nmr spectra run on the 100-ppm scale. The probable error is ±5 cps. Attempts to expand these spectra for a more precise measurement of this coupling constant were unsatisfactory. [f] Attempts to obtain ^{19}F nmr spectra of these compounds in both tetrahydrofuran and CH₂Cl₂ were unsatisfactory.

$C_5H_5V(CO)_2(PF_2NC_5H_{10})_2$ The infrared spectrum of this compound exhibited the expected two $\nu(CO)$ frequencies (1925 and 1842 cm^{-1}) which are considerably higher than the $\nu(CO)$ frequencies of the tributylphosphine derivative[17] $C_5H_5V(CO)_2[P(C_4H_9)_3]_2$ (1856 and 1762 cm^{-1}) in accord with the higher π-acceptor strength of a dialkylaminodifluorophosphine relative to a trialkylphosphine. Compounds of the type $C_5H_5V(CO)_2(PF_2NR_2)_2$ were relatively unstable and decomposed extensively during their purification. Thus the yield of $C_5H_5V(CO)_2(PF_2NC_5H_{10})_2$ from $C_5H_5V(CO)_4$ and N-piperidinodifluorophosphine was only 6%. Furthermore, the reaction between C_5H_5-$V(CO)_4$ and dimethylaminodifluorophosphine gave a product indicated by approximate elemental analyses and its infrared spectrum ($\nu(CO)$ at 1930 and 1850 cm^{-1}) to be the analogous derivative $C_5H_5V(CO)_2$-$[PF_2N(CH_3)_2]_2$ but this compound could not be obtained entirely pure. The temperature at which the reaction between $C_5H_5V(CO)_4$ and the dialkylaminodifluorophosphines was carried out was somewhat critical since if boiling benzene (80°) instead of boiling toluene (111°) was used as the reaction solvent, the $C_5H_5V(CO)_4$ was recovered unchanged.

Reactions of the methylmolybdenum derivative $CH_3Mo(CO)_3C_5H_5$ with trivalent phosphorus derivatives preferably in a polar solvent such as acetonitrile have been reported[18] to give the acetyl derivatives $CH_3COMo(CO)_2(L)(C_5H_5)$. In this reaction the carbonyl group displaced by the trivalent phosphorus ligand is not liberated as free carbon monoxide but instead inserts into the methyl–molybdenum bond to form an acetyl group. The reaction between CH_3Mo-$(CO)_3C_5H_5$ and dimethylaminodifluorophosphine in acetonitrile at room temperature proceeded analogously to give yellow $C_5H_5Mo(CO)_2(COCH_3)[PF_2N(CH_3)_2]$. The infrared spectrum of this complex exhibited the expected two terminal $\nu(CO)$ frequencies (1964 and 1892 cm^{-1}) and single acyl $\nu(CO)$ frequency (1652 cm^{-1}) in accord with the proposed formulation. This infrared spectrum clearly excludes an alternative formulation as $C_5H_5Mo(CO)_3[PF_2N(CH_3)_2CH_3]$ where the dimethylaminodifluorophosphine rather than a carbonyl group has inserted into the methyl–molybdenum bond.

The analogous reaction of the methylmolybdenum derivative $CH_3Mo(CO)_3C_5H_5$ with N-piperidinodifluorophosphine in boiling acetonitrile was also investigated. The only molybdenum carbonyl derivative that could be isolated from the reaction mixture was the known[8] compound cis-$(C_5H_{10}NPF_2)_4Mo(CO)_2$ indicating that loss of both the cyclopentadienyl and methyl groups of $CH_3Mo(CO)_3C_5H_5$ had occurred. The reaction between $CH_3Mo(CO)_3C_5H_5$ and N-piperidinodifluorophosphine to give cis-$(C_5H_{10}NPF_2)_4Mo(CO)_2$ is thus analogous to the reported[19] reaction between $CH_3Mo(CO)_3C_5H_5$ and the unsaturated chelating ditertiary phosphine cis-$(C_6H_5)_2PCH=CHP(C_6H_5)_2$ to give the analogous cis-$[(C_6H_5)_2PCH=CHP(C_6H_5)_2]_2Mo$-$(CO)_2$.

The reactions of trivalent phosphorus derivatives with $CH_3Mo(CO)_3C_5H_5$ to give compounds of the types

(17) E. O. Fischer and R. J. J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **6**, 569 (1967); *Ber.*, **103**, 3684 (1970).

(18) P. J. Craig and M. Green, *J. Chem. Soc. A*, 1978 (1968).

(19) R. B. King, L. W. Houk, and P. N. Kapoor, *Inorg. Chem.*, **8**, 1792 (1969).

$C_5H_5Mo(CO)_2(COCH_3)(PR_3)$ or cis-$(R_3P)_4Mo(CO)_2$ made of interest the reactions of trivalent phosphorus derivatives with other types of cyclopentadienylmolybdenum carbonyl derivatives also containing other carbon ligands. One such cyclopentadienylmolybdenum carbonyl derivative is the π-allyl derivative C_3H_5Mo-$(CO)_2C_5H_5$ (I, L = CO). The reactions of C_3H_5-$Mo(CO)_2C_5H_5$ (I, L = CO) with trivalent phosphorus derivatives were of interest because of the possibility for conversion of the π-allyl group to a σ-allyl group in order to generate a vacancy for coordination of a trivalent phosphorus atom to the molybdenum atom. Ultraviolet irradiation of the π-allyl derivative C_3H_5Mo-$(CO)_2C_5H_5$ (I, L = CO) with diethylaminodifluorophosphine gave the monocarbonyl $C_5H_5Mo(CO)(C_3H_5)$-$[PF_2N(C_2H_5)_2]$. The proton nmr spectrum of this allyl derivative indicated that the π-allyl group was retained rather than converted to a σ-allyl group. This indicates structure I (L = $(C_2H_5)_2NPF_2$) for the com-

L → Mo—CO

I
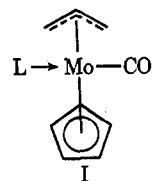
plex $C_5H_5Mo(CO)(C_3H_5)[PF_2N(C_2H_5)_2]$. This complex is thus a routine substitution product of the starting material $C_3H_5Mo(CO)_2C_5H_5$ (I, L = CO). However, it is apparently the first reported example of a substitution product of $C_3H_5Mo(CO)_2C_5H_5$.

The reactions between $C_5H_5Mo(CO)_3Cl$ and the dialkylaminodifluorophosphines in boiling benzene could be made to give either the monosubstituted derivative $C_5H_5Mo(CO)_2(PF_2NR_2)Cl$ or the disubstituted derivative $C_5H_5Mo(CO)(PF_2NR_2)_2Cl$ depending upon the mole ratios of reactants. These two types of substitution products of $C_5H_5Mo(CO)_3Cl$ could be separated easily by chromatography on alumina. If an excess of the dialkylaminodifluorophosphine was used in its reaction with $C_5H_5Mo(CO)_3Cl$ in boiling benzene, pure samples of the disubstituted products C_5H_5Mo-$(CO)(PF_2NR_2)_2Cl$ could be obtained without the need for chromatographic purification. No trisubstituted derivatives of the type $C_5H_5Mo(PF_2NR_2)_3Cl$ were observed in this work. In one attempt to prepare such a trisubstituted derivative, a mixture of C_5H_5Mo-$(CO)_3Cl$ and excess diethylaminodifluorophosphine was heated in boiling toluene. A black product was obtained which exhibited no $\nu(CO)$ frequencies. The proton nmr spectrum of this black solid exhibited no C_5H_5 resonances indicating that it was not the desired $C_5H_5No[PF_2N(C_2H_5)_2]_3Cl$.

The reaction between $C_5H_5W(CO)_3I$ and excess N-piperidinodifluorophosphine in boiling benzene was investigated in order to see what the maximum degree of substitution of the tungsten halide derivative would be under conditions where the molybdenum halide $C_5H_5Mo(CO)_3Cl$ gave the disubstituted derivative $C_5H_5Mo(CO)[PF_2NC_5H_{10}]_2Cl$. This reaction gave only the monosubstituted derivative $C_5H_5W(CO)_2(PF_2N$-$C_5H_{10})I$ indicating the greater difficulty in substituting carbonyl groups in $C_5H_5W(CO)_3I$ than in C_5H_5Mo-$(CO)_3Cl$.

One objective in this research was the preparation

of metal carbonyl anions with dialkylaminodifluorophosphine substituents. If such metal carbonyl anions were available, their reactions with various halides and related electrophilic reagents would provide possible routes to a wide variety of additional dialkylaminodifluorophosphine derivatives.[20] Reaction of C_5-$H_5Mo(CO)[PF_2N(CH_3)_2]_2Cl$ with excess sodium amalgam in tetrahydrofuran solution at room temperature for 1 hr followed by addition of either methyl iodide or trimethyltin chloride to trap any $Na[C_5H_5Mo(CO)\text{-}$ $[PF_2N(CH_3)_2]_2]$ reactive intermediate as either the σ-methyl derivative $C_5H_5Mo(CO)(CH_3)[PF_2N(CH_3)_2]_2$ or the trimethyltin derivative $C_5H_5Mo(CO)[Sn(CH_3)_3]\text{-}$ $[PF_2N(CH_3)_2]_2$, respectively, instead gave only unchanged $C_5H_5Mo(CO)[PF_2N(CH_3)_2]_2Cl$.

The molybdenum compound $C_5H_5Mo(CO)_3Cl$ reacts with various trialkylphosphines and triarylphosphines to form either nonionic products of the type $C_5H_5Mo(CO)_2(PR_3)Cl$ with replacement of one carbonyl group or ionic products containing the cation $[C_5H_5Mo(CO)_3PR_3]^+$ with replacement of the chloride.[21] The analogous reaction of $C_5H_5Mo(CO)[PF_2N\text{-}$ $(CH_3)_2]_2Cl$ with triphenylphosphine in boiling benzene resulted in the replacement of one dimethylaminodifluorophosphine ligand to give $C_5H_5Mo(CO)[PF_2N\text{-}$ $(CH_3)_2][P(C_6H_5)_3]Cl$. This compound exhibited a single $\nu(CO)$ frequency (1829 cm^{-1}) confirming the indication by analyses that the carbonyl group had been retained. The downward shift in the $\nu(CO)$ frequency and the upward shift in the cyclopentadienyl nmr resonance in $C_5H_5Mo(CO)[PF_2N(CH_3)_2][P(C_6\text{-}$ $H_5)_3]Cl$ relative to $C_5H_5Mo(CO)[PF_2N(CH_3)_2]_2Cl$ are the expected trends for replacement of a dimethylaminodifluorophosphine ligand with the more weakly π-accepting triphenylphosphine ligand. The compound $C_5H_5Mo(CO)[PF_2N(CH_3)_2][P(C_6H_5)_3]Cl$ is presently unique in having five completely different groups bonded to a single transition metal.

The photochemical reactions between $C_5H_5Mn(CO)_3$ and various tertiary phosphines give derivatives of the types $C_5H_5Mn(CO)_2PR_3$ and $C_5H_5MnCO(PR_3)_2$.[22] The photochemical reactions of $C_5H_5Mn(CO)_3$ with exessses of the dialkylaminodifluorophosphines, R_2NPF_2 ($R = CH_3$, $R_2 = C_5H_{10}$), gave the yellow crystalline disubstituted derivatives $C_5H_5Mn(CO)(PF_2NR_2)_2$. No unambiguous evidence either for intermediate monosubstituted derivatives $C_5H_5Mn(CO)_2PF_2NR_2$ or for the carbonyl-free trisubstituted derivatives $C_5H_5Mn\text{-}$ $(PF_2NR_2)_3$ was observed in this work.

The manganese compound $[C_5H_5Mn(CO)_2NO][PF_6]$ has been reported to react with tertiary phosphines in boiling methanol or acetone to give monosubstituted derivatives of the type $[C_5H_5Mn(CO)(NO)(PR_3)]\text{-}$ $[PF_6]$.[23,24] Reaction of $[C_5H_5Mn(CO)_2NO][PF_6]$ with diethylaminodifluorophosphine in boiling methanol gave the trimethyl phosphite derivative $[C_5H_5Mn\text{-}$ $(CO)(NO)P(OCH_3)_3][PF_6]$ which was shown to be identical with the compound obtained by reaction of $[C_5H_5Mn(CO)_2NO][PF_6]$ with trimethyl phosphite

in boiling acetone. Methanol thus cannot be used as a solvent in reactions of this type because of methanolysis of the ligand.

The reaction of $[C_5H_5MnCONO]_2$[13] with diethylaminodifluorophosphine in boiling benzene was also investigated. A green-black crystalline solid was obtained. This was shown by its infrared spectrum to be the reported[13,25] compound $(C_5H_5)_3Mn_3(NO)_4$ which was previously[13] prepared by the ultraviolet irradiation of $[C_5H_5MnCONO]_2$ in benzene solution. Subsequently, the bimetallic manganese compound $[C_5H_5\text{-}$ $MnCONO]_2$ was shown to give $(C_5H_5)_3Mn_3(NO)_4$ in quantitative yield by boiling under reflux in benzene solution for 6 hr. Thus, the thermal conversion of $[C_5H_5MnCONO]_2$ to $(C_5H_5)_3Mn_3(NO)_4$ does not appear to be affected by the presence of trivalent phosphorus complexing agents like diethylaminodifluorophosphine.

The bimetallic iron compound $[C_5H_5Fe(CO)_2]_2$, although isoelectronic with $[C_5H_5MnCONO]_2$, reacts differently with trivalent phosphorus derivatives. Thus the reaction of $[C_5H_5Fe(CO)_2]_2$ with various monodentate trivalent phosphorus derivatives in boiling benzene results in the replacement of one terminal carbonyl group to give $(C_5H_5)_2Fe_2(CO)_3PR_3$ derivatives of structure II ($L = PR_3$).[26] A similar reaction of
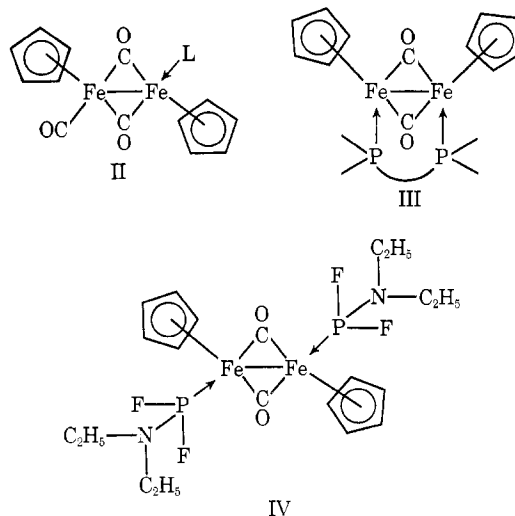
$[C_5H_5Fe(CO)_2]_2$ with various chelating bidentate trivalent phosphorus derivatives results in the replacement of both terminal carbonyl groups to give $(C_5H_5)_2\text{-}$ $Fe_2(CO)_2(diphos)$ derivatives of structure III.[27] The reaction of $[C_5H_5Fe(CO)_2]_2$ with diethylaminodifluorophosphine in boiling benzene gave products of both types which could be separated by chromatography. The gray monosubstituted derivative $(C_5H_5)_2Fe_2(CO)_3\text{-}$ $PF_2N(C_2H_5)_2$ (II, $L = (C_2H_5)_2NPF_2$) exhibited two closely spaced terminal carbonyl $\nu(CO)$ frequencies and three bridging $\nu(CO)$ frequencies. This suggests that a terminal carbonyl group in $[C_5H_5Fe(CO)_2]_2$ is replaced by the diethylaminodifluorophosphine ligand. The multiple infrared bands in the $\nu(CO)$ regions can be rationalized by the presence of conformational isomers arising from restricted rotation around the iron–phosphorus bond similar to the isomers arising from

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restricted rotation around the iron–silicon bond reported[28] in $CH_3SiCl_2Fe(CO)_2C_5H_5$ and related compounds. The green disubstituted derivative $(C_5H_5)_2$-$Fe_2(CO)_2[PF_2N(C_2H_5)_2]_2$ exhibited no terminal $\nu(CO)$ frequencies and a single bridging $\nu(CO)$ frequency. This is consistent with structure IV closely related to structure III. In both cases both terminal carbonyl groups of $[C_5H_5Fe(CO)_2]_2$ have been replaced by trivalent phosphorus ligands. This study on the reaction of diethylaminodifluorophosphine with $[C_5H_5Fe(CO)_2]_2$ demonstrates that diethylaminodifluorophosphine, like all other trivalent phosphorus derivatives which have been investigated, is capable of replacing only the terminal carbonyl groups in $[C_5H_5Fe(CO)_2]_2$.

Reactions of the methyliron compound $CH_3Fe(CO)_2$-C_5H_5 with trivalent phosphorus derivatives have been reported to give acetyl derivatives of the type CH_3CO-$Fe(CO)(L)(C_5H_5)$.[29] The reactions between CH_3Fe-$(CO)_2C_5H_5$ and the three dialkylaminodifluorophosphines investigated in this work were found to give the analogous acetyliron derivatives $C_5H_5Fe(CO)(COCH_3)$-$[PF_2NR_2]$ as yellowish liquids or low-melting solids. The infrared spectra of these complexes exhibited two closely terminal $\nu(CO)$ frequencies at 1959 ± 3 and 1944 ± 5 cm^{-1} in accord with a single terminal carbonyl group as in structure V but with the presence of conformational isomers similar to those found[28] for CH_3Si-$Cl_2Fe(CO)_2C_5H_5$ as discussed above. In addition the single acyl $\nu(CO)$ frequency as expected for structure V

V
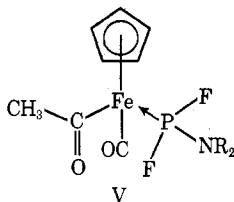
was found at 1625 ± 1 cm^{-1}. As is the case with the molybdenum compound $C_5H_5Mo(CO)_2(COCH_3)[PF_2$-$N(CH_3)_2]$ discussed above, the positions of these $\nu(CO)$ frequencies in the $C_5H_5Fe(CO)(COCH_3)(PF_2NR_2)$ derivatives indicate both that a carbonyl group rather than a dialkylaminodifluorophosphine ligand has inserted into the methyl–iron bond and that a dialkylaminodifluorophosphine ligand is a stronger π acceptor than trialkylphosphines or triarylphosphines such as triphenylphosphine (*i.e.*, for $C_5H_5Fe(CO)(COCH_3)$-$[P(C_6H_5)_3]$ $\nu(CO)$ frequencies occur at 1920 and 1598 cm^{-1}).

The reactions of the halides $C_5H_5Fe(CO)_2X$ (X = Cl, Br, or I) with trivalent phosphorus derivatives can give either nonionic products of the types $C_5H_5Fe(CO)$-$(L)X$ or $C_5H_5Fe(L)_2X$ or ionic derivatives of the cations $[C_5H_5Fe(CO)_2L]^+$ depending upon the reaction conditions.[30] Ultraviolet irradiation of the halides C_5H_5-$Fe(CO)_2X$ (X = Br or I) with excess dialkylaminodifluorophosphine gave the carbonyl-free nonionic derivatives $C_5H_5Fe(PF_2NR_2)_2X$. However, the ultraviolet irradiation of $C_5H_5Fe(CO)_2I$ with only about 1.2 equiv of diethylaminodifluorophosphine in benzene solution gave a mixture of the monosubstituted derivative $C_5H_5Fe(CO)[PF_2N(C_2H_5)_2]I$ and the disubstituted

derivative $C_5H_5Fe[PF_2N(C_2H_5)_2]_2I$ with the former predominating presumably because of the particular mole ratio of the reactants used. These two products could readily be separated by chromatography. The monocarbonyl $C_5H_5Fe(CO)[PF_2N(C_2H_5)_2]I$ exhibited a closely spaced pair of $\nu(CO)$ frequencies again indicative of conformational isomers because of restricted rotation around the iron–phosphorus bond (see above and ref 28). The position of the $\nu(CO)$ frequencies in $C_5H_5Fe(CO)[PF_2N(C_2H_5)_2]I$ (1999 and 1980 cm^{-1}) was between that of the $\nu(CO)$ frequency[31] (2021 cm^{-1}) in $C_5H_5Fe(CO)(PF_3)I$ containing the very strongly π-accepting trifluorophosphine ligand and that of the $\nu(CO)$ frequency[30] (1938 cm^{-1}) in $C_5H_5Fe(CO)[P$-$(C_6H_5)_3]I$ containing the relatively weakly π-accepting triphenylphosphine ligand thereby providing the most direct infrared spectroscopic indication of the intermediate π-acceptor strength of the dialkylaminodifluorophosphines.

Cations of the type $[C_5H_5Fe(CO)_2PF_2NR_2]^+$ were not obtained from any of the direct reactions of the $C_5H_5Fe(CO)_2X$ halides with the dialkylaminodifluorophosphines which were investigated in this work. However, the cation $[C_5H_5Fe(CO)_2PF_2NC_5H_{10}]^+$ was obtained through the intermediate 16-electron[32] cation[33] $[C_5H_5Fe(CO)_2]^+$ by reaction of $C_5H_5Fe(CO)_2I$ with the stoichiometric amount of silver tetrafluoroborate in tetrahydrofuran solution followed by addition of the N-piperidinodifluorophosphine to this coordinatively unsaturated intermediate. This cation was conveniently isolated as its hexafluorophosphate salt $[C_5H_5Fe(CO)_2PF_2NC_5H_{10}][PF_6]$. This salt exhibited the expected two $\nu(CO)$ frequencies for a cyclopentadienyliron dicarbonyl derivative.

Some attempts were made to prepare dialkylaminodifluorophosphine substitution products of the anion $[C_5H_5Fe(CO)_2]^-$ since this anion is a useful intermediate for the synthesis of a wide variety of organometallic derivatives.[20] The green color of a tetrahydrofuran solution of $(C_5H_5)_2Fe_2(CO)_2[PF_2N(C_2H_5)_2]_2$ became yellow upon stirring with sodium amalgam at room temperature. Reaction of this solution with excess hexafluorobenzene gave only the known[34] $C_6F_5Fe(CO)_2C_5H_5$ in low yield. No evidence for the formation of any C_6F_5Fe-$(CO)[PF_2N(C_2H_5)_2](C_5H_5)$ was obtained. This suggests that $(C_5H_5)_2Fe_2(CO)_2[PF_2N(C_2H_5)_2]_2$ reacts with sodium amalgam to form the sodium salt $Na[C_5H_5Fe(CO)_2]$ rather than the sodium salt $Na[C_5H_5Fe(CO)PF_2N$-$(C_2H_5)_2]$. In an attempt to prepare a mixed *penta-haptocyclopentadienylmonohaptocyclopentadienyl* derivative[35] $(h^5-C_5H_5)Fe[PF_2N(C_2H_5)_2]_2(h^1-C_5H_5)$, the reaction of $C_5H_5Fe[PF_2N(C_2H_5)_2]_2I$ with thallium cyclopentadienide in tetrahydrofuran at room temperature was investigated. However, the only product isolated after chromatography of the reaction mixture was unchanged starting material $C_5H_5Fe[PF_2N(C_2$-$H_5)_2]_2I$ (46% recovery).

B. Mass Spectra.—The mass spectra of relatively

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(35) For a description of this nomenclature system see F. A. Cotton, *J. Amer. Chem. Soc.*, **90**, 6230 (1968).

few of the dialkylaminodifluorophosphine complexes prepared in this work could be obtained apparently because of limited thermal stability at temperatures where they exhibited appreciable vapor pressure. The molybdenum compounds $C_5H_5Mo(CO)(PF_2NR_2)_2$ exhibited satisfactory mass spectra at the normal 220° chamber temperature except for the formation of a relatively small amount of an unidentified derivative containing two metal atoms and two cyclopentadienyl rings which apparently led to the ions $(C_5H_5)_2Mo_2Cl_2^+$, $(C_5H_5)_2Mo_2Cl^+$, $(C_5H_5)_2MoCl^+$, and $(C_5H_5)_2Mo^+$. The mass spectra of cyclopentadienyliron compounds such as the halides $C_5H_5Fe(PF_2NC_5H_{10})_2X$ (X = Br or I) exhibited only ions corresponding to the free ligand $C_5H_{10}NPF_2$ and ferrocene. However, by reducing the chamber temperature to 80° a satisfactory mass spectrum of the cyclopentadienyliron derivative $C_5H_5Fe(CO)(COCH_3)(PF_2NC_5H_{10})$ could be obtained. The mass spectrum of the vanadium compound $C_5H_5V(CO)_2(PF_2NC_5H_{10})_2$ showed only ions corresponding to the free ligand. The mass spectrum of $C_5H_5Mo(CO)_2(COCH_3)[PF_2N(CH_3)_2]$ showed only ions corresponding to the free ligand and to $CH_3Mo(CO)_3C_5H_5$ suggesting dissociation in the mass spectrometer into these components.

The molecular ions in the mass spectra of the $C_5H_5Mo(CO)(PF_2NR_2)_2Cl$ derivatives can undergo loss of CO to give the ion $C_5H_5Mo(PF_2NR_2)_2Cl^+$ or loss of the R_2NPF_2 ligand to give the ion $C_5H_5Mo(CO)(PF_2NR_2)Cl^+$. The latter ions predominate over the former ions suggesting that the R_2NPF_2 ligands are more readily lost from the $C_5H_5Mo(CO)(PF_2NR_2)_2Cl$ derivatives than the carbonyl ligands. This relates to the observation discussed above that $C_5H_5Mo(CO)[PF_2N(CH_3)_2]_2Cl$ reacts with triphenylphosphine to give $C_5H_5Mo(CO)[PF_2N(CH_3)_2][P(C_6H_5)_3]Cl$ with loss of the dimethylaminodifluorophosphine ligand rather than $C_5H_5Mo[PF_2N(CH_3)_2]_2[P(C_6H_5)_3]Cl$ with loss of the carbonyl ligand. Other ions observed in the mass spectra of the $C_5H_5Mo(CO)(PF_2NR_2)_2Cl$ derivatives are of routine types for transition metal carbonyl, cyclopentadienyl, and halide derivatives[36] and thus do not merit detailed discussion.

The molecular ion in the mass spectrum of the iron compound $C_5H_5Fe(CO)(COCH_3)(PF_2NC_5H_{10})$ can undergo loss of either a neutral CO or CH_3 fragment as was found[37] for the unsubstituted acetyliron derivative $CH_3COFe(CO)_2C_5H_5$. Dehydrogenations of ions containing the $CH_3FeC_5H_5$ fragment, particularly $C_5H_5Fe(CH_3)(PF_2NC_5H_{10})^+$, to give corresponding ions clearly containing C_6H_6Fe or C_6H_5Fe units are observed. The unambiguously observed metastable ions in this mass spectrum all correspond to well-established types of carbonyl losses.[36]

C. Nmr Spectra.

—The proton nmr spectra (Table IV) of all of the cyclopentadienylmetal complexes of dialkylaminodifluorophosphines were in agreement with their proposed structures. The position of the cyclopentadienyl resonance increases in the expected manner[38] as the π-acceptor strengths of other ligands bonded to the same metal atom are decreased. Thus the cyclopentadienyl resonance in $C_5H_5Mo(CO)[PF_2N(CH_3)_2]_2Cl$ occurs at τ 4.59 whereas the cyclopent-

adienyl resonance in $C_5H_5Mo(CO)[PF_2N(CH_3)_2][P(C_6H_5)_3]Cl$ occurs at τ 4.92 in accord with the higher π-acceptor strength of dimethylaminofluorophosphine relative to triphenylphosphine. Similarly the cyclopentadienyl resonance in $C_5H_5Fe(CO)[PF_2N(C_2H_5)_2]I$ occurs at τ 5.22 whereas the cyclopentadienyl resonance in $C_5H_5Fe[PF_2N(C_2H_5)_2]_2I$ occurs at τ 5.55 in accord with the lower π-acceptor strength of diethylaminodifluorophosphine relative to carbon monoxide. The proton nmr spectrum of $(C_5H_5)_2Fe_2(CO)_3PF_2N(C_2H_5)_2$ exhibited two cyclopentadienyl resonances at τ 5.32 and 5.46 in accord with the presence of two nonequivalent cyclopentadienyl groups as required by structure II (L = $(C_2H_5)_2N$). The higher field cyclopentadienyl resonance in this compound can also be assigned to the cyclopentadienyl ring bonded to the iron atom which is bonded to the diethylaminodifluorophosphine ligand both on the basis of the higher π-acceptor strength of carbon monoxide relative to diethylaminodifluorophosphine as discussed above and on the basis of the similarity of the chemical shift of this resonance to that of the single observed cyclopentadienyl resonance in $(C_5H_5)_2Fe_2(CO)_2[PF_2N(C_2H_5)_2]_2$ (IV). The proton nmr spectrum of the molybdenum compound $C_5H_5Mo(CO)_2(COCH_3)[PF_2N(CH_3)_2]$ exhibited only one cyclopentadienyl resonance and one acetyl resonance indicating this compound to be either a single pure isomer or two isomers rapidly interconverting at room temperature.[39] Temperature dependence studies to differentiate between these two possibilities have not yet been performed.

The cyclopentadienyl resonances in the proton nmr spectra of the cyclopentadienylmetal complexes of the dialkylaminodifluorophosphines were split by the phosphorus atoms but this splitting (1–2 cps) was near the resolution limits in these spectra and thus could not be unambiguously observed in all cases. Examples of compounds with two dialkylaminodifluorophosphine ligands which exhibit triplet cyclopentadienyl resonances include $C_5H_5V(CO)_2(PF_2NC_5H_{10})_2$, $C_5H_5Mn(CO)(PF_2NC_5H_{10})_2$, and $C_5H_5Fe(PF_2NR_2)_2I$ (R = ethyl or $R_2 = C_5H_{10}$). Examples of compounds with a single dialkylaminodifluorophosphine ligand which exhibit doublet cyclopentadienyl resonances include $C_5H_5Mo(CO)_2(COCH_3)[PF_2N(CH_3)_2]$ and $C_5H_5Fe(CO)(COCH_3)[PF_2N(C_2H_5)_2]$. The ability to observe this coupling between the cyclopentadienyl protons and the ligand phosphorus atoms in certain cases supports the bonding of the R_2NPF_2 ligands to transition metals through phosphorus rather than nitrogen. If the R_2NPF_2 ligands are bonded to the metals through phosphorus, this coupling is occurring through three bonds (P–M, M–C, and C–H), whereas if the R_2NPF_2 ligands are bonded to the metals through nitrogen, this coupling is occurring through four bonds (P–N, N–M, M–C, and C–H).

The fluorine nmr spectra of the cyclopentadienylmetal complexes of dialkylaminodifluorophosphines were unusually interesting since the PF_2 portions of the R_2NPF_2 ligands exhibited either AX_2, AXY, or AMX patterns (Figure 1 and Table IV; A = P; M, X, and Y = F) depending upon the types and arrangement of ligands coordinated to the metal atom. The observa-

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C₅H₅Mo(CO)₂(COCH₃)PF₂N(CH₃)₂

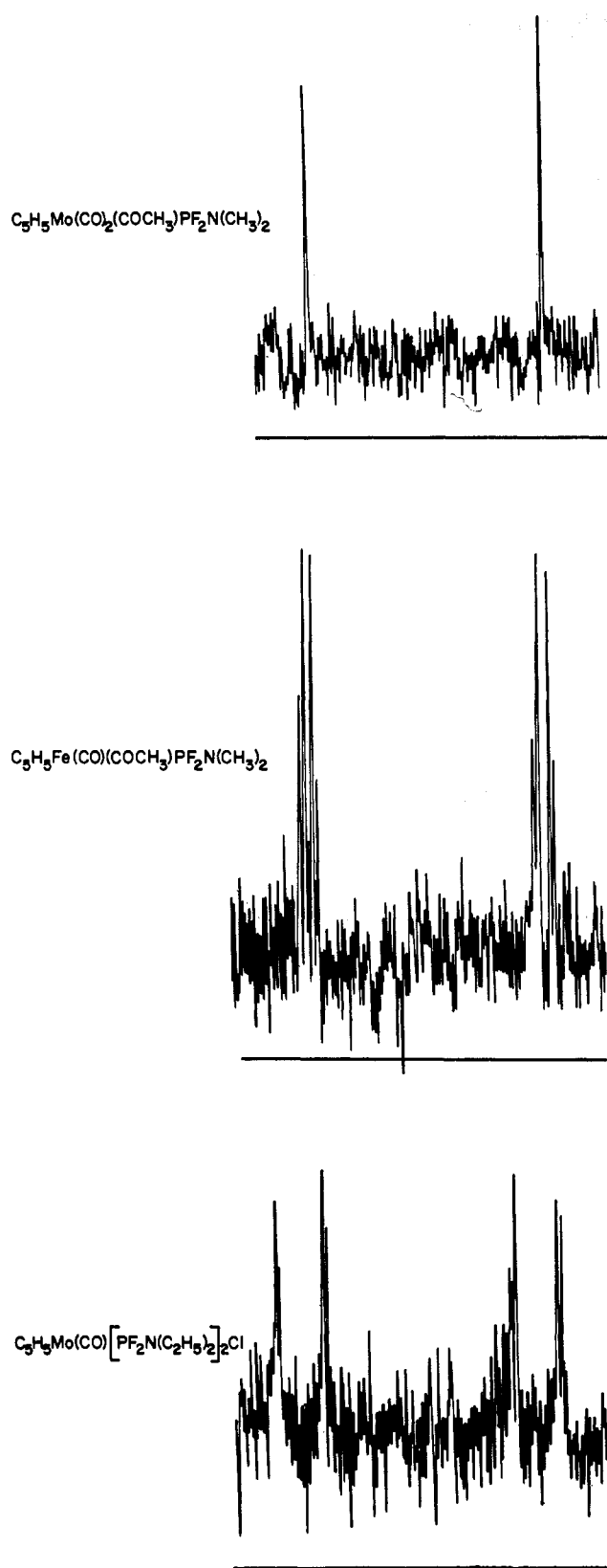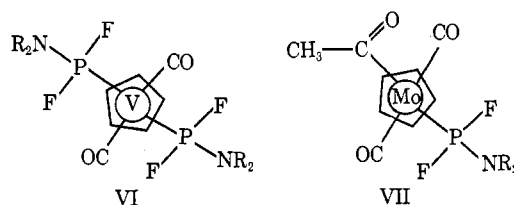C₅H₅Fe(CO)(COCH₃)PF₂N(CH₃)₂

C₅H₅Mo(CO)[PF₂N(C₂H₅)₂]₂Cl

Figure 1.—Fluorine nmr spectra of selected cyclopentadienyl-metal complexes of dialkylaminodifluorophosphines.

tion of an AXY or AMX pattern for the PF_2 portion of the coordinated dialkylaminodifluorophosphine ligand indicates that the two fluorine atoms of the PF_2 group have different chemical shifts. In order for the two fluorine atoms of a PF_2 group of a coordinated dialkyl-

aminodifluorophosphine to have different chemical shifts, restriction of the rotation around the metal-phosphorus bond between the transition metal and the dialkylaminodifluorophosphine must occur. In addition the magnetic environments on each side of the dialkylaminodifluorophosphine ligand must be different. Measurements of the chemical shift difference between the two fluorine atoms in a PF_2 group of a coordinated dialkylaminodifluorophosphine provide a useful indication of the relative magnetic shielding of different ligands that can be bonded to transition metals. Some interesting preliminary results of this type are presented in this paper. Measurements of the temperature dependence of the PF_2 fluorine resonances provide a useful indication of the barrier to rotation around the metal–phosphorus bond between the transition metal and the coordinated dialkylaminodifluorophosphine. The dependence of this rotation barrier on the structure of the transition metal–dialkylaminodifluorophosphine complex represents an interesting area for future investigations.

The AX_2 pattern (e.g., $C_5H_5Mo(CO)_2(COCH_3)$ [PF$_2$N-(CH$_3$)$_2$] in Figure 1) is found when both fluorine atoms of the PF_2 group have identical chemical shifts (i.e., $\Delta\phi = 0$). This pattern consists of a simple doublet with the separation corresponding to the $^1J(PF)$ coupling constant. The AX_2 pattern is necessarily found in the free dialkylaminodifluorophosphine ligands where the two fluorine atoms must have identical environments. In addition the AX_2 pattern with sharp doublet peaks is found in the two compounds C_5H_5V-$(CO)_2(PF_2NC_5H_{10})_2$ and $C_5H_5Mo(CO)_2(COCH_3)$[PF$_2$N-(CH$_3$)$_2$]. This demonstrates that both sides of the dialkylaminodifluorophosphine ligands in these two complexes are identical indicating that these complexes are the diagonal[38] isomers VI and VII rather than the cor-
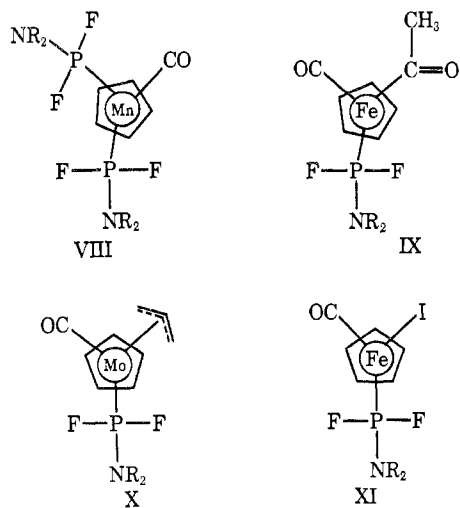

VI   VII

responding lateral isomers.

The AXY pattern (e.g., $C_5H_5Fe(CO)(COCH_3)$-[PF$_2$N(CH$_3$)$_2$] in Figure 1) is found when the two fluorine atoms of the PF_2 group have different chemical shifts but when this chemical shift difference is not sufficiently large (i.e., $\Delta\phi \approx 1$) relative to the $^2J(FF')$ coupling constant (about 15–30 cps). The AXY pattern consists of a pair of quartets. The separation between the pair of quartets corresponds to the $^1J(PF)$ coupling constant (generally about 1100 cps). The outer lines of each quartet of the AXY pattern are weak relative to the inner lines and may not be observable when the signal-to-noise ratio of the nmr spectrum is too poor. Examples of compounds exhibiting the AXY pattern include $C_5H_5Mo(CO)(C_3H_5)$[PF$_2$N-(C$_2$H$_5$)$_2$] and the compounds $C_5H_5Fe(CO)(COCH_3)$-(PF_2NR_2) (R = methyl or ethyl or R$_2$ = C$_5$H$_{10}$).

The AMX pattern (e.g., $C_5H_5Mo(CO)$[PF$_2$N(C$_2$H$_5$)$_2$]$_2$-Cl in Figure 1) is found when the chemical shift difference between the two fluorine atoms of the PF_2 group is large (i.e., $\Delta\phi > 3$) relative to the $^2J(FF')$ coupling con-

stant of 15–30 cps (*i.e.*, 0.3–0.6 ppm at 56.456 Mc). This pattern consists of a pair of quartets with all eight lines of approximately equal relative intensities. The AMX pattern is found in the nmr spectra of the halide derivatives investigated in this work such as C_5H_5Mo-$(CO)(PF_2NR_2)_2Cl$ ($R = CH_3$ or C_2H_5 or $R_2 = C_5H_{10}$), $C_5H_5Fe(CO)[PF_2N(C_2H_5)_2]I$, and $C_5H_5Fe(PF_2N$-$C_5H_{10})_2I$.

As the chemical shift difference of the two fluorine atoms in the PF_2 group increases from zero to infinity, the spectrum of the PF_2 group changes from the AX_2 pattern through the AXY pattern to the AMX pattern. During this process the sharp resonances of the AX_2 doublet first broaden. They next split into the quartet of the AXY pattern. Finally the relative intensities of the outer and inner lines of each quartet of the AXY pattern gradually become equal giving ultimately the idealized AMX pattern with all eight lines of equal relative intensities.
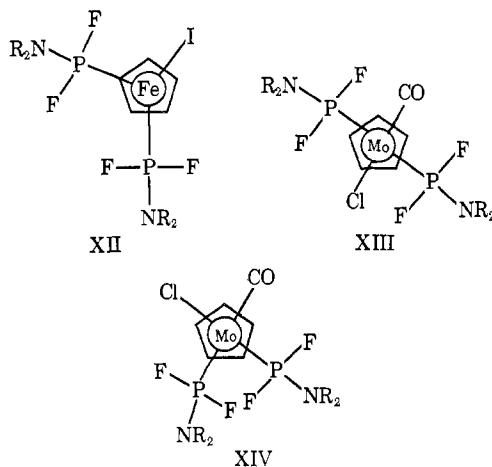
Measurement of the $\Delta\phi$ values in the fluorine nmr spectra of compounds of the type $C_5H_5M(X)(Y)$-(PF_2NR_2) provides a clear indication of the relative shielding characteristics of the X and Y groups. The data presented in this paper allow a comparison between the shielding of the carbonyl group and several other groups encountered in transition metal chemistry. Thus the $\Delta\phi$ values of the compounds $C_5H_5Mn(CO)$-$(PF_2NR_2)_2$ (VIII) are close to the minimum detectable

compounds $C_5H_5Fe(CO)(COCH_3)(PF_2NR_2)$ (IX) fall in the intermediate range 1.2–1.8 consistent with the different modes of bonding of the carbonyl and acetyl groups to the metal atom but with the presence of a carbon–oxygen multiple bond in both ligands. The $\Delta\phi$ value of the π-allyl derivative $C_5H_5Mo(CO)(C_3H_5)$-$[PF_2N(C_2H_5)_2]$ (X) (0.9) also falls into the intermediate range. The $\Delta\phi$ value of the halide $C_5H_5Fe(CO)$-$[PF_2N(C_2H_5)_2]I$ (XI) is one of the highest found in this work indicating considerable difference in the shielding characteristics of the carbonyl and halide ligands. This relatively large difference in the shielding characteristics of carbonyl and halide ligands could arise from the magnetic shielding effects of the three lone pairs on the halogen atom. The $\Delta\phi$ value of the compound $C_5H_5Fe(PF_2NC_5H_{10})_2I$ (XII) is also relatively high (4.2) indicating a rather large difference in the shielding characteristics of halide and dialkylaminofluorophosphine ligands.

The fluorine nmr spectra of the compounds C_5H_5Mo-$(CO)(PF_2NR_2)_2Cl$ exhibited an AMX pattern with a $\Delta\phi$ value in the range 3.2–3.9. This indicates that these compounds are the isomers XIII with the dialkylaminodifluorophosphine ligands in diagonal positions. The corresponding lateral isomers XIV would have all four fluorine atoms nonequivalent and thus would give more complex fluorine nmr spectra. The relatively high $\Delta\phi$ values for the compounds $C_5H_5Mo(CO)(PF_2$-$NR_2)_2Cl$ of structure XIII may thus be taken as a further indication of the different relative shielding of carbonyl and halide ligands.

VIII   IX   X   XI

nonzero values indicating near-equivalence of the shielding characteristics of the carbonyl and dialkylaminodifluorophosphine ligands which bond to the transition metal in similar ways although with different amounts of retroactive bonding. The $\Delta\phi$ values of the

XII   XIII   XIV