(15 mm.), which was found to be of 98% purity by v.p.c. Found: $n^{24}D$ 1.4568 *vs.* $n^{26}D$ 1.4552.[25] The identity of the material as pure α,α-difluorotoluene was further established by v.p.c. and infrared spectrum (comparison with authentic material).

Anal. Calcd. for $C_7H_6F_2$: C, 65.6; H, 4.7. Found: C, 65.3; H, 5.0.

(F) Reaction of Hexamethyldisiloxane with Phenyltetrafluorophosphorane.—With exclusion of moisture, 12.1 g. (0.075 mole) of hexamethyldisiloxane was placed in a 50-ml. three-necked flask, equipped with a Dry Ice reflux condenser, a thermometer, and a dropping funnel. From the dropping funnel was added 18.4 g. (0.1 mole) of phenyltetrafluorophosphorane, an exothermic reaction with formation of a low boiling material being observed. The mixture was refluxed for 1 hr. at $\leq 40°$. A total of 12.9 g. trimethylfluorosilane (93.5%) was collected on distillation, b.p. *ca.* 20° (lit.[26] b.p. 16.4°). The infrared spectrum (gas) was found in complete agreement with the reported spectrum.[27]

Distillation of the higher-boiling residue gave 3.5 g. of unreacted phenyltetrafluorophosphorane [b.p. 34° (13 mm.), identified by infrared analysis], followed by 10.8 g. (89%) of phenylphosphonic difluoride, b.p. 73° (13 mm.); $n^{25}D$ 1.4640, in agreement with the known data.[9] The stoichiometry of the reaction is thus established.

(G) Reaction of *n*-Butyric Anhydride with Phenyltetrafluorophosphorane.—The apparatus used was the same as in the above experiment. No immediate reaction was observed when 20 g. (*ca.* 0.11 mole) of phenyltetrafluorophosphorane was gradually added with stirring to 15.8 g. (0.1 mole) of butyric anhydride. Reflux of a low boiling material occurred on heating to 80° inner temperature (1 hr.). Distillation gave 16.4 g. (91%) of *n*-butyric fluoride, b.p. 69–70° (reported[28] b.p. 69–70°).

Anal. Calcd. for C_4H_7FO: C, 53.3; H, 7.8. Found: C, 53.6; H, 7.9.

Continued distillation *in vacuo* after removal of the acid fluoride gave 15.9 g. (98%) of phenylphosphonic difluoride, b.p. 71–73° (11 mm.); $n^{27}D$ 1.4610. The compound contained a small amount of impurity.

(H) Reaction of Succinic Anhydride with Phenyltetrafluorophosphorane.—A mixture of 10.1 g. (0.1 mole) of succinic anhydride and 20 g. (*ca.* 0.11 mole) of phenyltetrafluorophosphorane was heated with stirring for 6 hr. at 120–140°. The presence of the desired acid fluoride was detected by gas chromatographic investigation of the crude reaction product. The product was separated first by distillation through a 10-in. glass helix packed column [b.p. 30–60° (12 mm.)], 6.5 g. of product containing 80% of succinic fluoride (by v.p.c.) being collected. Pure succinic fluoride was obtained by preparative v.p.c. separation and was characterized by analysis and infrared spectrum.

Anal. Calcd. for $C_4H_4F_2O_2$: C, 39.4; H, 3.3. Found: C, 39.5; H, 3.2.

Continued distillation gave 12.0 g. of phenylphosphonic difluoride [b.p. 69° (10 mm.), identified by v.p.c. comparison with authentic material]. Finally, 3.1 g. of unreacted succinic anhydride was recovered. Succinic fluoride has been obtained by the fluorination of the corresponding dichloride with potassium fluorosulfinate,[29] reported b.p. 47° (12 mm.).

(25) W. A. Sheppard, personal communication.
(26) H. S. Booth and J. F. Suttle, *J. Am. Chem. Soc.*, **68**, 2658 (1946).
(27) H. Kriegsmann, *Z. anorg. allgem. Chem.*, **294**, 113 (1958).
(28) G. Olah, S. Kuhn, and S. Beke, *Chem. Ber.*, **89**, 2553 (1956).
(29) F. Seel and J. Langer, *ibid.*, **91**, 2553 (1958).

CONTRIBUTION FROM E. I. DU PONT DE NEMOURS AND COMPANY,
EXPLOSIVES DEPARTMENT, EXPERIMENTAL STATION, WILMINGTON, DELAWARE

Phosphorus–Fluorine Chemistry. V. Dialkylaminodifluorophosphines and Their Coordination Compounds with Transition Metals[1a]

BY R. SCHMUTZLER[1b]

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The substituted phosphorus fluorides $(CH_3)_2NPF_2$, $(C_2H_5)_2NPF_2$, and $C_5H_{10}NPF_2$ (C_5H_{10} = piperidyl) have been prepared by fluorinating the corresponding chlorides R_2NPCl_2 with SbF_3 or a suspension of NaF in tetramethylene sulfone. These substituted phosphorus fluorides serve as interesting ligands which will displace CO from nickel and molybdenum carbonyls to give compounds of the type $Ni(CO)_2L_2$, NiL_4, and $Mo(CO)_3L_3$ (L is any of the new fluorides).

As noted in the preceding papers,[2a,b] chlorophosphines undergo both oxidation and fluorination with SbF_3 or AsF_3 to give substitution products of PF_3.

$$3R_nPCl_{3-n} + (4-n)SbF_3 \longrightarrow 3R_nPF_{5-n} + 2Sb + (3-n)SbCl_3$$

$$3R_nPCl_{3-n} + (4-n)AsF_3 \longrightarrow 3R_nPF_{5-n} + 2As + (3-n)AsCl_3$$

R = hydrocarbon group; n = 1 or 2

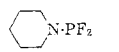
If, however, R in the above equation is replaced by either a dialkylamino group, R_2N–, or an alkoxy group, RO–, normal exchange reaction with either SbF_3 or NaF occurs to give the compounds R_2NPF_2 or $ROPF_2$, respectively.[3,4] No evidence for the compounds R_2NPF_4 or $ROPF_4$, analogous to alkyl- or aryltetrafluorophosphoranes described earlier,[2] has yet been obtained in these reactions.

Details of the fluorination with SbF_3 for the dialkylaminodichlorophosphines are contained in Table I and

(1) (a) The author has been informed by personal communications of Prof. R. W. Parry and Dr. H. Nöth [*cf.* also H. Nöth and H. J. Vetter, *Chem. Ber.*, **96**, 1109, 1298 (1963)] that they have studied independently the synthesis and coordination chemistry of dimethylaminodifluorophosphine. (b) University Chemical Laboratory, Cambridge, England.
(2) (a) R. Schmutzler, *Chem. Ind.* (London), 1868 (1962); (b) R. Schmutzler, *Inorg. Chem.*, **3**, 410 (1964).
(3) The early patent literature [*cf.* (a) French Patent 807,769 (to I. G. Farbenindustrie A.G., Oct. 26, 1936); (b) G. Schrader and O. Bayer (to I. G. Farbenindustrie A.G.), German Patent 664,438 (Aug. 26, 1938); (c) G. Schrader and O. Bayer (to Winthrop Chemical Co.), U. S. Patent 2,146,356 (Feb. 7, 1939)] refers to the fluorination of $(C_2H_5)_2NPCl_2$ and reports $(C_2H_5)_2NPF_2$ as a gas which was condensed to a liquid at −78°. These properties are in sharp disagreement with those found in this study (b.p. of $(C_2H_5)_2NPF_2$ 96° at atmospheric pressure).
(4) The reaction of $ROPCl_2$ with SbF_3 was studied earlier (D. R. Martin and P. J. Pizzolato, *J. Am. Chem. Soc.*, **72**, 4584 (1950); D. R. Martin, W. D. Cooper, D. R. Spessard, and H. S. Booth, *ibid.*, **74**, 809 (1952)). The compounds CH_3OPClF, CH_3OPF_2, and $ClCH_2CH_2OPF_2$ were isolated and characterized.

TABLE I

DIALKYLAMINOFLUOROPHOSPHINES

Compound	Method	Reactants, moles		Reaction conditions, hr. (temp.)	Yield, %	B.p., °C. (mm.); refractive index		Analyses[e] C	H	F	N	P
$(CH_3)_2N\cdot PF_2$	A	$(CH_3)_2N\cdot PCl_2$[a]	0.7	2 (50°)	45.1	47°	Calcd.	21.3	5.4	33.6	...	...
		SbF_3	0.56			$n^{20}D$ 1.3580	Found	21.0	5.7	33.0	...	...
	B	$(CH_3)_2N\cdot PCl_2$	1.1	2.5 (80°)	60.4	48°	Calcd.	...	...	...	12.4	...
		NaF	3.3			$n^{20}D$ 1.3580[e]	Found	...	...	...	12.0	...
		TMSO[b]	(250 ml.)									
$(C_2H_5)_2N\cdot PF_2$	A	$(C_2H_5)_2N\cdot PCl_2$[c]	0.15	2.5 (50–60°)	67	42° (95)	Calcd.	34.0	7.1	26.9	9.9	22.0
		SbF_3	0.2			$n^{20}D$ 1.3840	Found	34.9	7.5	26.9	9.7	21.7
	B	$(C_2H_5)_2N\cdot PCl_2$	0.55	2 (120°)	71.7	47° (100)	Calcd.	...	...	...	9.9	...
		NaF	1.7			$n^{25.5}D$ 1.3840[e]	Found	...	...	...	10.1	...
		TMSO[b]	(130 ml.)									
	A	$C_5H_{10}N\cdot PCl_2$[d]	0.7	3 (50°)	56	47° (30)	Calcd.	39.2	6.6	24.8	...	20.2
		SbF_3	0.56			$n^{26}D$ 1.4252	Found	39.2	7.0	25.3	...	19.4
	B	$C_5H_{10}N\cdot PCl_2$	1	3 (100–150°)	42.5	47° (30)	Calcd.	...	...	...	...	...
		NaF	3			$n^{25}D$ 1.4256[e]	Found	...	...	...	...	...
		TMSO[b]	(200 ml.)									

[a] A. B. Burg and P. J. Slota, *J. Am. Chem. Soc.*, **80**, 1107 (1958). [b] TMSO = tetramethylene sulfone. [c] K. Issleib and W. Seidel, *Chem. Ber.*, **92**, 2681 (1959). [d] A. Michaelis, *Ann.*, **326**, 129 (1903). [e] The identity of the products obtained according to (A) or (B) was further established by a comparison of their infrared spectra.

the properties of the corresponding R_2NPF_2 fluorides are given.

Another suitable preparative reaction for R_2NPF_2 compounds involved the fluorination of the chlorophosphines with a suspension of NaF in tetramethylene sulfone. The procedure was patterned after that of Tullock and Coffman.[5] Potassium fluorosulfinate, KSO_2F,[6] was also effective as a fluorinating agent in this reaction.

Coordination compounds of zerovalent transition metals involving the new ligand molecules were synthesized.

Experimental

Since most of the compounds described are sensitive toward moisture or oxygen, the reactions were run throughout in an atmosphere of dry nitrogen.

Materials.—Solvents such as ether or benzene were dried over sodium. Antimony trifluoride was obtained from Ozark Mahoning Co. Sodium fluoride (Baker & Adamson) was dried at 600° for 10 hr. and allowed to cool in a desiccator. Nickel carbonyl was used as obtained from the Matheson Co., and molybdenum hexacarbonyl used in the preparation of cycloheptatrienemolybdenum tricarbonyl was purchased from Climax Molybdenum Co. Cycloheptatriene (purity >95% by v.p.c.) was obtained from Shell Chemical Co.

(1) **Preparation of Dialkylaminodifluorophosphines** (*cf.* **Table I**).—Two procedures were employed, as reported below.

(A) In a three-necked flask, equipped with a thermometer, a reflux condenser with drying tube, and a solid addition funnel, a slight excess of antimony trifluoride was added in small portions from the solid addition funnel to the stirred dialkylaminodichlorophosphine in the absence of a solvent. A mildly exothermic reaction occurred which was controlled by the rate of addition of the antimony trifluoride. Formation of a gas, fuming in the atmosphere, was observed at temperatures as low as 50°, and viscous residues were left after recovering the volatile fluorination products by distillation. Varying amounts of elementary antimony, characterized by analysis, were found in these residues, indicating some side reaction had occurred.

(B) To a mechanically stirred suspension of sodium fluoride in tetramethylene sulfone was added dropwise at gradually increasing temperature (*cf.* reaction conditions in Table I) the dialkylaminodichlorophosphine. Recovery of products was by distillation.

The dialkylaminodifluorophosphines thus prepared were colorless liquids. Their boiling points were approximately 100° lower than those of the corresponding dichloro compounds. Dialkylaminodifluorophosphines were found to be stable upon brief exposure toward the atmosphere. No changes were noted on prolonged storage in closed containers at room temperature. Both during their preparation and in further reactions the compounds were handled in an atmosphere of dry nitrogen.

Infrared Absorptions of Dialkylaminodifluorophosphines.—Infrared spectra reported in this paper were taken of the pure liquids, solutions of liquids, or solids in certain solvents, or of solids in potassium bromide wafers on a Perkin-Elmer Model 221 instrument.

$(CH_3)_2N\cdot PF_2$ (pure liquid): 2908 (s), 2800 (s); 1691 (w); 1484 (s), 1468 (w), 1450 (s), 1308 (vs), 1182 (vs), 1068 (s), 990 (vs); 800, 743 (vs) (P–F); 705 (s).

$(C_2H_5)_2N\cdot PF_2$ (pure liquid): 2970 (s), 2925 (w), 2876 (w); 1464 (m), 1382 (s), 1290 (m), 1208, 1176 (s), 1103, 1064 (m), 1029 (s), 948 (s); 792, 738 (vs) (P–F); 680 (m).

$C_5H_{10}N\cdot PF_2$ (pure liquid): 2908, 2830 (s); 1449, 1373, 1334 (m), 1274 (w), 1209, 1162, 1117 (m), 1060 (s), 1023 (w), 960 (s), 849 (w); 793, 737 (vs) (P–F); 691 (m).

F^{19} N.m.r. Spectra.—The spectra were obtained on the pure liquids at 56.4 Mc. and were found similar for all three compounds and also comparable to those of other fluorides of trivalent phosphorus. The spectra consist basically of doublets, arising from F^{19}–P^{31} coupling, the doublets being further split by coupling of F^{19} with protons. Thus, a septuplet fine structure is observed for the $(CH_3)_2N\cdot PF_2$ spectrum. Chemical shifts are given in p.p.m. from an internal CCl_3F reference.

	J_{F-F}, c.p.s.	δ, p.p.m.
$(CH_3)_2N\cdot PF_2$	1196	+65.3
$(C_2H_5)_2N\cdot PF_2$	1195	+64.9
$C_5H_{10}N\cdot PF_2$	1192	+65.2

(2) **Preparation of Coordination Compounds Containing Dialkylaminodifluorophosphine Ligands** (*cf.* **Table II**). **(A) Nickel(0) Derivatives. (a) Bis(ligand)dicarbonylnickel(0) Complexes.**—The preparation of bis(piperidine-N-difluorophosphine)-dicarbonylnickel(0) is typical: a three-necked flask was equipped with a thermometer reaching to its bottom, a dropping funnel, and a water-cooled reflux condenser with a Dry Ice condenser on top. The latter was connected to a mercury valve, which pre-

(5) C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2016 (1960).

(6) (a) F. Seel, H. Jonas, L. Riehl, and J. Langer, *Angew. Chem.*, **67**, 32 (1955); (b) F. Seel and L. Riehl, *Z. anorg. allgem. Chem.*, **282**, 293 (1955).

TABLE II

COORDINATION COMPOUNDS CONTAINING DIALKYLAMINODIFLUOROPHOSPHINE LIGANDS

Compound	Reactants	Reaction conditions	Yield, %	Physical properties		Analyses C	H	F	Metal	N	P	Mol wt.
$Ni(CO)_2[(CH_3)_2N\cdot PF_2]_2$	$Ni(CO)_4$ 34.14 g. (0.2 mole); $(CH_3)_2N\cdot PF_2$ 45.2 g. (0.4 mole)	Stirred 40 hr., room temp.[a]	Essentially quantitative	Colorless, nondistillable, viscous liquid	Calcd.	21.1	3.6	22.3	17.2	8.2	18.2	341
					Found	21.3	3.7	22.4	16.9	8.5	18.2	370[b]
$Ni(CO)_2(C_5H_{10}N\cdot PF_2)_2$	$Ni(CO)_4$ 8.5 g. (0.05 mole); $C_5H_{10}N\cdot PF_2$ 15.3 g. (0.1 mole)	Room temp., 50° (1 hr.)	Essentially quantitative	Crystals,[c] m.p. 39.5°	Calcd.	34.2	4.8	18.1	13.9	6.7	14.7	421
					Found	34.4	5.0	17.7	13.9	6.4	14.7	413, 421[b]
$Ni[(CH_3)_2N\cdot PF_2]_4$	$Ni(CO)_4$ 4.58 g. (0.027 mole); $(CH_3)_2N\cdot PF_2$ 18.1 g. (0.16 mole)	Room temp., 3 hr.; reflux 50° (5 hr.); heated under aut. press. 16 hr. (120–140°), $(CH_3)_2N\cdot PF_2$ (0.1 mole) added[d]	59.5	Crystals, m.p. 110.5–111.5°	Calcd.	18.8	4.7	29.7	11.5	11.0	24.2	...
					Found	18.6	4.9	29.5	11.6	10.8	24.7	...
$Ni(C_5H_{10}N\cdot PF_2)_4$	$Ni(CO)_4$ 6.83 g. (0.04 mole); $C_5H_{10}N\cdot PF_2$ 46 g. (0.3 mole)	25–100° (7 hr.)	Quantitative	Crystals, m.p. 164–165.5°	Calcd.	35.8	6.0	22.6	8.8	8.3	18.5	671
					Found	35.7	6.1	22.8	8.8	8.3	18.5	670[b]
$Mo(CO)_3[(CH_3)_2N\cdot PF_2]_3$	$Mo(CO)_3(C_7H_8)$ 2.72 g. (0.01 mole); $(CH_3)_2N\cdot PF_2$ 17 g. (0.15 mole)	20–45° (25 min.)	58	Crystals, m.p. 56–57°	Calcd.	20.8	3.5	22.0	18.5	8.1	17.9	519
					Found	20.7	3.4	22.1	19.0	7.9	16.8	510[b]
$Mo(CO)_3[(C_2H_5)_2N\cdot PF_2]_3$	$Mo(CO)_3(C_7H_8)$ 2.72 g. (0.01 mole); $(C_2H_5)_2N\cdot PF_2$ 12 g. (0.085 mole)	20–45° (25 min.)	...	Colorless, nondistillable oil[e]	Calcd.	29.9	5.0	7.0	...	...	...	...
					Found	30.3	5.2	7.3	...	...	...	...
$Mo(CO)_3(C_5H_{10}N\cdot PF_2)_3$	$Mo(CO)_3(C_7H_8)$ 2.72 g. (0.01 mole); $C_5H_{10}N\cdot PF_2$ 17 g. (0.11 mole)	20–45° (25 min.)	62.6	Crystals, m.p. 100°[f]	Calcd.	33.8	4.7	17.8	15.0	6.6	14.6	639
					Found	33.6	4.6	18.4	16.7	6.4	14.0	600[b]
$Mo(CO)_2(C_5H_{10}N\cdot PF_2)_4$	$Mo(CO)_6$ 10.5 g. (0.04 mole); $C_5H_{10}N\cdot PF_2$ 30.6 g. (0.2 mole)	13 hr. (120–140°) (autogenous pressure)	...	Crystals, m.p. (sealed capillary) 142.0–142.8° dec.	Calcd.	34.6	5.3	19.9	12.6	7.3	16.2	764
					Found	34.8	5.7	19.5	13.6	7.1	16.6	756, 735[b]

[a] In order to remove volatile impurities the reaction mixture was held under vacuum (25°, 0.1 mm.) for 0.7 hr. Distillation of the complex (b.p. 50–60° (0.05 mm.)) was accompanied by extensive decomposition. $Ni(CO)_2[(CH_3)_2N\cdot PF_2]_2$ turned very viscous, but did not solidify upon cooling the pure liquid to −80°. [b] Molecular weights were determined cryoscopically in benzene. [c] The complex is extremely soluble in all common organic solvents. Excellent crystals, 20–30 mm. long, were grown by dissolving the product in the minimum amount of cyclohexane, which was allowed to evaporate slowly in the atmosphere. [d] The reflux temperature of $(CH_3)_2N\cdot PF_2$ was insufficient to effect complete substitution of CO in $Ni(CO)_4$. The reaction vessel (300-ml. Monel cylinder) was repeatedly cooled to −80° during the heating period in order to bleed off CO and to check for the presence of carbonyl groups (infrared). The complex was finally crystallized from ether. Magnetic susceptibility: $\chi_M = -253 \times 10^{-6}$ [c.g.s.] corresponding to a magnetic moment $\mu_{eff} = 0.33$ B.M., after allowing for the diamagnetic corrections. [e] Volatile impurities were pumped off at 40–50° (0.05 mm.) prior to analysis. [f] The volatility of the complex was insufficient for high-vacuum sublimation.

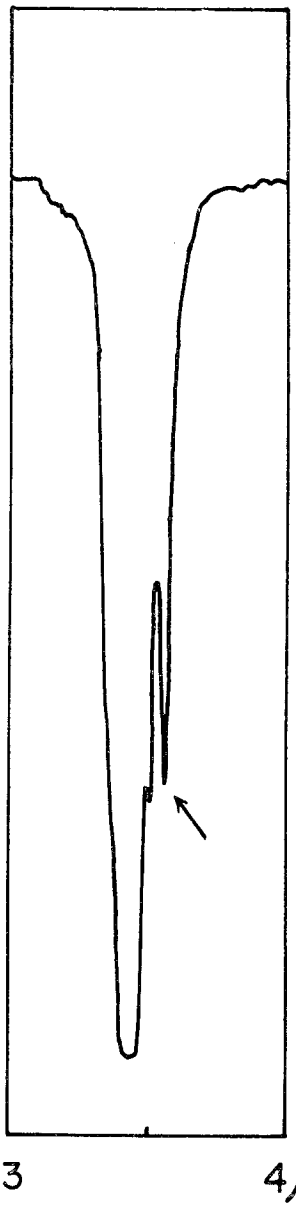


Fig. 1.—Infrared spectrum of $(CH_3)_2N\cdot PF_2$ (pure liquid) in the 3–4 μ region.

vented contact with the air. The system was evacuated and filled with nitrogen. Nickel carbonyl (8.5 g., 0.05 mole) was placed in the flask and 15.3 g. of piperidine-N-difluorophosphine (0.1 mole) was added from the dropping funnel. Carbon monoxide was evolved briskly at room temperature. After 16 hr. stirring at room temperature, the reaction mixture had solidified completely, and no unreacted carbonyl was present. Upon heating to *ca.* 50° inner temperature, the colorless solid melted, but no further gas evolution occurred, and the reaction was considered complete. The complex was extremely soluble in all common organic solvents and recrystallization was difficult. It was found, however, that even the crude material as obtained in the reaction is analytically pure.

Infrared Spectra. $Ni(CO)_2[(CH_3)_2N\cdot PF_2]_2$ (pure liquid): 2910 (m), 2840 (vw), 2800 (w); 2083 (w), 2040, 1993 (vs) (C–O); 1482, 1451 (m); 1300, 1181 (s); 1068 (m); 985 (vs); 829, 800, 775 (vs); 706 (vs).

$Ni(CO)_2(C_5H_{10}N\cdot PF_2)_2$ (in Nujol): 2041, 1993 (vs) (C–O); 1335, 1274 (m); 1205, 1160, 1112, 1060 (vs); 1023 (m); 958 (vs); 894 (m); 850 (w); 828, 802, 780 (vs); 696 (s). Absorptions coinciding with Nujol bands are omitted.

(b) **Tetrasubstituted Nickel(0) Complexes.**—A typical preparation is as follows. **Tetrakis(piperidine-N-difluorophosphine)-nickel(0).** The reaction was carried out in the apparatus described above, which was evacuated and filled with nitrogen. In a countercurrent of nitrogen, 46 g. (0.3 mole) of piperidine-N-difluorophosphine was placed in the flask while 6.83 g. (0.04 mole) of nickel carbonyl was added dropwise with stirring within 40 min., carbon monoxide being vigorously evolved. After 7 hr. stirring at gradually increased temperature, when the inner temperature was 100°, a sudden increase in temperature occurred and the contents of the flask solidified. Infrared analysis indicated almost complete substitution of the carbonyl groups, m.p. of the crude material 157°. An analytical sample was recrystallized from benzene, m.p. 164–165.5°. Upon further heating in the atmosphere the product turned yellow only slowly at temperatures as high as 240°.

The volatility of the material was insufficient to permit its sublimation under high vacuum without sizable decomposition. The stability of the complex in the atmosphere, even in solution in organic solvents and toward aqueous (nonoxidizing) acids and even aqueous 20% sodium hydroxide, is noteworthy.

Weissenberg photographs, powder diffraction studies, and density measurements by the flotation method[7] indicate the unit cell of the compound to be tetragonal, containing two molecules with the nickel atoms at (000) and ($^1/_2$, $^1/_2$, $^1/_2$); $a = b = 13.32 \pm 0.02$ Å.; $c = 8.249 \pm 0.009$ Å.

Magnetic susceptibility of $Ni(C_5H_{10}N\cdot PF_2)_4$: $\chi_M = -337.5 \times 10^{-6}$ [c.g.s.] at 297°K., corresponding to a magnetic moment $\mu_{eff} = 0.44$ B.M.

Infrared Spectra. $Ni(C_5H_{10}N\cdot PF_2)_4$ (solid in KBr): 2934 (s), 2858 (m); 1465 (w), 1451 (m), 1375 (s), 1341 (m), 1278 (m), 1256 (w), 1206 (s), 1166 (s), 1114 (s), 1060 (vs), 1025 (m), 958 (vs), 896 (m), 854 (s), 834 (m), 813 (w); 776 (vs), 762 (m), 744 (w) (P–F); 696 (vs).

$Ni[(CH_3)_2N\cdot PF_2]_4$ (solid in KBr): 2924 (s); 2858 (w), 2818 (m); 1484, 1454 (s); 1439, 1412 (w); 1295, 1182, 1067 (s), 981 (vs); 874 (w); 799, 760, 702 (vs).

(B) **Substitution Products of Molybdenum Hexacarbonyl.**—The starting compound, cycloheptatrienetricarbonylmolybdenum(0), was obtained according to the method of Wilkinson, *et al.*[8]

The reactions of cycloheptatrienetricarbonylmolybdenum(0) with the various ligands[9] were conducted by mixing 0.01 mole of the π-complex with excess of the ligand below room temperature in a 25-ml. three-necked flask, equipped with a reflux condenser, a thermometer, and a stopcock adapter. The apparatus was evacuated and filled with nitrogen.

The mildly exothermic exchange reaction was controlled by ice cooling (temperatures not exceeding 45–50°). The red-brown mixtures were stirred for 20 to 30 min.; the volatile products were then removed *in vacuo* (*ca.* 1 mm., temperature $\leq$30°). The residue thus left was extracted with several 10-ml. portions of hexane, and the combined extracts were decolorized by brief boiling with charcoal. After partial evaporation of the solvent, crystallization was effected by chilling with ice or Dry Ice. For further details, *cf.* Table II.

Infrared Spectra of Tricarbonyl–Molybdenum(0) Derivatives. $Mo(CO)_3[(CH_3)_2N\cdot PF_2]_3$ (in KBr): 2925 (m), 2858, 2818 (sh); 2000, 1923 (vs) (C–H); 1481 (m), 1456 (m), 1299 (s), 1175 (s), 1067 (m), 985 (vs), 826 (sh), 808 (vs, bd), 777 (s, bd); 714 (sh), 705 (vs).

$Mo(CO)_3[(C_2H_5)_2N\cdot PF_2]_3$ (solution in benzene): 2970 (m), 2915 (sh); 1995, 1919 (vs) (C–O); 1460 (m); 1381 (m), 1289 (w), 1205 (s), 1166 (s), 1098 (w), 1064 (w), 1021 (s), 950 (s), 922 (m); 834 (s), 804 (s, bd), 790 (s, bd).

$Mo(CO)_3(C_5H_{10}N\cdot PF_2)_3$ (in KBr): 2924 (m), 2849 (m); 1996, 1934 (vs), 1890 (sh) (C–O); 1453, 1444 (m), 1375 (s), 1361 (w); 1336 (s), 1277 (m), 1203 (s), 1152 (s), 1112 (s), 1067, 1060

(7) B. Greenberg, A. Amendola, and R. Schmutzler, *Naturwissenschaften*, **50**, 518 (1963).

(8) E. W. Abel, M. A. Bennett, R. Burton, and G. Wilkinson, *J. Chem. Soc.*, 4559 (1958).

(9) E. W. Abel, M. A. Bennett, and G. Wilkinson, *ibid.*, 2323 (1959).

(s), 1025 (m), 959 (vs), 896 (vs), 853 (s); 834 (m), 816, 802 (vs), 766 (vs); 695 (vs).

Tetrakis(piperidine-N-difluorophosphine)dicarbonylmolybdenum(0). A 75-ml. Monel cylinder was flushed with nitrogen and charged with a mixture of 30.6 g. (0.2 mole) of piperidine-N-difluorophosphine and 10.5 g. (0.04 mole) of molybdenum hexacarbonyl. The cylinder was sealed, cooled to −190°, evacuated to 0.05 mm., and heated for 5 hr. in an oil bath at 120°. Strong carbon monoxide pressure was noted when the cylinder was opened at −80°. The cylinder was sealed again as described before and heated for two further 4-hr. periods at 120–140°. There was little carbon monoxide pressure when the cylinder was opened finally.

A faintly yellow liquid was obtained which was rinsed out with ether and decolorized by brief boiling with charcoal. Evaporation *in vacuo* (first aspirator, then oil pump) at room temperature left a viscous oil [2-hr. pumping at 30° (0.5 mm.)]. This oil was dissolved in the minimum amount of hot ether and hexane was added until precipitation commenced. Upon cooling in a refrigerator, 2.6 g. of a white solid precipitated which was once recrystallized from ether–hexane and dried *in vacuo;* m.p. (sealed tube) 142.0–142.8° (with darkening).

Infrared Spectrum (solid in KBr): 2917, 2840 (s); 1946, 1897 (vs) (C–O) (*cis*); 1450, 1442 (m); 1373 (s); 1333, 1277 (m); 1204, 1160, 1110 (s); 1064 (vs); 1025 (m); 957 (vs); 898, 855 (m); 827, 796, 779 (vs), 769 (sh) (P–F); 752 (vw); 693 (vs). The CO absorptions were found at the same position when the spectrum was taken in CCl_4 solution.

Discussion

A number of coordination compounds of zerovalent transition metals, such as nickel and molybdenum, involving the new dialkylaminodifluorophosphines as donor molecules, could readily be obtained according to

$$Ni(CO)_4 + 2L \longrightarrow Ni(CO)_2L_2 + 2CO \quad (a)$$

$$Ni(CO)_4 + 4L \longrightarrow NiL_4 + 4CO \quad (b)$$

$$Mo(CO)_3(C_7H_8) + 3L \longrightarrow Mo(CO)_3L_3 + C_7H_8 \quad (c)$$

C_7H_8 = cycloheptatriene; L = $(CH_3)_2N\cdot PF_2$, $(C_2H_5)_2N\cdot PF_2$, or $C_5H_{10}N\cdot PF_2$)

Exchange of carbon monoxide in nickel carbonyl commenced readily at room temperature and, depending on the ratio of reactants and reaction conditions, partially or completely substituted derivatives of nickel carbonyl could be obtained. Thus, the dicarbonylnickel(0) complexes were formed by stirring $Ni(CO)_4$ and the ligand (molar ratio 1:2) for several hours at room temperature without further heating. Furthermore, the dicarbonyl was formed, regardless of whether the ligand was added to the carbonyl or *vice versa*, indicating an equilibrium reaction. Both dicarbonylnickel(0) complexes were obtained directly in analytical purity. A tendency to disproportionate to $Ni(CO)_4$ and the completely substituted products, NiL_4, was apparent; thus upon attempted high-vacuum distillation of $Ni(CO)_2[(CH_3)_2N\cdot PF_2]_2$, the still residue approached the composition $Ni[(CH_3)_2N\cdot PF_2]_4$. Diethylaminodifluorophosphine at atmospheric pressure (maximum temperature *ca.* 85°) replaced close to three CO groups in $Ni(CO)_4$.

Heating under autogenous pressure was required to effect complete substitution of CO groups in $Ni(CO)_4$ with $(CH_3)_2N\cdot PF_2$, while $C_5H_{10}N\cdot PF_2$ reacted completely at atmospheric pressure, $Ni(C_5H_{10}N\cdot PF_2)_4$ crystallizing at *ca.* 100° in quantitative yield.

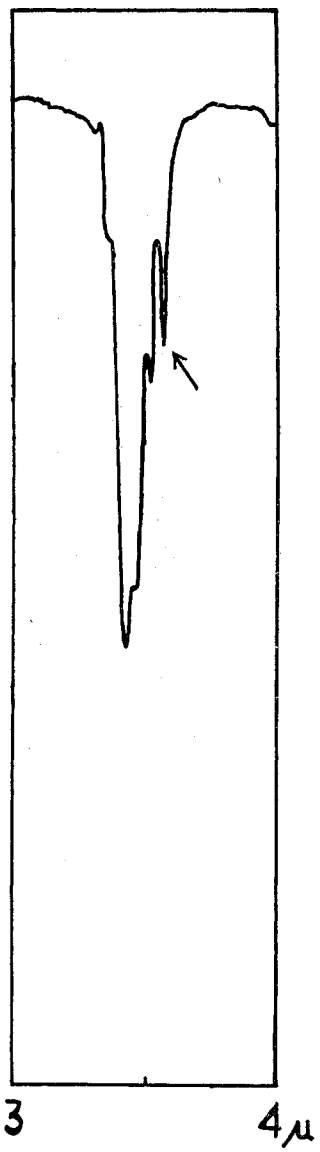


Fig. 2.—Infrared spectrum of $Ni(CO)_2[(CH_3)_2N\cdot PF_2]_2$ (pure liquid) in the 3–4 μ region.

Several tricarbonyl–molybdenum(0) derivatives were obtained by the exchange of the hydrocarbon ligand in cycloheptatrienetricarbonylmolybdenum(0)[8,9] with excess of the appropriate dialkylaminodifluorophosphine (eq. c). The exchange reactions proceeded readily with slight evolution of heat; reaction periods as short as 20–30 min. were sufficient. Especially interesting is the substitution of four CO groups in $Mo(CO)_6$ upon heating the hexacarbonyl with $C_5H_{10}N\cdot PF_2$ in a molar ratio of *ca.* 1:5. Tetrasubstitution of carbon monoxide in a group VI hexacarbonyl has previously been described only with the bidentate ligand *o*-phenylene-bis-dimethylarsine,[10] where the chelating properties of the ligand may be a driving force for the replacement of carbon monoxide. No

(10) (a) H. L. Nigam and R. S. Nyholm, *Proc. Chem. Soc.*, 321 (1957); (b) H. L. Nigam, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.*, 1803 (1960).

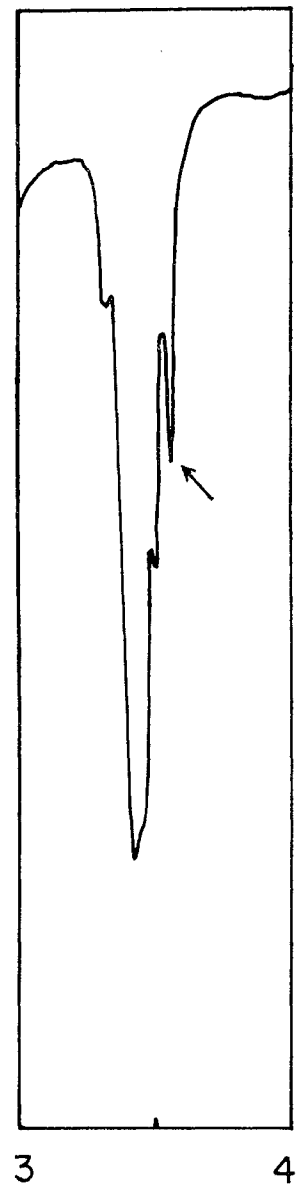


Fig. 3.—Infrared spectrum of $Ni[(CH_3)_2N \cdot PF_2]_4$ (in KBr) in the 3–4 μ region.

monodentate ligand has been reported to replace directly more than three CO groups in a group VI hexacarbonyl.

The ease of these new fluorine-containing phosphine ligands to coordinate is noteworthy in view of the known sluggish reaction between the parent compound, PF_3, and $Ni(CO)_4$, for instance.[11-13] Substitution of only one fluorine atom in phosphorus trifluoride thus leads to a marked change in Lewis basicity, which evidently can be controlled by the choice of proper substituents on the trivalent phosphorus. It has been reported recently that phosphorus trifluoride was not sufficiently basic to stabilize B_4H_8CO, whereas trimethylamine was too strongly basic and led to further attack on the B_4H_8 group.[14] A stable B_4H_8 adduct could be obtained when dimethylaminodifluorophosphine was employed, its Lewis basicity being intermediate between trimethylamine and phosphorus trifluoride.

Similar considerations presumably hold for the coordination of dialkylaminodifluorophosphines to transition metals. It is apparent that the stability of the transition metal complexes involving dialkylaminodifluorophosphine ligands is greatly increased, compared to complexes containing fluorophosphine, RPF_2, ligands,[15,16] the latter containing a direct carbon–phosphorus bond. Dialkylaminodifluorophosphine (and fluorophosphite[17]) complexes are more stable than fluorophosphine complexes, both as pure compounds and, especially, in solution in organic solvents.

Some information has been obtained on the bonding site in dialkylaminodifluorophosphines, and it is suggested that their coordination to transition metals occurs through phosphorus rather than nitrogen. Thus, $p\pi$–$d\pi$ interaction between nitrogen and phosphorus (promoted by the electronegative fluorine atoms) is expected to reduce the basicity of nitrogen and increase the tendency of phosphorus to coordinate.[18] In the case of tetrakis(piperidine-N-difluorophosphine)-nickel(0), strong support for coordination *via* phosphorus is provided by the determination of the crystal structure, which is currently in progress.[7] Especially informative as to the bonding site in transition metal complexes of dialkylaminodifluorophosphines is a comparison of the C–H stretching region in the infrared spectrum both in uncoordinated $(CH_3)_2N \cdot PF_2$ and in its metal complexes.

It is known that the presence of a CH_3 group bonded to nitrogen which also bears a lone pair of electrons, *i.e.*, $>\bar{N}-CH_3$, gives rise to a characteristic symmetric C–H stretching frequency in the 2760–2820 $cm.^{-1}$ region.[19] If the lone pair of electrons is tied up by coordination, this absorption will disappear. As the infrared spectra, for instance, of $(CH_3)_2N \cdot PF_2$, $Ni(CO)_2[(CH_3)_2N \cdot PF_2]_2$, and $Ni[(CH_3)_2N \cdot PF_2]_4$ (Fig. 1–3) show, this absorption is virtually unaffected in the metal complexes, lending strong support to donation through phosphorus rather than nitrogen in $(CH_3)_2N \cdot PF_2$ complexes.

Also of interest are the infrared absorptions due to carbonyl groups in the partially substituted derivatives of nickel and molybdenum carbonyl, which are listed, together with some previously reported data, in Tables III and IV.

(11) J. Chatt and A. A. Williams, *J. Chem. Soc.*, 3061 (1959).
(12) G. Wilkinson, *J. Am. Chem. Soc.*, **73**, 5501 (1951).
(13) Only very recently, complete exchange of CO in $Ni(CO)_4$ by direct interaction with PF_3 could be accomplished for the first time, temperature and rate of addition being very carefully controlled: M. Bigorgne and A. Zelwer, *Bull. Soc. Chim. France*, 1986 (1960).
(14) G. Ter Haar, Sr. M. A. Fleming, and R. W. Parry, *J. Am. Chem. Soc.*, **84**, 1767 (1962).
(15) F. Seel, K. Ballreich, and R. Schmutzler, *Chem. Ber.*, **94**, 1173 (1961).
(16) R. Schmutzler, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p. 150.
(17) R. Schmutzler, *Chem. Ber.*, **96**, 2435 (1963).
(18) *Cf.* G. Ewart, A. P. Lane, and D. S. Payne, VII International Conference on Coordination Chemistry, Stockholm and Uppsala, June 25–29, 1962, Abstracts, p. 229.
(19) J. T. Braunholtz, E. A. V. Ebsworth, F. G. Mann, and N. Sheppard, *J. Chem. Soc.*, 2780 (1958); the author is indebted to a referee for drawing his attention to this reference.

TABLE III

INFRARED CARBONYL FREQUENCIES IN NICKEL DICARBONYL DERIVATIVES

Compound	ν_{C-O}, cm.$^{-1}$	Conditions	Ref.
$Ni(CO)_4$	2050, 2043	Gas	[a]
$Ni(CO)_2[P(n\text{-}C_4H_9)_3]_2$	2000, 1935	Soln. in cyclohexane	[b]
$Ni(CO)_2[P(C_6H_5)_3]_2$	2010, 1955	Soln. in cyclohexane	[b]
$Ni(CO)_2[P(OC_6H_5)_3]_2$	2034, 1975	Soln. in cyclohexane	[b]
$Ni(CO)_2[(CH_3)_2N \cdot PF_2]_2$	2040, 1993	Pure liquid	This work
	2049, 1997	Soln. in chloroform	This work
$Ni(CO)_2(C_5H_{10}N \cdot PF_2)_2$	2041, 1993	Nujol mull	This work
	2049, 1996	Soln. in chloroform	This work
$Ni(CO)_2(PCl_3)_2$	2090, 2065	Soln. in cyclohexane	[b]

[a] B. L. Crawford and P. C. Cross, *J. Chem. Phys.*, **6**, 525 (1938). [b] L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.*, **81**, 4200 (1959).

TABLE IV

INFRARED CARBONYL FREQUENCIES IN MOLYBDENUM TRICARBONYL DERIVATIVES

Compound	ν_{C-O}, cm.$^{-1}$	Conditions	Ref.
$Mo(CO)_6$	2000	Gas	[a]
$[(C_2H_5)_2N \cdot PF_2]_3Mo(CO)_3$	1995, 1919	Soln. in C_6H_6	This work
$(C_5H_{10}N \cdot PF_2)_3Mo(CO)_3$	1996, 1934	Solid in KBr	This work
$[(CH_3)_2N \cdot PF_2]_3Mo(CO)_3$	2000, 1923	Solid in KBr	This work
$C_7H_8Mo(CO)_3$	2000, 1935, 1911	Soln. in cyclohexane	[b]
$[(C_6H_5O)_2P]_3Mo(CO)_3$	2020, 1923	Soln. in CCl_4	[c]
$(ClCH_2PF_2)_3Mo(CO)_3$	2038, 1970	Soln. in C_6H_6	16
$(PCl_3)_3Mo(CO)_3$	2040, 1990	Solid in KBr	16
	2041, 1989, 1960(sh)	Soln. in CCl_4	9
$(PF_3)_3Mo(CO)_3$	2085, 2055, 1990	Solid in KBr	16

[a] N. J. Hawkins, H. C. Mattraw, W. W. Sabol, and D. R. Carpenter, *J. Chem. Phys.*, **23**, 2422 (1955). [b] R. D. Fischer, *Chem. Ber.*, **93**, 165 (1960). [c] T. A. Magee, C. N. Matthews, T. S. Wang, and J. H. Wotiz, *J. Am. Chem. Soc.*, **83**, 3200 (1961).

The CO stretching absorptions for both nickel dicarbonyl and molybdenum tricarbonyl derivatives were found in the region typical for terminal CO groups. A pronounced increase in the CO frequencies of phosphine-substituted metal carbonyls, as compared with those of derivatives containing nitrogen donor molecules, has been attributed to the π-character of the metal–ligand bond in the phosphine complexes.[9] The multiple bond character of the metal–phosphorus bond is increased with increasing availability of donor atom d-orbitals due to the influence of the electronegative fluorine substituents. This effect is reflected in the steady rise of the carbonyl stretching frequencies in both series (Tables III and IV).

CONTRIBUTION FROM E. I. DU PONT DE NEMOURS AND COMPANY, EXPLOSIVES DEPARTMENT, EXPERIMENTAL STATION, WILMINGTON, DELAWARE

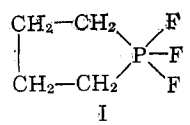
Phosphorus–Fluorine Chemistry. VI. A New Synthesis of Heterocyclic Phosphorus Compounds: Preparation of Di- and Trifluorophosphoranes *via* Phosphine Sulfide Intermediates[1a]

BY R. SCHMUTZLER[1b]

Received March 19, 1963

Reaction of α,ω-di-Grignard reagents with thiophosphoryl chloride led to the formation of novel heterocyclic biphosphine disulfides, bis(cyclotetramethylene)biphosphine disulfide and bis(cyclopentamethylene)biphosphine disulfide. Both were converted to the corresponding cyclic trifluorophosphoranes by means of antimony trifluoride. Further trifluorophosphoranes were prepared from tetraalkyl biphosphine disulfides and antimony trifluoride. Difluorophosphoranes could be obtained in a similar manner from tertiary phosphine sulfides by fluorination with antimony trifluoride.

In the course of a stereochemical study on fluorophosphoranes, R_nPF_{5-n} (R = organic hydrocarbon group; n = 1, 2, 3) by means of F^{19} n.m.r. spectroscopy, special interest arose in fluorophosphoranes containing a PF_3 group as part of a cyclic system, such as



I

where a rapid intramolecular exchange of equatorial and apical fluorine atoms in the trigonal bipyramidal structure was found to occur.[2]

Cyclotetramethylenetrifluorophosphorane (I) was readily obtained as a volatile liquid, b.p. 62° (90 mm.), upon reaction of cyclotetramethylenemonochlorophosphine (II) with antimony trifluoride.[3] The chlorophosphine II, however, is available only by a rather complex, low-yield, three-step sequence,[4] and it appeared desirable to synthesize a heterocyclic phosphorus intermediate which might permit a more facile access to a fluorophosphorane such as I. The synthesis of I can be realized *via* a novel biphosphine disulfide intermediate III as shown in Scheme I.

The reaction of thiophosphoryl chloride with the double Grignard reagent from 1,5-dibromopentane gave the corresponding six-membered heterocycle IV, which

(1) (a) Preceding paper in this series: R. Schmutzler, *Inorg. Chem.*, **3**, 415 (1964); (b) University Chemical Laboratory, Cambridge, England.

(2) E. L. Muetterties, W. Mahler and R. Schmutzler, *ibid.*, **2**, 613 (1963).

(3) R. Schmutzler, *ibid.*, **3**, 410 (1964).

(4) A. B. Burg and P. J. Slota, *J. Am. Chem. Soc.*, **82**, 2148 (1960).