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## Phosphorus-Fluorine Chemistry. XVIII.<sup>1a</sup> Nuclear Magnetic Resonance Studies on Coordination Compounds Involving Fluorine-Containing Phosphine Ligands

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$P^{31}$  and  $F^{19}$  nmr data have been obtained for a wide variety of coordination compounds of zerovalent nickel and molybdenum of the types  $Ni(CO)_2L_2$ ,  $NiL_4$ , and  $Mo(CO)_3L_3$  ( $L$  = fluorophosphite, dialkylaminofluorophosphine, or fluorophosphine). Both  $P^{31}$  and  $F^{19}$  chemical shifts were found to be at lower field in the complexes, compared to the free ligands. Likewise, a decrease in  $J_{P-F}$  on complexation is almost invariably observed. These trends are discussed qualitatively in terms of the following factors: formation of a  $\sigma$  bond between phosphorus and the metal, magnetic anisotropy of the metal atom, increased paramagnetic contribution, changes in the coordination number of phosphorus and/or the bond angles of the ligands, polarization of lone-pair electron orbitals, and  $d_{\pi}-d_{\pi}$  bonding between phosphorus and the metal. The preparation of some new coordination compounds is also described.

### Introduction

$P^{31}$  nuclear magnetic resonance spectroscopy has developed into a major probe in the characterization and structural elucidation of phosphorus compounds.<sup>2</sup> It is noteworthy, therefore, that very little work has been reported on the use of  $P^{31}$  nmr spectroscopy in the study of transition metal complexes containing phosphine ligands.<sup>3,4</sup> Numerous other physical methods have been employed in attempts to elucidate the nature of the metal-ligand bond in these compounds.

We have had occasion to study the  $P^{31}$  nmr spectra of a series of transition metal coordination compounds involving fluorophosphite,<sup>5</sup> dialkylaminofluorophosphine,<sup>6,7</sup> and fluorophosphine<sup>8</sup> ligands. In these compounds, conclusions as to the nature of the metal-ligand bond may be based not only on the observation of changes in the  $P^{31}$  chemical shift of coordinated *vs.* free ligand but also on  $F^{19}$  nmr data for free and coordinated ligands. Furthermore, a useful feature is the existence of spin-spin coupling between  $P^{31}$  and directly bonded  $F^{19}$ , and P-F coupling constants are expected to provide further insight into the properties of the metal-phosphorus bond. Pertinent nmr data have been reported, thus far, only for the compounds  $Ni(PF_3)_4$ <sup>3,9</sup> and  $Pd(PF_3)_4$ .<sup>9</sup>

### Experimental Section

$P^{31}$  and  $F^{19}$  nmr spectra were obtained on a Varian Associates HR-60 spectrometer at 24.3 and 56.4 Mc/sec, respectively.

(1) (a) For No. XVII in this series see: G. S. Reddy and R. Schmutzler, *Inorg. Chem.*, **5**, 164 (1966); (b) Explosives Department, Repauno Development Laboratory, Gibbstown, N. J.; present address: Experimental Station, Wilmington, Del.; (c) Experimental Station, Wilmington, Del.; present address: Department of Chemistry, University of Technology, Loughborough, Leicestershire, England.

(2) For a review of  $P^{31}$  nmr spectroscopy see: E. Fluck, "Die Kernmagnetische Resonanz und ihre Anwendung in der Anorganischen Chemie," Springer Verlag, Berlin, Göttingen, Heidelberg, 1963.

(3) L. S. Meriwether and J. R. Leto, *J. Am. Chem. Soc.*, **83**, 3192 (1961).

(4) A. Pidcock, R. E. Richards, and L. M. Venanzi, *Proc. Chem. Soc.*, 184 (1962); *J. Chem. Soc., Sect. A*, 1707 (1966).

(5) R. Schmutzler, *Chem. Ber.*, **96**, 2435 (1963).

(6) R. Schmutzler, *Inorg. Chem.*, **3**, 415 (1964).

(7) R. Schmutzler, *J. Chem. Soc.*, 5630 (1965).

(8) R. Schmutzler, *Chem. Ber.*, **98**, 552 (1965).

A Varian Associates A-60 spectrometer was used for the  $H^1$  spectra. In the case of solid samples, saturated solutions in the appropriate solvents (see tables) were used. No solvent was used for liquid samples. Calibrations were carried out by either the side-band or the superposition technique, depending on the complexity of the spectra. Eighty-five per cent aqueous  $H_3PO_4$  was the external reference for  $P^{31}$ , and  $CFCl_3$  was the internal reference for  $F^{19}$  spectra. Tetramethylsilane was used as internal reference for  $H^1$  spectra.

All compounds were prepared by published procedures (see list of references), except for the following.

**1. Tetrakis(2-chloro-1,3,2-benzodioxaphosphole)nickel(0).**—The reaction was conducted with exclusion of air and moisture, as outlined in previous reports.<sup>5-8</sup> Nickel carbonyl (12.0 g, 0.07 mole) was added dropwise with stirring to 70 g (0.4 mole) of 2-chloro-1,3,2-benzodioxaphosphole, CO being vigorously evolved. After 3 hr of stirring at room temperature, the mixture was heated slowly to 75° over a period of 4 hr, when it suddenly solidified. The solid product was sucked dry and washed with petroleum ether (bp 60–80°). The yield was 50.0 g (94%). An analytical sample was recrystallized once from benzene-petroleum ether.

*Anal.* Calcd for  $Ni(C_6H_4O_2PCl)_4$ : C, 38.1; H, 2.1; Cl, 18.7; Ni, 7.8; P, 16.4; mol wt, 756.82. Found: C, 37.9; H, 2.3; Cl, 18.5; Ni, 7.4; P, 16.4; mol wt, 728 (cryoscopic in benzene).

Infrared spectrum (KBr pellet):  $\sim 3000$  (vw); 1615 (w); 1469 (vs); 1325 (s); 1270 (w); 1212 (vs); 1144, 1090 (m); 1008 (m); 926, 881 (s); 827 (vs); 778 (s, b); 754 (sh); 746, 739 (vs); 717 (w)  $cm^{-1}$ .

**2. Bis(diethylaminodifluorophosphine)dicarbonylnickel(0).**—Under the usual anaerobic conditions, 11.3 g (0.08 mole) of diethylaminodifluorophosphine<sup>9</sup> was added dropwise with stirring to 6.85 g (0.04 mole) of nickel carbonyl. The mixture was stirred for 20 hr at room temperature and for 3 hr at 50°, until evolution of carbon monoxide had ceased. No volatile material came off on pumping at room temperature (0.3 mm), indicating that all the diethylaminodifluorophosphine had reacted. An infrared spectrum of the liquid left after 0.7 hr of pumping at room temperature showed two very strong CO bands, as expected for a  $Ni(CO)_2$  derivative. The yield was 15.2 g (96%).

*Anal.* Calcd for  $Ni[(C_2H_5)_2NPF_2]_2(CO)_2$ : C, 30.3; H, 5.1; F, 19.1; N, 7.1; Ni, 14.8; P, 15.6; mol wt, 396.94. Found: C, 30.5; H, 5.3; F, 20.4; N, 7.2; Ni, 14.9; P, 16.0; mol wt, 435 (cryoscopic in benzene).

Infrared spectrum (neat): 2970 (s); 2930 (m); 2890, 2865 (w); 2090 (w); 2046, 1992 (vs); 1460 (m); 1380 (s); 1367 (w); 1295

(9) G. F. Svatos and E. E. Flagg, *Inorg. Chem.*, **4**, 422 (1965).

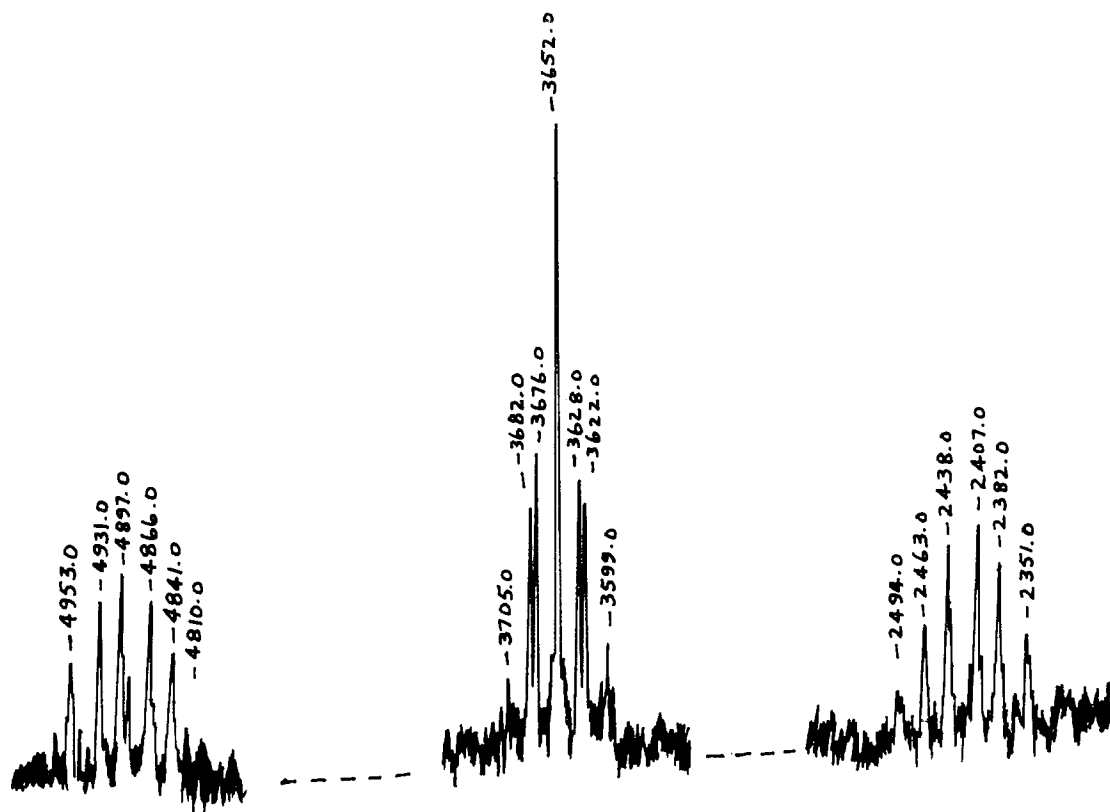


Figure 1.  $P^{31}$  nmr spectrum of  $Mo(CO)_3(C_6H_5OPF_2)_3$  (benzene solution). Calibration is in cycles per second from  $H_3PO_4$  external reference.

(m); 1210, 1174 (vs); 1011, 1066 (m); 1026 (vs, b); 950 (vs); 924 (m); 826, 789 (vs, b); 685 (vs); 520 (s); 476, 445 (m, b)  $cm^{-1}$ . An infrared spectrum recorded in carbon tetrachloride solution was completely identical with that of the neat compound.

**3. Tetrakis(diethylaminodifluorophosphine)nickel(0).**—Nickel carbonyl (15.35 g, 0.09 mole) was added dropwise with stirring to 67 g (0.475 mole) of diethylaminodifluorophosphine,<sup>6</sup> vigorous evolution of carbon monoxide taking place. The reaction mixture was heated with stirring for 16 hr at 45–50°. After addition of 7 g (0.05 mole) of diethylaminodifluorophosphine, the product was transferred to a steel cylinder which was evacuated to 0.3 mm at  $-80^\circ$  and heated for 6 hr at 150–160°. The cylinder was still under vacuum when opened at room temperature. The infrared spectrum of the product showed a band at 2000  $cm^{-1}$ , indicating a simple species, presumably a trisubstituted derivative of nickel carbonyl. No change was observed when the mixture was once more heated for 4 hr to 170° as above, after another 7 g (0.05 mole) of diethylaminodifluorophosphine had been added.

The crude product was rinsed out of the reaction tube with ether. A virtually quantitative yield of crude, tetrasubstituted product was obtained upon evaporation of volatile products. The observed CO absorption was thus due only to a small amount of impurity. After three recrystallizations from petroleum ether, colorless crystals, mp 46°, were obtained.

*Anal.* Calcd for  $Ni[(C_2H_5)_2N \cdot PF_2]_4$ : C, 30.8; H, 6.5; F, 24.4; N, 9.0; Ni, 9.4; P, 19.7; mol wt, 623.14. Found: C, 31.4; H, 6.6; F, 24.2; N, 9.2; Ni, 9.6; P, 19.9; mol wt, 582 (cryptoscopic in benzene).

The infrared spectrum was recorded in KBr; CO absorptions were completely absent: 2980 (s), 2940 (m); 2902, 2875 (w); 1462 (s); 1450 (sh); 1380 (vs); 1370 (m); 1347 (m); 1294 (m); 1210, 1174 (vs); 1100, 1069 (s); 1022 (vs); 950 (vs); 924 (s);  $\sim 790$  (vs, b); 751 (vs); 681 (vs); 518, 493 (vs); 423 (m, b)  $cm^{-1}$ . The infrared spectrum in  $CCl_4$  solution was superimposable on that in KBr.

## Results

The  $P^{31}$  and  $F^{19}$  nmr spectra of our compounds showed mirror image patterns.  $P^{31}$  and  $F^{19}$  spectra of two typical compounds are shown in Figures 1–4. In the case of  $Ni(CO)_2L_2$  ( $L$  = fluorine-containing phosphine ligand) and  $NiL_4$ , where nickel is in a tetrahedral environment and all the ligands are magnetically equivalent, the mirror-image pattern can be rationalized only on the basis of long-range P–P, P–F, and F–F coupling through the complexing metal atom. In order to obtain these long-range coupling constants, it would be necessary to carry out a complicated nmr analysis. This is not practical to do in the case of complexes where the number of magnetic nuclei exceeds eight, and no attempts were made to obtain these parameters, although their importance in gaining a better understanding of the metal–ligand bonding should be underlined. In the case of the octahedral molybdenum complexes, nonequivalence of the ligands in the case of the *trans* compounds will complicate the situation further, and the analysis will be still more difficult. Despite the complexity of the spectra, chemical shifts are readily obtained as the centers of the mirror-image components. P–F coupling constants, however, are more difficult to obtain without analysis in the case of the  $F^{19}$  spectra.  $P^{31}$  spectra are symmetrical within each group, and  $J_{P-F}$  values obtained from them are believed to be accurate within  $\pm 10$  cps. The estimated uncertainties in  $\delta_P$  and  $\delta_F$  are less than 0.5 and 0.2 ppm, respectively.

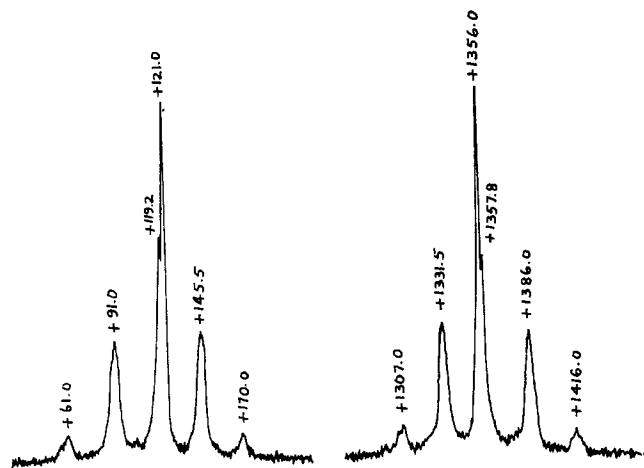


Figure 2.— $F^{19}$  nmr spectrum of  $Mo(CO)_3(C_6H_5OPF_2)_3$  (benzene solution). Calibration is in cycles per second from  $CFCl_3$  internal reference.

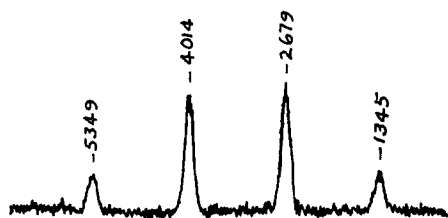


Figure 3.— $P^{31}$  nmr spectrum of  $Ni(PF_3)_4$  (neat liquid). Calibration is in cycles per second from  $H_3PO_4$  external reference.

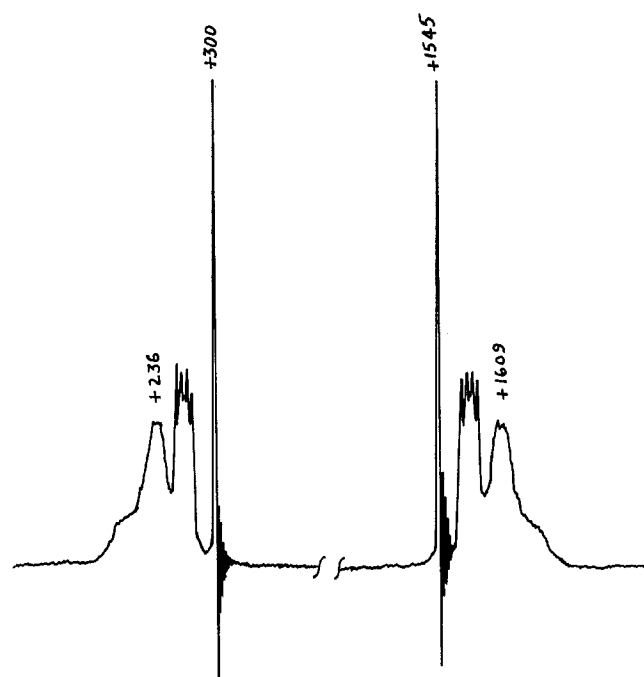


Figure 4.— $F^{19}$  nmr spectrum of  $Ni(PF_3)_4$  (neat liquid). Calibration is in cycles per second from  $CFCl_3$  internal reference.

The nmr data for the series  $F_2P-X$  are given in Table I; those for the coordination compounds are listed in Tables II-IV, where they are arranged according to the metal atom, the degree of substitution of the parent carbonyl, and the nature of the substituents on the phosphorus atom. Table II contains data for compounds

TABLE I  
NMR DATA FOR THE SERIES  $F_2P-X$

Compound	$\delta_P$ , ppm	$\delta_F$ , ppm	$J_{P-F}$ , cps	Electronegativity of atom adjacent to phosphorus	Ref
$F_2P-CH_3$	-250.7	+92.9	1157	<2.5	a
$F_2P-C_6H_5$	-208.3	+92.3	1174	2.6	b
$F_2P-N(C_2H_5)_2$	-144.0	+64.8	1194	3.1	c
$F_2P-O-n-C_3H_7$	-111.5	+94.1	1288	3.55	c
$F_2P-F$	-97.0	+34.0	1441	3.95	d

<sup>a</sup> F. Seel, K. Rudolph, and R. Budenz, *Z. Anorg. Allgem. Chem.*, **341**, 196 (1965). <sup>b</sup> See ref 8. <sup>c</sup> G. S. Reddy and R. Schmutzler, *Z. Naturforsch.*, **20b**, 104 (1965). <sup>d</sup> H. S. Gutowsky and D. W. McCall, *J. Chem. Phys.*, **21**, 279 (1953); **22**, 162 (1954).

of the type  $Ni(CO)_2L_2$ . The choice of substituents on the phosphorus atom is limited in this case to nitrogen-containing groups, as partially substituted derivatives of  $Ni(CO)_4$  containing fluorophosphite substituents are not stable enough to be isolated. In all cases,  $\delta_P$  is shifted to lower field in the complexes, compared to the free ligand, and so is  $\delta_F$ .  $J_{P-F}$  is also smaller in the complexes than for the uncoordinated ligands with the exception of  $Ni(CO)_2[CH_3PFN(CH_3)_2]_2$ .

In Table III, data for completely substituted derivatives of  $Ni(CO)_4$  are given. In these complexes,  $\delta_P$  and  $\delta_F$  are to lower field and  $J_{P-F}$  is also smaller than in the free ligand. Table IV contains nmr data for a series of molybdenum complexes of the type  $Mo(CO)_3L_3$ . Again,  $\delta_P$  and  $\delta_F$  are shifted to lower field and  $J_{P-F}$  decreases on complexation, except in the cases where L is  $CH_3PFN(CH_3)_2$  and  $C_6H_5PFN(C_2H_5)_2$ . In these cases  $J_{P-F}$  is slightly larger in the complex than in the free ligand, an observation which has also been made in the case of the  $Ni(CO)_2$  derivative of the former compound.


A marked difference in these trends is noticed when the analogous complexes are considered in which fluorine is replaced by chlorine. In both the molybdenum and the nickel series the changes in  $\delta_P$  on complexation are positive or slightly negative, when analogous complexes containing a P-Cl ligand instead of a P-F ligand are compared (Table V).

## Discussion

**A. Free Ligands.**—It has been noticed that  $P^{31}$  and  $F^{19}$  chemical shifts in fluorides of trivalent phosphorus vary with the electronegativity of the substituent atom X, attached to the phosphorus atom.<sup>10</sup> In the series  $F_2P-X$  (Table I) where X is F, O, N, or C (phenyl or methyl),  $\delta_P$  increases (shifts to higher field) and  $\delta_F$  decreases (shifts to lower field) with increasing electronegativity of the atom X directly attached to the phosphorus atom. The P-F coupling constants,  $J_{P-F}$ , were found to increase with increasing electronegativity of X. The observed decrease of  $\delta_F$  and the increase in  $J_{P-F}$  can be explained mostly on the basis of electronegativity considerations. It is well established, for example, that in compounds of the type  $CH_3-X$


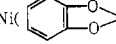
(10) G. S. Reddy and R. Schmutzler, *Z. Naturforsch.*, **20b**, 104 (1965).

TABLE II  
 P<sup>31</sup> AND F<sup>19</sup> NMR DATA FOR THE SERIES Ni(CO)<sub>2</sub>L<sub>2</sub><sup>a</sup>

Compound	Ref	$\delta_P$ , ppm			$\delta_F$ , ppm			$J_{P-F}$ , cps		$\Delta J_{P-F}$ , cps	Remarks
		Free ligand	Complex	$\Delta\delta_P$ , ppm	Free ligand	Complex	$\Delta\delta_F$ , ppm	Free ligand	Complex		
Ni(CO) <sub>2</sub> [(CH <sub>3</sub> ) <sub>2</sub> N·PF <sub>2</sub> ] <sub>2</sub>	6	-143.0	-168.5	-25.5	+65.3	+43.3	-22.0	1197	1150	-47	
Ni(CO) <sub>2</sub> [(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N·PF <sub>2</sub> ] <sub>2</sub>	<i>b</i>	-144.0	-168.8	-24.8	+64.8	+41.4	-23.4	1194	1140	-54	
Ni(CO) <sub>2</sub> (  N·PF <sub>2</sub> ) <sub>2</sub>	6	-139.1	-164.6	-25.5	+65.2	+43.1	-22.1	1193	1147	-46	Spectra recorded in toluene solution
Ni(CO) <sub>2</sub> [(CH <sub>3</sub> ) <sub>2</sub> N]PF <sub>2</sub>	7	-150.8	-181.0	-30.2	+99.6	+68.8	-30.8	1042	1041	-1	
Ni(CO) <sub>2</sub> [CH <sub>3</sub> PF[N(CH <sub>3</sub> ) <sub>2</sub> ]] <sub>2</sub>	7	-168.9	-184.4	-15.5	+117.5	+84.0	-33.5	919	940	+21	


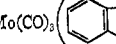

<sup>a</sup>  $\Delta\delta_X = \delta_X(\text{complex}) - \delta_X(\text{ligand})$  (X = P, F);  $\Delta J_{P-F} = J_{P-F}(\text{complex}) - J_{P-F}(\text{ligand})$ . Compounds were run as neat samples, unless stated otherwise. <sup>b</sup> This work.

 TABLE III  
 P<sup>31</sup> AND F<sup>19</sup> NMR DATA FOR THE SERIES NiL<sub>4</sub>

Compound	Ref	$\delta_P$ , ppm			$\delta_F$ , ppm			$J_{P-F}$ , cps		$\Delta J_{P-F}$ , cps	Remarks
		Free ligand	Complex	$\Delta\delta_P$ , ppm	Free ligand	Complex	$\Delta\delta_F$ , ppm	Free ligand	Complex		
Ni(PF <sub>2</sub> ) <sub>4</sub>	<i>a</i>	-97.0 <sup>b</sup>	-137.7	-40.7	+33.7 <sup>b</sup>	+16.7	-17.0	1441 <sup>b</sup>	~1320	-121	
Ni(C <sub>6</sub> H <sub>5</sub> PF <sub>2</sub> ) <sub>4</sub>	8	-208.3	-214.8	-6.5	+92.3	+55.8	-36.5	1174	1113	-61	CDCl <sub>3</sub> solution
Ni(  N·PF <sub>2</sub> ) <sub>4</sub>	6	-139.1	<i>c</i>	...	+65.2	+39.6	-25.6	1193	1123	-70	Benzene solution
Ni( <i>n</i> -C <sub>3</sub> H <sub>7</sub> OPF <sub>2</sub> ) <sub>4</sub>	5	-111.5	-146.0	-34.5	+49.1	+29.2	-19.9	1288	1230	-58	
Ni(C <sub>6</sub> H <sub>5</sub> OPF <sub>2</sub> ) <sub>4</sub>	5	-110.1	-139.6	-29.5	+44.5	+24.6	-19.9	1326	1258	-68	
Ni(  P-F) <sub>4</sub>	5	-123.1	-157.1	-34.0	+37.5	+13.9	-23.6	1307	1280	-27	Benzene solution
Ni[(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N·PF <sub>2</sub> ] <sub>4</sub>	This work	-144.0	-167.9	-23.9	+64.3	+38.8	-25.5	1197	1115	-82	
Ni[(CH <sub>3</sub> ) <sub>2</sub> NPF <sub>2</sub> ] <sub>4</sub>	6	-143.0	<i>c</i>	...	+65.3	+38.9	-26.4	1197	1104	-93	

<sup>a</sup> G. Wilkinson, *J. Am. Chem. Soc.*, **73**, 5501 (1951). <sup>b</sup> H. S. Gutowsky and D. W. McCall, *J. Chem. Phys.*, **21**, 279 (1953); **22**, 162 (1954). <sup>c</sup>  $\delta_P$  not obtained, owing to insufficient solubility.

 TABLE IV  
 P<sup>31</sup> AND F<sup>19</sup> NMR DATA FOR THE SERIES Mo(CO)<sub>2</sub>L<sub>3</sub>

Compound	Ref	$\delta_P$ , ppm			$\delta_F$ , ppm			$J_{P-F}$ , cps		$\Delta J_{P-F}$ , cps	Remarks
		Free ligand	Complex	$\Delta\delta_P$ , ppm	Free ligand	Complex	$\Delta\delta_F$ , ppm	Free ligand	Complex		
Mo(CO) <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> PF <sub>2</sub> ) <sub>3</sub>	8	-208.3	-233.6	-25.3	+92.3	+46.1	-46.2	1174	1113	-61	
Mo(CO) <sub>2</sub> [(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N·PF <sub>2</sub> ] <sub>3</sub>	6	-144.0	-182.4	-38.4	+64.8	+29.2	-35.6	1194	1104	-90	CCl <sub>4</sub> solution
Mo(CO) <sub>2</sub> (  N·PF <sub>2</sub> ) <sub>3</sub>	6	-139.1	-177.4	-38.3	+65.2	+30.8	-34.4	1193	1120	-73	
Mo(CO) <sub>2</sub> ( <i>n</i> -C <sub>3</sub> H <sub>7</sub> OPF <sub>2</sub> ) <sub>3</sub>	5	-111.5	-157.5	-46.0	+49.1	+19.7	-29.4	1288	~1220	-68	
Mo(CO) <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> OPF <sub>2</sub> ) <sub>3</sub>	5	-110.1	-150.1	-40.0	+44.5	+13.1	-31.4	1326	1240	-86	
Mo(CO) <sub>2</sub> [CH <sub>3</sub> PF[N(CH <sub>3</sub> ) <sub>2</sub> ]] <sub>3</sub>	7	-168.9	-194.6	-25.7	+117.5	+77.7	-39.8	919	930	+11	
Mo(CO) <sub>2</sub> [C <sub>6</sub> H <sub>5</sub> PF[N(CH <sub>3</sub> ) <sub>2</sub> ]] <sub>3</sub>	7	-156.0	-185.5	-29.5	+125.7	+84.7	-41.0	989	990	+1	
Mo(CO) <sub>2</sub> [(CH <sub>3</sub> ) <sub>2</sub> N]PF <sub>2</sub>	7	-150.8	-182.3	-31.5	+99.6	+59.7	-39.9	1042	1034	-8	CDCl <sub>3</sub> solution
Mo(CO) <sub>2</sub> (  P-F) <sub>3</sub>	5	-123.1	-171.6	-48.5	+37.0	-1.0	-38.0	1307	1270	-37	Benzene solution
Mo(CO) <sub>2</sub> (  N·PF <sub>2</sub> ) <sub>3</sub>	6	-139.1	-183.1	-42.0	+65.2	+26.9	-38.3	1193	1079	-114	
Mo(CO) <sub>2</sub> (PF <sub>3</sub> ) <sub>3</sub>	<i>a</i>	-97.0	-150.6	-53.6	+33.7	+3.0	-30.7	1441	~1300	~ -141	Benzene solution

<sup>a</sup> Th. Kruck and A. Prash, *Z. Naturforsch.*, **19b**, 669 (1964); R. J. Clark and P. I. Hoberman, *Inorg. Chem.*, **4**, 1771 (1965).

H<sup>1</sup> chemical shift decreases and  $J_{C^{13}-H}$  increases with increasing electronegativity of X, although they are approximately the same in methyl halides.<sup>11</sup> The decrease in  $\delta_H$  is because electrons being withdrawn from carbon are rendering it more electronegative. The increase in  $J_{C^{13}-H}$  is due to the increase in the s character of the C-H bonds as a consequence of the electronega-

tivity of X. This suggestion is substantiated by the observed increase in  $J_{C^{13}-H}$  in ethylene, as compared to methane. It was shown by Goldstein and Reddy<sup>12-14</sup> that an inverse linear relationship exists between  $\delta_H$  and  $J_{C^{13}-H}$  in the systems where the neighboring-group

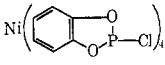
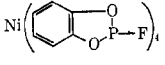
(12) J. H. Goldstein and G. S. Reddy, *ibid.*, **36**, 2644 (1962).

(13) G. S. Reddy and J. H. Goldstein, *ibid.*, **38**, 2736 (1963).

(14) G. S. Reddy and J. H. Goldstein, *ibid.*, **39**, 3509 (1963).

(11) C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2198 (1962).

TABLE V  
 COMPARISON OF P<sup>31</sup> CHEMICAL SHIFTS FOR SOME CHLOROPHOSPHINE COMPLEXES AND THEIR FLUOROPHOSPHINE ANALOGS

Compound	Ref	$\delta_P$ , ppm		$\Delta\delta_P^a$ ppm	Remarks
		Free ligand	Complex		
Ni(PCl <sub>3</sub> ) <sub>4</sub>	<i>b</i>	-219.5	-171.8	+47.7	Benzene solution
Ni(PF <sub>3</sub> ) <sub>4</sub>	<i>c</i>	-97.0	-137.7	-40.7	
Mo(CO) <sub>3</sub> (PCl <sub>3</sub> ) <sub>3</sub>	<i>d</i>	-219.5	-162.6	+56.9	Benzene solution
Mo(CO) <sub>3</sub> (PF <sub>3</sub> ) <sub>3</sub>	<i>e</i>	-97.0	-150.6	-53.6	
Ni(C <sub>6</sub> H <sub>5</sub> PCl <sub>2</sub> ) <sub>4</sub>	<i>f</i>	-161.1	-152.0	+9.1	Benzene solution
Ni(C <sub>6</sub> H <sub>5</sub> PF <sub>2</sub> ) <sub>4</sub>	8	-208.3	-214.8	-6.5	
Ni(  ) <sub>4</sub>	This work	-173.0	-177.4	-4.4	Nitrobenzene solution
Ni(  ) <sub>4</sub>	5	-123.1	-157.1	-34.0	
Mo(CO) <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> PCl <sub>2</sub> ) <sub>3</sub>	<i>d</i>	-161.1	-172.0	-10.9	Benzene solution
Mo(CO) <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> PF <sub>2</sub> ) <sub>3</sub>	8	-208.3	-233.6	-25.3	

<sup>a</sup>  $\Delta\delta_P = \delta_P(\text{complex}) - \delta_P(\text{free ligand})$ . <sup>b</sup> J. W. Irvine and G. Wilkinson, *Science*, **113**, 742 (1951). <sup>c</sup> G. Wilkinson, *J. Am. Chem. Soc.*, **73**, 5501 (1951). <sup>d</sup> E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 2323 (1959). <sup>e</sup> Th. Kruck and A. Prasz, *Z. Naturforsch.*, **19b**, 669 (1964). <sup>f</sup> L. Malatesta and A. Sacco, *Ann. Chim. (Rome)*, **44**, 134 (1954).

anisotropy effects are negligible. Similarly, in the series F<sub>2</sub>P-X it is expected that  $\delta_F$  decreases and  $J_{P-F}$  increases with increasing electronegativity of X, as is borne out in the data listed in Table I. Besides the electronegativity of X, the paramagnetic term may have some contribution to the chemical shifts of fluorine.<sup>15</sup>

The increase in  $\delta_P$  with increasing electronegativity of X cannot be rationalized on the basis of these simple considerations. Gutowsky and Larmann<sup>16</sup> have shown from theoretical calculations that in compounds of the type PX<sub>3</sub> (X = H, CH<sub>3</sub>, or halogen) the paramagnetic contribution is very dominant in determining the P<sup>31</sup> chemical shift. In their theoretical calculation of P<sup>31</sup> chemical shifts Gutowsky and Larmann<sup>16</sup> have neglected the  $\pi$  bonding which may exist between phosphorus and the substituent atom. In the ligands employed in the present study, all of the substituent atoms either have  $\pi$  electrons (phenyl group) or unshared electrons (N, O, and F), and the possibility of a partial double bond must be considered. The effect of the  $\pi$  bonding will be such as to lower further the chemical shift of phosphorus. In conclusion, in the present series of ligands it appears reasonable to assume that the paramagnetic term overshadows the effects due to the electronegativity differences of the substituent atoms.

A third factor which may contribute to changes in  $\delta_P$  in the compounds under discussion is the polarization of the unshared electrons by the group X. In compounds of the type F<sub>2</sub>P-X this polarization depends on the electronegativity of X, and its contribution to  $\delta_P$  is always negative.

**B. Complexes.**—The bond between phosphorus and the metal atom in these complexes is a dative bond, formed by the donation of two electrons by the phosphorus atom. There are several factors which can influence the nmr parameters in these complexes.

**1. Changes in the Electronegativity of the Phosphorus Atom.**—Donation of its two lone-pair electrons

to form the dative bond with the metal atom renders phosphorus more electronegative, thereby increasing its capability to form  $\pi$  bonds by accepting d electrons from the metal atom into its vacant d orbitals. It is expected that d <sub>$\pi$</sub> -d <sub>$\pi$</sub>  bonding will make a negative contribution to  $\delta_P$  by increasing the paramagnetic term, its magnitude depending on the extent of  $\pi$ -bond formation. It should also be noted that a  $\pi$  bond can be formed between the substituent atom and the phosphorus atom if the substituent atom has lone-pair electrons.

**2. Anisotropy of the Metal Atom.**—On complexation, the phosphorus atom is placed in the magnetic anisotropy region of the metal atom and its contribution to  $\delta_P$  is also negative. This has been discussed by Pitcher, *et al.*,<sup>17</sup> in the case of fluorine chemical shifts in perfluoroalkyl transition metal complexes and by Siddall and Prohaska<sup>18</sup> for the proton chemical shifts in uranyl nitrate adducts of tetraalkylmethylenediphosphonates. The direction of the anisotropy effect can be either negative or positive, depending on the position of the phosphorus atom, relative to the center of the anisotropy. However, the magnitude is believed to be small and the effect will not be considered further here.

**3. Increase in the Coordination Number of Phosphorus.**—On formation of the  $\sigma$  bond in the complex the coordination number of phosphorus increases and, as a result,  $\delta_P$  is expected to increase while  $J_{P-F}$  decreases. It is known from previous work that  $\delta_P$  and, less characteristically,  $J_{P-F}$ , in P-F compounds containing phosphorus in different coordination number, fall into distinct regions, as shown in Table VI.

It may be seen that the changes in  $\delta_P$  and  $J_{P-F}$  in going from one coordination number to the other are usually appreciable, and there is little overlap, except in the case of compounds containing P=S bonds, for which unusually negative values of  $\delta_P$  have been observed.<sup>19</sup>

(17) E. Pitcher, A. D. Buckingham, and F. G. A. Stone, *J. Chem. Phys.*, **36**, 124 (1962).

(18) T. H. Siddall and C. A. Prohaska, *Inorg. Chem.*, **4**, 783 (1965).

(19) G. S. Reddy and R. Schmutzler, publication in preparation.

(15) A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

(16) H. S. Gutowsky and J. Larmann, *J. Am. Chem. Soc.*, **87**, 3815 (1965).

TABLE VI

Coordn no.	$\delta_P$ , ppm from $H_3PO_4$	$J_{P-F}$ , cps	$\delta_F$ , ppm from $CFCI_3$
3	ca. -150 to -100	1200-1400	ca. 40-120
4	-100 to 0	1000-1200	40-70
5	0 to +100	600-1000	40-70
6	+100 to +150	650-800	40-70

#### 4. Changes in the Bond Angles of the Ligand.—

It is expected that the bond angles in the phosphine ligands will change on complexation, and it has been shown by several workers that bond angles critically affect  $\delta_P$ .<sup>20,21</sup> However, since bond angles neither in ligands, except for  $PF_3$ , nor in any of our complexes are known, this effect will not be discussed further, in spite of its importance.

#### 5. Polarization of the Lone-Pair Orbitals.—

Since most of the ligands included in this study are unsymmetrically substituted, polarization of the lone-pair electron orbitals by the unsymmetrical field of the substituent atoms can give rise to a further downfield shift of  $\delta_P$  in the free ligands, which will be reduced on complexation since the lone-pair electrons are shared in the complex and are thus less susceptible to polarization.<sup>22</sup>

It is obvious that factors 1 and 2 will tend to reduce  $\delta_P$  while factors 3 and 5 will tend to increase  $\delta_P$  on complexation. In all the complexes studied,  $\delta_P$  decreases on complexation (Tables II-IV) except in the case of chlorophosphines (Table V). It can be concluded that the combined effect of factors 1 and 2 outweighs the combined effect of factors 3 and 5. This is also borne out in the case of  $\delta_F$ . It is not the purpose of this study to obtain quantitative estimates but to study the relative importance of these effects. Figures 5-8 will serve to illustrate further these points.

Figure 5 shows a plot of the electronegativity of the substituent atom X in the series  $F_2PX$  vs.  $\delta_P$  in the free ligand and also vs.  $\Delta\delta_P$  ( $\delta_{P,complex} - \delta_{P,ligand}$ ) in the series  $NiL_4$  and  $Mo(CO)_3L_3$ . It can be seen that all of the plots are approximately straight lines. The plot for molybdenum complexes is lower than that for nickel complexes. This can be assumed to be due to a larger magnetic anisotropic contribution of molybdenum, compared to nickel atoms. The slopes of the lines are negative suggesting that there is a significant paramagnetic contribution to the chemical shift of phosphorus from the metal-phosphorus bond formed on complexation. It was already pointed out that changes in the bond angles on complexation can be responsible for part of the observed changes in  $\delta_P$ . It is conceivable that part of this paramagnetic contribution to  $\delta_P$  is due to  $d_\pi-d_\pi$  bonding between the metal atom and the phosphorus atom. There is a definite, though small, difference in the slopes of the lines for

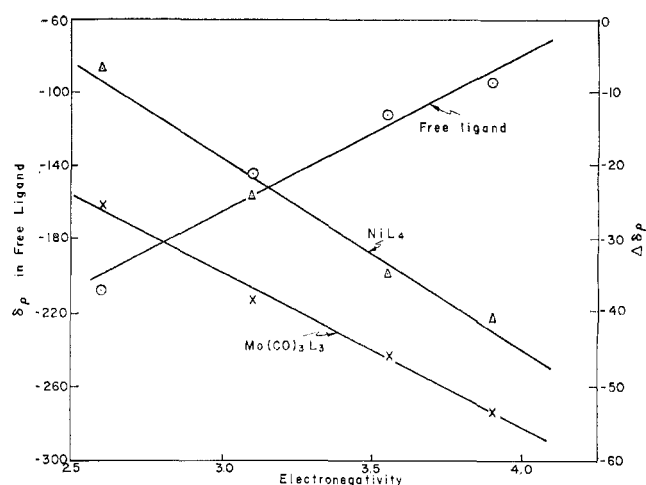


Figure 5.—Plot of  $P^{31}$  chemical shift in free ligands,  $F_2P-X$ , vs. electronegativity of X and vs. change in  $\delta_P$  of ligand on complexation ( $\Delta\delta_P$ ) in the series  $NiL_4$  and  $Mo(CO)_3L_3$ .

nickel and molybdenum complexes, the slope for the former being more negative.

Figure 6 shows a similar plot for  $\delta_F$  and  $\Delta\delta_F$ . In this case the lines for nickel and molybdenum are almost parallel, suggesting the  $\pi$ -bond contribution to  $\delta_F$  is negligible. Only the anisotropy of the metal atom, the paramagnetic term,<sup>17</sup> and the changes in bond angles are expected to be responsible for the observed changes in  $\delta_F$  with the electronegativity of X. The line for molybdenum complexes is lower, suggesting again that the paramagnetic term in the case of molybdenum complexes is larger than in nickel complexes.

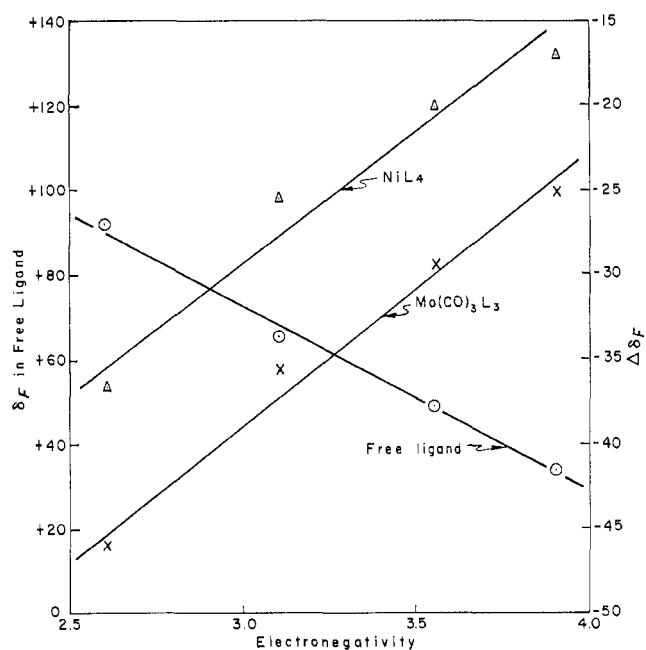


Figure 6.—Plot of  $F^{19}$  chemical shift in free ligands,  $F_2P-X$ , vs. electronegativity of X and vs. change in  $\delta_F$  of ligand on complexation ( $\Delta\delta_F$ ) in the series  $NiL_4$  and  $Mo(CO)_3L_3$ .

Figures 7 and 8 show the plots of  $\delta_P$  vs.  $\Delta\delta_P$  and  $\Delta\delta_F$ , respectively. Figure 7 shows that the higher the chemical shift of phosphorus in the free ligand, the larger is the low-field shift on complexation. On the other hand, in the case of the fluorine resonance it is

(20) D. Purdela, *Rev. Roumaine Chim.*, **10**, 949 (1965); D. Purdela and R. Vilceanu, "Chimia Compusilor Organici ai Fosforului si ai Acizilor Lui," Editura Academiei Republicii Socialiste, Romania, 1965, p 41.

(21) J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, **44**, 815 (1966). We are indebted to Dr. Van Wazer for providing us with a copy of this paper prior to its publication.

(22) The authors wish to thank Professor R. S. Nyholm for pointing out this factor.

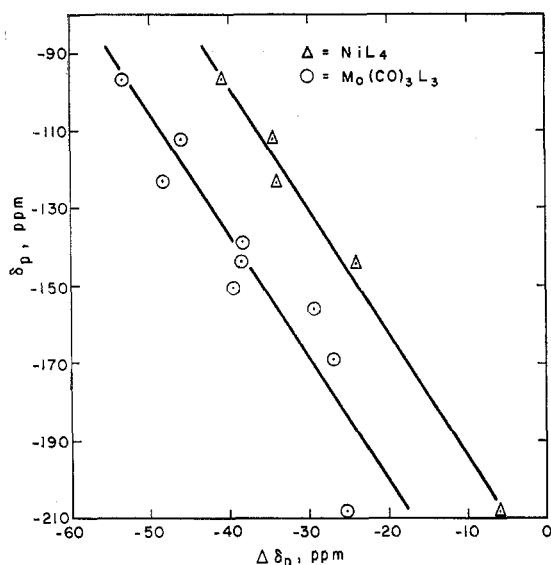


Figure 7.—Plot of  $P^{31}$  chemical shift of uncoordinated ligands vs. change in  $\delta_P$  on complexation ( $\Delta\delta_P$ ) in the series  $NiL_4$  and  $Mo(CO)_3L_3$ .

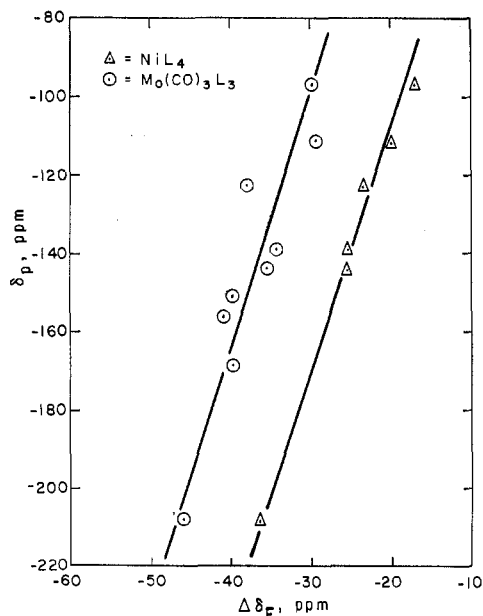


Figure 8.—Plot of  $P^{31}$  chemical shift of uncoordinated ligands vs. change in  $\delta_P$  on complexation ( $\Delta\delta_P$ ) in the series  $NiL_4$  and  $Mo(CO)_3L_3$ .

noticed (Figure 8) that the larger the chemical shift of phosphorus in the free ligand, the smaller the low-field shift of fluorine on complexation.

The coupling constants between phosphorus and fluorine in all of these complexes are smaller than those in the free ligands except in a few cases where the phosphorus is bonded to two dialkylamino groups. Since only the P-F bond property determines these values, it can be said that on complexation the  $s$  electrons of phosphorus are tied up to form a  $\sigma$  bond. As a result, the hybridization of the phosphorus orbitals involved in forming bonds with fluorine atoms, as well as the bond angles, will change, and it is believed that these changes are responsible for the changes in  $J_{P-F}$  on complexation.

Finally, comparative data for some complexes involving fluorophosphine and the corresponding chlorophosphine ligands are presented in Table V. It is noticed that for the chlorophosphine ligands,  $\Delta\delta_P$  is either positive or only slightly negative. It seems that the largest discrepancies occur in trichlorophosphine complexes. The reason for this abnormal behavior is suggested to be the larger changes in the hybridization and bond angles on complexation, because of the larger size of the chlorine atoms. It is also possible that the electron-donating properties of chlorine are so different from those of fluorine as to give the observed anomaly.

The carbonyl stretching frequencies in the infrared spectra have long been used to study the degree of  $\pi$  bonding in similar transition metal complexes.<sup>23</sup> In order to compare the trends in the carbonyl stretching frequencies and the chemical shift changes in a number of our complexes, pertinent data are presented in Table VII.  $PF_3$  has been shown to be the strongest  $\pi$ -bond-

TABLE VII  
CO STRETCHING FREQUENCIES AND  $\Delta\delta_P$  VALUES  
IN SOME  $Ni(CO)_2L_2$  AND  $Mo(CO)_3L_3$  COMPLEXES

Compound	$\nu_{CO}$ , cm <sup>-1</sup>	$\Delta\delta_P$ , ppm	Ref
$Ni(CO)_2[(CH_3)_2P(N(CH_3)_2)]_2$	2020, 1961	-15.5	7
$Ni(CO)_2[(C_2H_5)_2N \cdot PF_2]_2$	2046, 1992	-24.5	This work
$Ni(CO)_2[(CH_3)_2N \cdot PF_2]_2$	2040, 1993	-25.5	6
$Ni(CO)_2(\text{Cyclohexane ring with N-PF}_2)_2$	2041, 1993	-25.5	6
$Ni(CO)_2[(CH_3)_2N]_2PF_2$	2019, 1961	-30.2	7
$Mo(CO)_3(C_6H_5PF_2)_3$	2034, 1969	-25.3	8
$Mo(CO)_3[CH_3PF(N(CH_3)_2)]_3$	1970, 1882	-25.7	7
$Mo(CO)_3[C_6H_5PF(N(CH_3)_2)]_3$	1960, 1873	-29.5	7
$Mo(CO)_3[(CH_3)_2N]_2PF_3$	1969, 1878	-31.5	7
$Mo(CO)_3(\text{Cyclohexane ring with N-PF}_2)_3$	1996, 1934	-38.3	6
$Mo(CO)_3[(C_2H_5)_2N \cdot PF_2]_3$	1995, 1919	-38.4	6
$Mo(CO)_3(C_6H_5OPF_2)_3$	2025, 1954	-40.0	5
$Mo(CO)_3(\eta-C_3H_7OPF_2)_3$	2020, 1947	-46.0	5
$Mo(CO)_3(\text{Benzene ring with O-P-F})_3$	2041, 1990, 1970	-48.5	5
$Mo(CO)_3(PF_3)_3$	2090, 2055	-53.6	21

ing ligand from infrared spectroscopic studies.<sup>23</sup> It can be reasoned that the high electronegativity of fluorine makes the phosphorus atom more electronegative and hence increases its capability of forming  $\pi$  bonds with the metal atom. Since it was suggested that part of the downfield shift of the phosphorus resonance on complexation is due to this  $\pi$  bonding and as fluorine is successively substituted by less electronegative atoms or groups, this  $\pi$  bonding should decrease. Hence, there should be a direct correlation between the carbonyl stretching frequency and  $\Delta\delta_P$ . An examination of the data in Table VII shows that such a trend indeed exists. This further supports the earlier observation that the less electronegative the substituent atom on the phosphorus is, the less  $\pi$  bonding exists between phosphorus and the metal atom.

From these studies the following conclusions are drawn.

(1) The paramagnetic contribution to the screening

(23) For a detailed account on this subject see F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

constants of phosphorus and fluorine atoms, which is due to the presence of low-lying excited states in the metal-phosphorus bond, is increased on complexation. This contribution is larger in the case of molybdenum complexes than in nickel complexes.

(2) The data may best be interpreted as providing evidence in support of the view that there is an appreciable amount of  $d_{\pi}$ - $d_{\pi}$  bonding between the phosphorus atom and the metal atom. The extent of  $d_{\pi}$ - $d_{\pi}$  bonding appears to be larger in the case of the nickel complexes than in molybdenum complexes.

(3) The hybridization and bond angles of the ligand change (phosphorus orbitals possess less  $s$  character) on complexation. These changes are presumably more pronounced for chlorophosphine ligands than for the corresponding fluorophosphine ligands.

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## Notes

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TULANE UNIVERSITY, NEW ORLEANS, LOUISIANA 70118

### Synthesis and Properties of Some Metal Chelates of 2-Pyrrolealdimines<sup>1</sup>

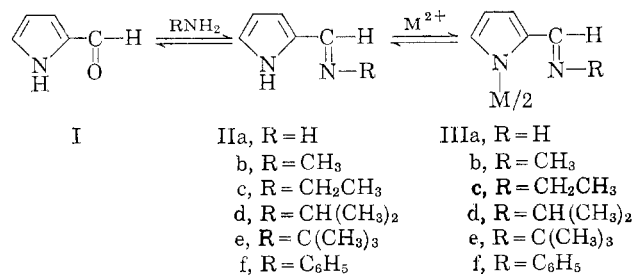
BY KWAN-NAN YEH AND ROBERT H. BARKER

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Because of their high degree of stability and their prominence in areas of biological interest, the metal chelate complexes of condensed pyrrole ring systems have been quite thoroughly studied and characterized.<sup>2</sup> Metal derivatives of the dipyrromethenes, the phthalocyanines, and the complex porphyrins have been known for almost 50 years. It is thus somewhat surprising that only a few complexes have been reported in which the ligand contains a single pyrrole ring. The use of pyridylpyrrole as a ligand for nickel(II), aluminum(III), and cadmium(II) was reported by Emmert in 1929.<sup>3</sup> Pyrrole-2-carboxaldehyde (I) and its methylimine (IIb) were also used. Organopalladous compounds of pyrrole and indole have been claimed as products from the interaction of the heterocycle with palladium(II) chloride in aqueous solution, but this has been questioned recently.<sup>4</sup> The X-ray structure of bis(2-pyrrolealdimethylimino)copper(II) (IIIb,  $M = \text{Cu}$ ) has been determined and the compound was found to be bimolecular, *trans*, and probably planar.<sup>5</sup>

The previously described procedures for the synthesis of the complexes of both the aldehyde and its methylimine with copper(II) involved heating the ligand together with the metal oxide at reflux in a high-boiling solvent such as xylene or anisole.<sup>3</sup> Since the methylimine was known to be quite unstable toward heat, light, and moisture and since there was no reason to

expect the higher homologous imines to be any more stable, such high-temperature methods did not seem to offer the best routes to the desired chelates. The work described herein provides more widely applicable synthetic routes to the pyrrolealdimines and their copper(II), mercury(II), and palladium(II) complexes.



The free methyl-, ethyl-, and phenylpyrrolealdimines were prepared by a modification of the procedure used by Emmert and co-workers for the methyl compound.<sup>3</sup> The instability of these materials precluded the usual characterization by elemental analysis but their infrared and nuclear magnetic resonance spectra were in complete agreement with the proposed structures. This instability is apparently greater for those imines having larger N-alkyl groups and all attempts to isolate the analogous N-isopropyl- and N-*t*-butylimines, II d and II e, were unsuccessful. That this was due to unfavorable equilibria in the additions and not failure of the amines to add to the pyrrolealdehyde was shown by the fact that treatment of the crude amine-aldehyde reaction mixture with copper(II) produced the corresponding pyrrolealdimine chelates. Similar procedures were used for the synthesis of the mercury(II) and palladium(II) complexes of the isopropyl and *t*-butyl imine ligands. The N-methyl and N-ethyl complexes of mercury(II) and palladium(II) were best prepared from the purified ligands. The much more stable N-phenyl ligand, II f, was also isolated and purified before complexation. The resulting chelates were characterized by elemental analysis, melting point, infrared spectra, and, when possible, nuclear magnetic resonance spectra.

(1) Taken from a thesis submitted by Kwan-nan Yeh to the Graduate School of Tulane University in partial fulfillment of the requirements for the M.S. degree.

(2) See, for example, A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952.

(3) B. Emmert, K. Diehl, and F. Gollwitzer, *Ber.*, **62**, 1733 (1929).

(4) F. A. Cotton, *Chem. Rev.*, **55**, 551 (1955).

(5) M. V. Stackelberg, *Z. Anorg. Chem.*, **253**, 136 (1947).