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# Trifluorophosphine Complexes of Nickel

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Mixtures of the $Ni(CO)_x(PF_3)_{4-x}$ compounds can best be prepared by either the interaction of $Ni(CO)_4$ and $Ni(PF_3)_4$ at about 70° or the reaction between $PF_3$ and $Ni(CO)_4$ at 100° in a pressure vessel. The presence of finely divided nickel metal in the latter approach increases the yield. The composition of the mixtures represents a nearly random arrangement of ligands among the various species. The pure compounds, isolated by means of vapor phase chromatography, have physical properties quite similar to those of the parent compounds and infrared and nuclear magnetic resonance studies clearly pointout the very great similarity between CO and $PF_3$ as ligands.

## Introduction

Nickel complexes of phosphorus trifluoride were first prepared by two different groups of workers. Irvine and Wilkinson[2] prepared $Ni(PF_3)_4$ from $PF_3$ and $Ni(PCl_3)_4$, with this latter compound being prepared from $Ni(CO)_4$ and $PCl_3$. Nearly simultaneously Chatt and Williams[3] attempted to prepare $Ni(PF_3)_4$ by the direct replacement of carbonyl groups from $Ni(CO)_4$ by $PF_3$. Although they did not obtain the desired compound, they did succeed in preparing materials having the composition of a di- to trisubstituted nickel carbonyl. No information was obtained to show whether these materials were mixtures of $Ni(CO)_4$ and $Ni(PF_3)_4$ or mixtures of intermediate compounds that can be formulated as $Ni(CO)_x(PF_3)_{4-x}$. $Ni(PF_3)_4$ was also prepared later by the fluorination of $Ni(PCl_3)_4$ with potassium fluorosulfinate.[4]

In this article, the preparation, isolation, and characterization of the compounds intermediate between $Ni(CO)_4$ and $Ni(PF_3)_4$ will be described.

## Experimental

Some of the general techniques are reported in an earlier publication.[5]

**Preparation of $Ni(PF_3)_4$.**—The procedure differed from that used by Irvine and Wilkinson[2] only in the use of a reaction temperature of 75° to give a slight improvement in yield and in the use of a stainless steel pressure vessel for greater safety. Their procedure for separating the products $PCl_3$ and $Ni(PF_3)_4$ was changed by hydrolyzing the $PCl_3$ with cold water, which does not affect $Ni(PF_3)_4$. The $Ni(PF_3)_4$ was separated from excess $H_2O$ by distilling the product *in vacuo* through a bed of Linde 4A Molecular Sieves. The $Ni(PF_3)_4$ is too large to be adsorbed in the internal pore structure, but the water is not.

Tetrakis(trifluorophosphine)nickel(0) of better than 90% purity could be prepared by the direct reaction of $Ni(CO)_4$ and $PF_3$ in a pressure vessel. About 2 g. of $Ni(CO)_4$ and sufficient $PF_3$ to create a pressure of 200 p.s.i. at room temperature were heated to 150° in a 150-ml. pressure vessel for 12 hr. The vessel was next cooled to −195° and the evolved carbon monoxide pumped out. The heating, cooling, and evacuation was continued through a total of five cycles. The final product contained better than 90% tetraphosphine with the triphosphine being the only other product.

**Preparation of $Ni(CO)_x(PF_3)_{4-x}$ Mixture.**—Two procedures were developed for the preparation of these mixtures. The first was similar to the reaction used by Chatt and Williams.[3] $Ni(CO)_4$ (1–2 ml.) was condensed into a 300-ml. capacity stainless steel pressure vessel at −195° followed by enough $PF_3$ to make a pressure of 200–400 p.s.i., at room temperature. Heating at 100° for several hours caused extensive reaction. The presence of several grams of active nickel prepared from nickel formate considerably increased the yield by reacting with most of the CO evolved on substitution.

Another procedure utilized the reaction between $Ni(CO)_4$ and $Ni(PF_3)_4$. These two materials were sealed in evacuated Pyrex tubes and heated to 75° for 24 to 48 hr. A very small amount of a nonvolatile, nonferromagnetic residue was formed during the process.

**Ligand Redistribution.**—This study was made by the second of the preparative techniques described above. Mixtures of $Ni(CO)_4$–$Ni(PF_3)_4$, varying in mole fraction by 0.125 increments, were equilibrated at 75°, and the products were analyzed by two different techniques.

One approach was vapor phase chromatography. The injection of small quantities of any of these mixtures onto a 2.5 m. × 5 mm. column of DC-710 silicone oil on Celite at room temperature resulted in five peaks in the chromatogram. The last component to elute had the same retention time as $Ni(CO)_4$. In the other approach, the $F^{19}$ n.m.r. spectra of the mixtures were measured. There were four sets of peaks whose relative height varied with the starting composition, but only the main peak for each species was considered in the interpretation. A typical set of spectra containing only the low-field half is shown in Figure 1.

**Isolation of $Ni(CO)_x(PF_3)_{4-x}$ Intermediates.**—These compounds were isolated by vapor phase chromatography on a

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(2) J. W. Irvine, Jr., and G. Wilkinson, *Science*, **113**, 742 (1951); G. Wilkinson, *J. Am. Chem. Soc.*, **73**, 5501 (1951).

(3) J. Chatt and A. A. Williams, *J. Chem. Soc.*, 3061 (1951).

(4) F. Seel, K. Ballreich, and R. Schmutzler, *Chem. Ber.*, **94**, 1173 (1961).

(5) R. J. Clark, *Inorg. Chem.*, **3**, 1395 (1964).

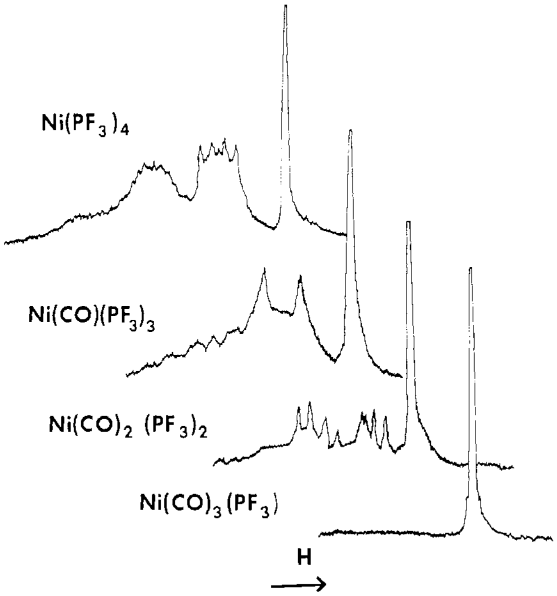

Figure 1.—$F^{19}$ n.m.r. spectra of $Ni(CO)_x(PF_3)_{4-x}$ species (low-field half). An exact mirror image of the peaks is found at higher magnetic field.

preparative scale. Many problems were encountered before the preparation was successful. The best conditions that were found are as follows: a 12 mm. × 2.5 m. column loaded with 40% DC 710 silicone oil on Celite, a column temperature of either 25 or 0°, and a flow of about 100 cc./min. of either hydrogen or carbon monoxide. The lower temperature and carbon monoxide carrier gas are of critical importance for the preparation of the labile $Ni(CO)_3(PF_3)$. Because of the extreme lability expected, the exit gas stream was split, sending only a small fraction to the thermal conductivity cell and the rest to the trapping system. Damage to detectors has been observed to occur at high filament currents. Sample sizes from 80 to 150 $\mu$l. were used for a first stage of purification, and a second cycle of 50 $\mu$l. was used for the final purification. Attempts to use longer columns to get better resolutions were not successful.

**Physical Measurements.**—The approximate melting point of the mono- and dicarbonyl were determined in a micro melting point apparatus as described by Sanderson.[6] Vapor pressure measurements were made at 0° in a system having dual monometer tubes immersed in a common well of mercury. One tube was connected to a high-vacuum system, and the other was connected to the sample which was thoroughly outgassed. The densities were determined in a semimicro pycnometer at 25°. The infrared data were obtained in hexane on a Perkin-Elmer Model 221 spectrometer. The $F^{19}$ n.m.r. data were obtained on a Varian 4300 B at 40 Mc. The $P^{31}$ n.m.r. spectra were kindly run by Dr. M. M. Crutchfield at Monsanto.

Kinetic data on the rate of disproportionation were obtained at room temperature from samples sealed in either evacuated tubes or tubes closed by silicone rubber septums. Samples were studied both in the presence and absence of carbon monoxide. Analytical vapor phase chromatography was used to determine the composition of the mixtures.

**Infrared** frequencies in the P–F region (cm.$^{-1}$): $Ni(CO)(PF_3)_3$; 927 (m), 892 (s), 879 (sh), 857 (s); $Ni(CO)_2(PF_3)_2$; 902 (s), 883 (s), 855 (s); $Ni(CO)_3(PF_3)$; 902 (s), 874 (vs), 855 (s).

**Analyses.**—Phosphorus was determined by the Linde Analytical Department and nickel was determined by the dimethylglyoxime procedure. The samples were taken into solution by nitric acid in closed and partially evacuated vessels to prevent loss of the compounds. The smallness of the samples used and the elaborate handling involved in the solution process prevented the analytical agreement from being better. *Anal.* Calcd. for $Ni(CO)(PF_3)_3$: Ni, 16.7; P 26.5. Found: Ni, 16.5, 16.0, 16.0; P, 25.6, 27.0. Calcd. for $Ni(CO)_2(PF_3)_2$: Ni, 20.2; P, 21.3. Found: Ni, 21.0; P 21.8. Calcd. for $Ni(CO)_3(PF_3)$: Ni, 25.4; P, 13.4. Found: Ni, 26.2; P, 12.3, 14.4.

## Results

Several reactions have been developed which allow the preparation of mixtures of $Ni(CO)_x(PF_3)_{4-x}$ compounds. These can be represented by the equations

$$Ni(CO)_4 + (4 - x)PF_3 = Ni(CO)_x(PF_3)_{4-x} + (4 - x)CO \quad (1)$$

$$(x/4)Ni(CO)_4 + (4 - x)PF_3 + (1 - x/4)Ni = Ni(CO)_x(PF_3)_{4-x} \quad (2)$$

$$(x/4)Ni(CO)_4 + (1 - x/4)Ni(PF_3)_4 = Ni(CO)_x(PF_3)_{4-x} \quad (3)$$

$$Ni + xCO + (4 - x)PF_3 = Ni(CO)_x(PF_3)_{4-x} \quad (4)$$

Only the last, which was carried out at atmospheric pressure, fails to give a good yield and will not be considered further. The reaction between $Ni(CO)_4$ and $Ni(PF_3)_4$ allows easy control of the over-all system composition, but requires the previous preparation of the phosphine complex. The reaction between $Ni(CO)_4$ and $PF_3$, either with or without the presence of nickel metal, is easily carried out to give a good yield of the mixtures. A study of variables such as temperature, time, and pressure should also allow good control of the composition.

Fluorine n.m.r. and vapor phase chromatography show that the products prepared by these techniques are not mixtures of $Ni(CO)_4$ and $Ni(PF_3)_4$. The gas chromatograms contain five peaks—the number to be expected in the $Ni(CO)_4$–$Ni(PF_3)_4$ system. The $F^{19}$ n.m.r. spectra of the mixtures contain even more peaks than the surprisingly complex pattern for $Ni(PF_3)_4$, indicating that several new fluorine-containing species are present.

The systematic study of the equilibrated $Ni(CO)_4$–$Ni(PF_3)_4$ mixtures over the complete composition range makes possible the identification of the various compounds. It is merely necessary to assume that any given species will have a maximum concentration when the over-all system composition is the same as that of the species. A plot showing the relative concentrations for the five species at various system compositions, as determined from the chromatograms of the various mixtures, has been published elsewhere.[7] It therefore appears that the compounds are, in order of elution: tetrakistrifluorophosphinenickel(0), $Ni(PF_3)_4$; carbonyltristrifluorophosphinenickel(0), $Ni(CO)(PF_3)_3$; dicarbonylbistrifluorosphosphinenickel(0), $Ni(CO)_2(PF_3)_2$; tricarbonyltrifluorophosphinenickel(0), $Ni(CO)_3PF_3$, and nickel tetracarbonyl, $Ni(CO)_4$.

Comparable observations and plots can be made for the n.m.r. data for the system.

The three intermediate compounds are isolated in a high state of purity by vapor phase chromatography. The procedure is moderately simple for the trisubstituted compound, but only the use of low temperature and carbon monoxide carrier gas makes possible the isolation of the di- and tricarbonyl compounds.

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(6) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 95.

(7) *Chem. Eng. News*, **42**, 52 (Oct. 26, 1964).

Strangely, it appears that there is an upper limit on the length of the column for maximum sensitivity, for on lengthening the column, beyond 3 to 4 m., the purity becomes worse. A wide variety of various organic partitioning phases and solid silicious supports which had been pretreated in a variety of ways were tried in an effort to alleviate some of the difficulties, but to no avail.

All the compounds in the system are colorless and mobile liquids. No odor was ever noticed for the substituted compounds, but a deliberate effort was made to avoid the circumstances leading to their being smelled. On the rare occasion that small amounts of $Ni(CO)_4$ got loose in the laboratory, a characteristic odor was observed. On the assumption that the substituted compounds also must have gotten loose at some time, it can be concluded that they can be detected even less easily than $Ni(CO)_4$. If they are as toxic as the tetracarbonyl, they present an even greater toxicity hazard.

The compounds $Ni(CO)(PF_3)_3$ and $Ni(CO)_2(PF_3)_2$ both melt fairly sharply at about −93°. The tricarbonyl appears to melt within 10° of this temperature, but it was never possible to keep it in the state of purity demanded for good melting point determinations. The vapor pressures and densities of the compounds, shown in Table I, are nearly linear functions of the system composition.

TABLE I

PHYSICAL PROPERTIES OF $Ni(CO)_x(PF_3)_{4-x}$ SPECIES

| | Vapor press., mm., at 0° | Density at room temp. |
|---|---|---|
| $Ni(CO)_4$ | 133 | 1.31[a] |
| $Ni(CO)_3PF_3$ | 88 | 1.49 |
| $Ni(CO)_2(PF_3)_2$ | 56 | 1.61 |
| $Ni(CO)(PF_3)_3$ | 41 | 1.71 |
| $Ni(PF_3)_4$ | 34[b] | 1.80[b] |

[a] N. H. Lange, Ed., "Handbook of Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1961. [b] Data from ref. 2.

The fluorine nuclear magnetic resonance spectra for the various $Ni(CO)_x(PF_3)_{4-x}$ species are shown in Figure 1. In this figure only the low-field half of the spectra is shown. At higher magnetic fields, an exact mirror image of peaks is found. The main features are as follows: (1) The spectra are split into two main parts caused by spin–spin coupling between the fluorine and phosphorus. The value for the splitting was not measured, but it is very similar to that of $PF_3$, which is reported to be 1441 c.p.s.[8] (2) Only a very small fluorine chemical shift is observed as the degree of substitution changes. The fluorine resonance shifts only slightly toward higher fields as the carbonyl groups are replaced by trifluorophosphine groups. (3) The spectra of many of these compounds are surprisingly complex. For example, one-half the spectrum of $Ni(PF_3)_4$ consists of a sharp spike, a quartet or a quintet, and an unresolved multiplet. The other half is an exact mirror image of this. Only the compound $Ni(PF_3)(CO)_3$ consists of a single peak—well split by P–F coupling.

The phosphorus resonance seems straightforward. The compound $Ni(PF_3)_4$, like $PF_3$, gives a four-line pattern of relative intensities 1:3:3:1 with a shift of −139 p.p.m. relative to phosphoric acid. A mixture of the $Ni(CO)_x(PF_3)_{4-x}$ complexes gave the same main pattern with essentially the same chemical shift, but having some fine structure within each peak. This fine structure is presumably caused by the nonequivalence of the phosphorus atoms in the various species. There is thus almost no chemical shift among the various $Ni(CO)_x(PF_3)_{4-x}$ species. The value of $J_{P-F}$ is about 1400 c.p.s.

The infrared data obtained for the carbonyl stretching frequencies agree fairly well with the values assigned by Bigorgne,[9] who did not actually isolate the compounds. The values obtained in this work were shifted six or eight wave numbers to lower values, probably owing to a solvent shift. The P–F data which have not been previously reported are given in the Experimental section. The assignment of the frequencies for $Ni(CO)_3(PF_3)$ is perhaps a little uncertain owing to its complexity and the lability of the compound.

The rate of disproportionation decreases significantly as the degree of phosphine substitution increases. The substitution is also markedly less when the material is in a carbon monoxide atmosphere as contrasted to when it has been well outgassed. The data are not good enough to attempt to determine the mechanism of the disproportionation, and are not actually reported here. However, the approximate time required for the disproportionation of 20% of the compounds $Ni(CO)_3(PF_3)$, $Ni(CO)_2(PF_3)_2$, and $Ni(CO)(PF_3)_3$ is about 10, 100, and 480 min., respectively. The dicarbonyl, saturated with carbon monoxide, requires 700 min. for the same degree of disproportionation. The effect of phosphorus trifluoride gas is not known.

## Discussion

The work reported in this paper combined with work done more recently[4] apparently represents the first use of vapor phase chromatography in the separation of various substituted metal carbonyls. For carbonyls that are, at least, somewhat volatile and of sufficient thermal stability, this technique provides an ideal solution to the frequently difficult problem of separating complex mixtures. Also for these systems, it can show whether a material having the composition of a probable compound is truly a single species. A further illustration of the use of v.p.c. is found in a system currently being studied.[10] Nearly all the compounds of the type $Mo(CO)_x(PF_3)_{6-x}$ have been prepared and isolated, including *cis* and *trans* isomers.

It has been assumed since the first phosphorus trifluoride complexes were prepared[2,3] that the phosphine and carbon monoxide had much in common as ligands. The current report provides a very good confirmation

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(8) E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.*, **79**, 322 (1957).

(9) M. Bigorgne, *Bull. soc. chim. France*, **53**, 1986 (1960).

(10) P. I. Hoberman and R. J. Clark, unpublished information.

of that belief. The physical similarity between the compounds $Ni(CO)_4$ and $Ni(PF_3)_4$ has been found to extend to all of the compounds intermediate between the two. The nearly linear change of vapor pressure and density among the series of compounds provides a particularly good example.

In addition to a physical similarity, one can conclude that the bonding must be similar. Not only are the carbonyl stretching frequencies only slightly effected by the presence of various numbers of phosphine groups, but there is only a very slight chemical shift for the resonance of both the phosphorus and fluorine nuclei as the carbonyl content varies.

Bigorgne[9] has studied the change in carbonyl frequency for nickel carbonyls containing $PF_3$ and a number of organic phosphines. He found that the shift of the carbonyl frequency for any given type of phosphine compound was least for the $PF_3$ complexes. He explained these results on the basis of inductive effects using Taft parameters. However, the present authors prefer the approach taken by Cotton.[11] Alternate to an explanation based on inductive effects, the behavior of $PF_3$ can be explained by attributing to $PF_3$ about the same ability to $\pi$-bond as is possessed by carbon monoxide. This then means that the $PF_3$-substituted carbonyls are unique in that the remaining carbonyl groups do not need to $\pi$-bond to a higher degree, as in other phosphine-substituted complexes, to compensate for the loss of substituted carbonyls; thus the carbonyl stretching frequency changes only slightly.

Further, the lack of any significant degree of n.m.r. chemical shift is consistent with this view. In fact, what little shift there is can be qualitatively explained by stating that $PF_3$ can $\pi$-bond slightly more effectively than carbon monoxide. This agrees with the conclusion reached by Cotton[11] on the basis of force constant calculations made for $PF_3$ bonded to molybdenum.

The $Ni(CO)_4$–$Ni(PF_3)_4$ system provides an excellent example of a system in which one can have a nearly random arrangement of ligands.[12] On heating $Ni(CO)_4$ plus $Ni(PF_3)_4$ or any one of the intermediates to only slightly elevated temperatures, a mixture of all five compounds results in which the concentration of the species appears to be based predominantly upon the relative concentration of the ligands. However, the study was not performed with sufficient accuracy to determine how closely this system comes to being truly random.

Two criteria are probably satisfied in this system in order for it to have a random ligand arrangement. First, the bonding and also the strength of the Ni–P and Ni–C bonds appear to be similar, and second, the kinetics are such that equilibrium is readily established. In the other CO–$PF_3$ systems[13] that are being studied, the first criterion is probably satisfied, but the second is not. Substitution requires such vigorous conditions that an excessive length of time is required to reach equilibrium in the absence of a catalyst. Still, mixtures are always obtained.

The ability of the ligands to rearrange creates a serious problem in purifying the compounds and keeping them pure. They have some tendency to disproportionate on the column. Further, once they have been purified, they rearrange and become mixtures again. Low temperature and the presence of carbon monoxide suppresses this tendency. This latter observation suggests that the disproportionation proceeds by a dissociation mechanism for which there is some precedent in the work by Meriweather.[14] These observations suggested the use of carbon monoxide as a carrier gas, which finally made possible the preparation of $Ni(CO)_3(PF_3)$ in high purity.

One unexplained phenomenon is the fluorine n.m.r. spectra. One can illustrate the problem by the spectrum of $Ni(PF_3)_4$, which was described earlier. Since this molecule is tetrahedral, one would expect that all twelve fluorines would be equivalent, assuming that the $PF_3$ groups are free rotating about the M–P axis. This should result in a spectrum consisting only of a doublet caused by spin–spin splitting between phosphorus and fluorine. Spin–spin decoupling and temperature studies will be done in an effort to resolve the problem.

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(11) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

(12) For a recent review, see J. R. Van Wazer, *Am. Scientist*, **50**, 450 (1962).

(13) Iron, molybdenum, chromium, cobalt, and manganese.

(14) L. S. Meriweather and M. L. Fiene, *J. Am. Chem. Soc.*, **81**, 4200 (1959).