by the ratio Δ/σ of the difference from its esd.

Acknowledgment. The authors are indebted to Prof. C. Guastini (University of Parma) for his help in the collection of X-ray data.

Supplementary Material Available: Figure A (IR spectra of $Ru(CO)_2(CH_3COO)_2[P(n\text{-}Bu)_3]_2$ and $Ru_4(CO)_8(CH_3COO)_4[P(n\text{-}Bu)_3]_2$ in heptane at 60, 100, 120, and 140 °C) and, for IV, Figure B (IR spectrum, KBr pellet) and Figure C (NMR spectrum, CD_2Cl_2 solution) and, for the structure determination, tables of anisotropic thermal parameters, hydrogen atom coordinates, bond distances, bond angles, and torsion angles (17 pages); a listing of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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Two New Nickel Difluorophosphine Species: Synthesis, Characterization, and Discussion Regarding the Nature of the Nickel–Difluorophosphine Interaction

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Received September 4, 1986

The study of the coordination chemistry of PF_2H has been expanded by the synthesis and characterization of $Ni(CO)_3(PF_2H)$ and $Ni(CO)_2(PF_2H)_2$. Spectral data for these complexes are compared with those of related compounds as a probe for investigating bonding interactions of PF_2H. Infrared carbonyl stretching frequency data and displacement reactions suggest that the electron-donor–electron-acceptor properties of PF_2H are intermediate between those of PF_3 and PH_3 when the ligands are bound to nickel. This observation contrasts sharply with the donor ability of PF_2H when BH_3 is the reference acid. In the latter case PF_2H is a much stronger base than PF_3 or PH_3. Acid–base arguments are considered.

The chemistry of PF_2H has been a widely discussed topic in the literature for several years.[1] $HF_2P{\cdot}BH_3$,[2] and $HF_2P{\cdot}B_4H_8$[3,4] show an unexpectedly high thermal stability when compared with the analogous complexes of PF_3 and PH_3. This anomalous behavior of PF_2H has been interpreted as evidence for the premise that PF_2H is a stronger σ base than either PF_3 or PH_3.[5] In contrast, $Ni(PF_2H)_4$ is intermediate in thermal stability between $Ni(PF_3)_4$ and $Ni(PH_3)_4$.[6]

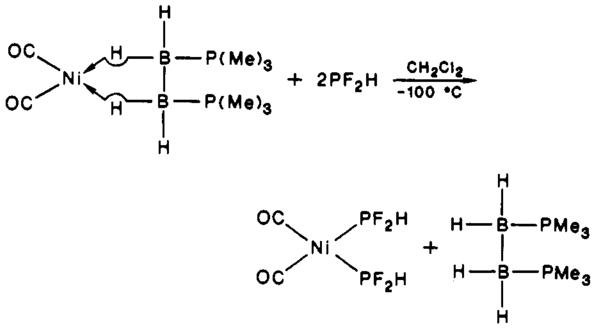
We were interested in synthesizing $Ni(CO)_3(PF_2H)$ and $Ni(CO)_2(PF_2H)_2$ to obtain more definitive information concerning the electron-donor–electron-acceptor properties of PF_2H. Carbonyl infrared stretching frequencies are generally free from extensive coupling with other modes and they usually are not obscured by the presence of other vibrations, so they provide a useful probe into bonding considerations. Tolman[7] and others[8] have previously used carbonyl infrared data as one measure of the relative electron-donor–electron-acceptor properties of phosphorus ligands bound to metal carbonyls. In this paper we have compared the infrared data for $Ni(CO)_3L$ and $Ni(CO)_2L_2$ where L = PF_3, PF_2H, and PH_3 in order to compare PF_2H to other related ligands. These results will be discussed. Some displacement results are also considered.

Prior to this study, $Ni(PF_2H)_4$ was the only well-characterized, isolatable metal complex of PF_2H.[6,9] So far PF_2H complexes are more difficult to prepare than most other analogous phosphine metal complexes,[6,10,11] because of the high reactivity of PF_2H itself. The compound is air and water sensitive and will begin to decompose or react readily when it is in an impure state, even at temperatures of 20 °C or lower. However, when PF_2H is pure, it can be held at room temperature for short periods of time with minimal decomposition and it can be handled very easily by using high-vacuum techniques.[12] $(CO)_3Ni(PF_2H)$ is easily prepared by using general procedures described earlier[13] for the preparation of $Ni(CO)_3L$ species where L is a phosphine. The equation is

$$PF_2H + Ni(CO)_4\ (\text{excess}) \xrightarrow[-80\ °C]{CH_2Cl_2} (CO)_3Ni(PF_2H) + CO \qquad (1)$$

$Ni(CO)_2(PF_2H)_2$ is also easily prepared by exploiting the reactive

bonds in the complex $Ni(CO)_2(B_2H_4{\cdot}2PMe_3)$.



(2)

This method has also been used to prepare $Ni(CO)_2L_2$ complexes where L = PPh_3, PF_3, and PH_3.[14]

Experimental Section

General Methods. All manipulations were carried out under an inert atmosphere or on a high-vacuum line. IR data were recorded on a Beckman IR-20 high-resolution spectrometer or on a Perkin-Elmer 1500 FTIR spectrometer. Mass spectral data were obtained by using a VG

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(9) (a) When Rudolph first prepared PF_2H, he obtained a product that he suggested was $Ni(CO)_3(PF_2H)$ from the reaction of excess PF_2H and $Ni(CO)_4$. Data presented here show that actually he obtained a mixture of $Ni(CO)_3(PF_2H)$ and $Ni(CO)_2(PF_2H)_2$. See ref 6. (b) Ebsworth et al. have presented in situ low-temperature NMR information on some extremely reactive iridium–PF_2H complexes. These decompose on warming and have not yet been isolated: Edsworth, E. A. V.; Gould, R. O.; McNapus, J. T.; Rankin, D. W. H.; Walkinshaw, M. D.; Whitelock, J. D. *J. Organomet. Chem.* **1983**, 249, 227.

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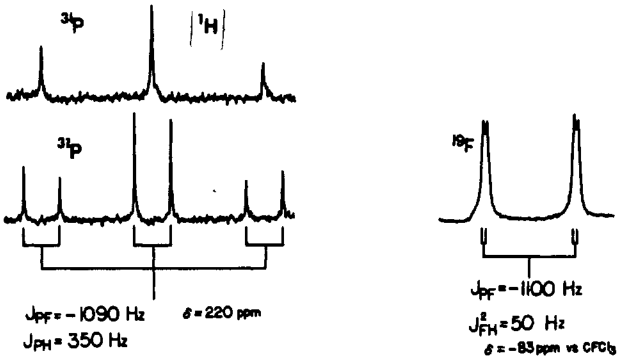

Figure 1. ^{31}P and ^{19}F NMR spectra of $(CO)_3Ni(PF_2H)$.

Table I. NMR Data for PF_2H and PF_2H–Nickel Complexes[d]

	chem shift, ppm			coupling const, Hz			
	^{31}P[a]	^{19}F[b]	^{1}H[c]	$^{1}J_{PF}$	$^{1}J_{PH}$	$^{3}J_{PF}$	$^{2}J_{FH}$
PF_2H[2,12]	224	-121.6	7.64	-1143	182	...	41.7
$(CO)_3Ni(PF_2H)$	219.6	-83.2		-1100	350	...	50
$(CO)_2Ni(PF_2H)_2$	220.3	-81.3	8.18	-1095	371.1	-42.5	47.5
$Ni(PF_2H)_4$	218	-77.1	8.30	-1040	374	-46	50

[a] 85% H_3PO_4 was external standard. [b] $CFCl_3$ was external standard. [c] Tetramethylsilane was external standard. [d] In all cases downfield shifts are positive.

micromass 7070 double-focusing high-resolution mass spectrometer with a VG Data System 2000 with electron-impact ionization at either 17 or 70 eV. NMR spectra were obtained on one of the following, a Varian XL-100, XL-300, or FT-80A spectrometer. External standards were used for all spectra, 85% H_3PO_4 for ^{31}P, Tetramethylsilane (Me_4Si) for ^{1}H, and $CFCl_3$ for ^{19}F NMR data. Downfield shifts have positive values.

Materials. PF_2H, prepared by using the method of Rudolph,[15,16] was obtained from laboratory stock. $Ni(CO)_4$ was obtained from Pfaltz and Bauer, Inc., and was fractionated before use. $(CO)_2Ni(B_2H_4{\cdot}2PMe_3)$ was obtained from S. A. Snow.[14] Solvent CH_2Cl_2 was distilled from P_2O_5 and degassed before use.

Preparation of $Ni(CO)_3(PF_2H)$. In a typical reaction, a carefully measured quantity (0.25 mmol) of PF_2H was condensed with liquid nitrogen into the bottom of a 9-mm-o.d. Pyrex reaction tube, which was sealed in its upper portion to a 100-mL gas expansion bulb. This tube was then sealed on its linear axis to a stopcock and ground-glass joint to permit attachment to the vacuum system. An excess of PF_2H (beyond 0.25 mmol) was carefully avoided. Approximately 0.75 mL of CH_2Cl_2 was then condensed (-196 °C) into the sample tube. The sample was warmed briefly to obtain a homogeneous solution and was then refrozen. A 1.0-mmol sample of $Ni(CO)_4$ was condensed with liquid nitrogen onto the frozen PF_2H/CH_2Cl_2 solution. The reaction sample, held at -196 °C, was removed from the vacuum line and allowed to warm to -80 °C in the NMR probe. To place the reaction tube in the NMR probe, the 9-mm reaction tube was placed inside a regular 10-mm NMR tube and the entire assembly was then placed in the appropriate opening of the probe. If the tube still had a stopcock in the assembly, it was not spun. If spinning was desired, the tube could be sealed off above or below the gas expansion bulb to give a balanced unit. Reaction progress was monitored by ^{31}P NMR spectroscopy. No reaction was observed after 0.5 h at -80 °C. The probe temperature was then raised to -60 °C, and in less than 10 min the new nickel complex containing coordinated difluorophosphine began to form. After 2 h at -60 °C approximately two-thirds of the PF_2H had reacted. After the initial period, the reaction progressed more slowly. After 2 h more at -60 °C and 15 h at -45 °C, low-temperature NMR spectra verified that only 2% of the original PF_2H was still present in the free state. An 86% yield of $Ni(CO)_3(PF_2H)$ and a 12% yield of $Ni(CO)_2(PF_2H)_2$ were found in the products by ^{31}P NMR. Since $Ni(CO)_3(PF_2H)$ is slighly more volatile than $Ni(CO)_2(PF_2H)_2$ or CH_2Cl_2, the monosubstituted compound can be further purified by a tedious trap-to-trap distillation. The sample was held at 0 °C, and the volatile components were collected in a -196 °C trap. The product and CH_2Cl_2 have very similar vapor pressures, and so separation procedures are time consuming. Both CH_2Cl_2 and $(CO)_3Ni(PF_2H)$ distill slowly from a -111 °C trap into a -196 °C trap. However, when the mixture is held at -126 °C, only the $(CO)_3Ni(PF_2H)$ will move into the -196 °C trap. The ^{31}P and ^{19}F NMR spectra are shown in Figure 1. Characterization data are present in Table I. Gas-phase infrared data for $Ni(CO)_3(PF_2H)$ are summarized here, with units of cm^{-1}: ν(PH), 2356 s, 2343 s, 2330 s (the multiplet in ν(PH) is assigned to rotational structure at the present; more work is in progress); ν(CO), 2110 w, 2058 vs; δ(PH), 1029 s; ν(PF), 883 vs. The ν(CO) data (Table II) and the NMR data are analyzed in the discussion section.

Table II. ν(CO) A_1 Mode Frequencies for $Ni(CO)_{4-n}L_n$ Species[a,b]

		ν(CO)					
	L	$Ni(CO)_3L$		$Ni(CO)_2L_2$		$Ni(CO)L_3$	
good π acid	CO	2131	...	2131	...	2131	...
poor σ base	PF_3	2117	(2111)	2101	(2094)	2084	(2076)
	PCl_3	...	(2103)	...	(2081)	...	(2059)
	PF_2H	2110	(2099)	2087		...	
	Me_2NPF_2	2102		2060	(2049)	2018	
	PH_3[c]		(2083)	2057		...	
poor π acid	$P(OMe)_3$		(2082)		(2028)	...	
good σ base	PMe_3		(2069)		(2002)		(1923)

[a] Values are given in cm^{-1}. [b] Values in parentheses are hydrocarbon solution data. All others are gas-phase data. See ref 21. [c] See ref 23.

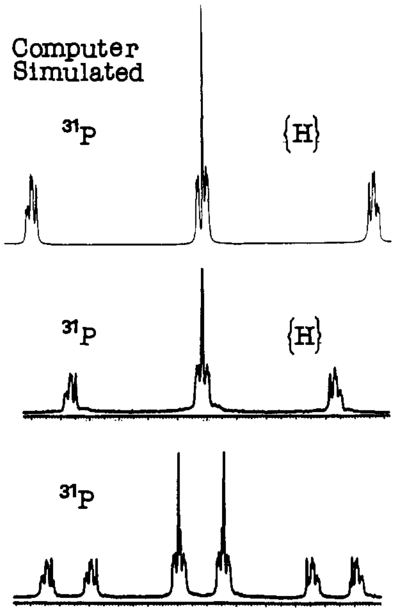

Figure 2. Observed and simulated ^{31}P NMR spectrum of $(CO)_2Ni(PF_2H)_2$.

Preparation of $(CO)_2Ni(PF_2H)_2$. In a typical reaction 1 mL of CH_2Cl_2 was condensed into a 9-mm-o.d. NMR/reaction tube, similar to that described previously except that the present unit was equipped with a capped side arm. With nitrogen gas flushing the system, 0.14 mmol of $(CO)_2Ni(B_2H_4{\cdot}2PMe_3)$ powder was added into the sample tube through the side arm. The yellow material readily dissolved in CH_2Cl_2 to give a yellow solution. After all of the nickel complex was dissolved, the sample was degassed by a series of freeze–thaw cycles. The solution was then frozen with a liquid nitrogen bath, and 0.27 mmol of PF_2H was condensed onto the frozen sample. The sample tube was removed from the vacuum line and placed in a -100 °C NMR probe and monitored by ^{31}P NMR. The tube was not spun during NMR measurements. The reaction occurred rapidly at -100 °C. In less than 0.5 h the reaction was virtually complete, yielding the new nickel complex $(CO)_2Ni(PF_2H)_2$ and the uncoordinated $B_2H_4{\cdot}2PMe_3$. The compound could be isolated from the clear yellow solution by trap-to-trap distillation. The yellow solution mixture was held at 0 °C and the volatile components were collected at -196 °C. This volatile sample from the -196 °C trap was then raised to 0 °C, and the trap contents were distilled through a -80 °C trap into a -196 °C trap. Solid $B_2H_4{\cdot}2PMe_3$ crystallized in the -80 °C trap. The product and CH_2Cl_2 were collected at -196 °C. If this last mixture was held at -111 °C, the CH_2Cl_2 distilled slowly into the -196 °C trap while

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(17) When L = PF_3, the ^{31}P NMR shift is approximately 138 ppm for n = 1-4. The ^{19}F shift for $Ni(CO)_2(PF_3)_2$ is -18.9 ppm, and that for $Ni(PF_3)_4$ is -16.8 ppm. When L = Me_2NPF_2, the ^{31}P NMR shift is approximately 169 ppm for n = 1-4. The ^{19}F NMR data are -44.3, -43.4, -41.6, and -38.9 ppm for n = 1-4, respectively: (a) Clark, R. J.; Brimm, E. O. *Inorg. Chem.*, **1965**, *4*, 651. (b) Nixon, J. F. *Adv. Inorg. Chem. Radiochem.* **1970**, *13*, 363. (c) See also ref 5.

Table III. Displacement of PF_3 by PF_2H in $Ni(CO)_2(PF_3)_2$ and of PF_2H by PF_3 in $Ni(CO)_2(PF_2H)_2$ at −80 °C

$$(CO)_2Ni(PF_3)_2 + 2PF_2H \xrightleftharpoons[-80\ ^\circ C]{CH_2Cl_2} (CO)_2Ni(PF_2H)_2 + 2PF_3$$

quantities mixed in 1 mL of dry CH_2Cl_2 in an NMR tube			
reactant	amt, mmol	time	ratio measd of A/B[a]
$Ni(CO)_2(PF_3)_2$ (A)	0.23	50 h	13/1
PF_2H	0.22	17 days	10/1
$Ni(CO)_2(PF_2H)_2$ (B)	0.23	50 h	1/7
PF_3	0.22	17 days	1/4

[a] This ratio is $[(CO)_2Ni(PF_3)_2]/[(CO)_2Ni(PF_2H)_2]$. Because equimolar quantities of complex and free ligand were taken, complete displacement would give a ratio of 1 in both cases.

the product remained in the −111 °C trap.

The undecoupled ^{31}P NMR spectrum is shown in Figure 2. Complete NMR characterization data are shown in Table I. The proton NMR data for $(CO)_2Ni(PF_2H)_2$ obtained in CH_2Cl_2 solution are also shown in Table I.

Gas-phase infrared spectroscopic data are summarized here in units of cm^{-1}: ν(PH), 2330 s; ν(OC), 2087 s, 2055 vs; δ(PH), 1019 s; δ(HPF), 970 w; ν(PF), 853 vs, 840 s.

Electron-impact mass spectral data were obtained at 17 and 70 eV. The expected isotopic pattern due to the five isotopes of nickel can be seen. The parent peak and structurally significant fragments are listed here. Only the most intense peak in each isotopic group is listed. The relative intensities of the peaks were normalized to the most abundant peak above *m/z* 32. The 17-eV assignments, *m/z* values, and relative intensities are given as follows: $Ni(CO)_2(PF_2H)_2^{\bullet+}$, 254 (9); $Ni(CO)(PF_2H)_2^+$, 226 (37); $Ni(CO)_3(PF_2H)^{\bullet+}$, 212 (23); $Ni(PF_2H)_2^+$, 198 (19); $Ni(CO)_2(PF_2H)^+$, 184 (68); $Ni(CO)(PF_2H)^+$, 156 (52); $Ni(CO)_3^+$, 142 (86); $Ni(PF_2H)^+$, 128 (29); $Ni(CO)_2^+$, 114 (100); $Ni(CO)^+$, 86 (59); Ni^+ 58 (9). Note that the peaks at *m/z* 212 and 142 can only be derived from a $Ni(CO)_2(PF_2H)_2$ impurity.

Displacement Reactions Involving $Ni(CO)_3PF_2H$ and $Ni(CO)_2(PF_2H)_2$. Experiments involved displacement of PF_3 in $(CO)_2Ni(PF_3)_2$ by PF_2H and displacement of PF_2H in $(CO)_2Ni(PF_2H)_2$ by PF_3. For the first process a 9-mm-o.d. NMR tube equipped with a gas expansion bulb, a stopcock, and a joint for fastening the tube to the vacuum line was used. An 0.23-mmol sample of $(CO)_2Ni(PF_3)_2$ was prepared on the vacuum line from $(CO)_2Ni(B_2H_4{\cdot}2PMe_3)$ by a method analogous to that used to prepare $(CO)_2Ni(PF_2H)_2$ (previous section). A 1-mL sample of dry CH_2Cl_2 was condensed on to the $(CO)_2Ni(PF_3)_2$, and then a 0.22-mmol sample of PF_2H was condensed in the tube at −196 °C. The system was then warmed to −80 °C for times as indicated. Analysis of the mixture was by ^{31}P NMR. The dominant compounds in the reaction mixture were $Ni(CO)_2(PF_3)_2$ and $Ni(CO)_2(PF_2H)_2$. Other side products were present in relatively small amounts. We did not see $Ni(CO)_2(PF_3)(PF_2H)$ as a significant species. Data on mixture composition are found in Table III.

The second process, the displacement of PF_2H from $(CO)_2Ni(PF_2H)_2$ by PF_3, was carried out under conditions identical with those described above for the first displacement. The dominant species in the final reaction mixture were again $(CO)_2Ni(PF_3)_2$ and $(CO)_2Ni(PF_2H)_2$ with smaller quantities of side products. Data are summaried in Table III.

Discussion

NMR Data. For $(CO)_3Ni(PF_2H)$ the undecoupled ^{31}P NMR spectrum shows clearly that the PF_2H unit remains intact. The P–H and P–F coupling constant values are consistent with those expected for a nickel-coordinated phosphine. The simplicity of both the ^{31}P and ^{19}F spectra provides evidence in support of a monosubstituted nickel carbonyl complex.

For $(CO)_2Ni(PF_2H)_2$ the NMR spectrum is more complex as one would expect, but the first-order triplet of doublets expected at about 220 ppm confirms that PF_2H is present in the molecule. Because of clear second-order behavior in the $(CO)_2Ni(PF_2H)_2$ spectrum a computer simulation experiment was undertaken. Chemical shifts and coupling constants obtained from ^{31}P and ^{19}F spectra using first-order approximations were used to start. The simulation program available to us on the Varian XL-300 NMR system was not sophisticated enough to allow simulation of the fully coupled ^{31}P spectrum of $(CO)_2Ni(PF_2H)_2$. However, simulated $^{31}P\{^1H\}$ matched the experimentally obtained spectrum very well. Actual and simulated spectra are shown in Figure 2. The ^{19}F spectrum is seen in Figure 3.

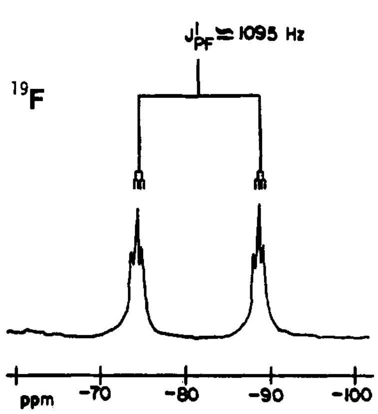

Figure 3. ^{19}F NMR spectrum of $(CO)_2Ni(PF_2H)_2$.

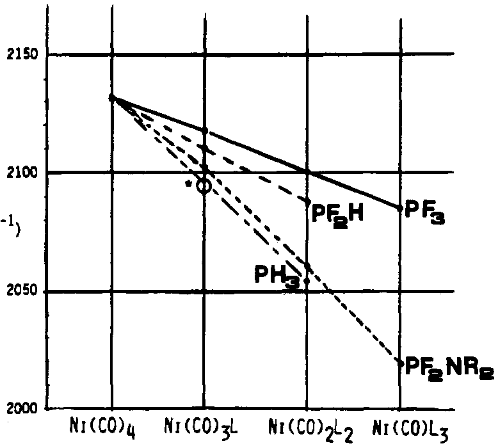

Figure 4. Carbon monoxide symmetric stretching frequencies (A_1 mode) for the series $(CO)_{4-x}NiL_x$. Gas-phase data except for $Ni(CO)_3PH_3$, which value is for a hydrocarbon solution corrected empirically to the vapor phase.

It is interesting to note that the ^{31}P chemical shifts for $(CO)_3Ni(PF_2H)$ and $(CO)_2Ni(PF_2H)_2$ are nearly identical (220 ppm) while the ^{19}F shifts are displaced through a small but measurable range. Similarly when the $\delta(^1H)$ values for PF_2H, $(CO)_2Ni(PF_2H)_2$, and $Ni(PF_2H)_4$ are examined, values follow a smooth curve over a small range of values. Since we do not have data from $(CO)_3Ni(PF_2H)$, there could still be an irregularity in the trend.

Infrared Data. Assignments of infrared spectral lines were made by using earlier work from this laboratory of Rudolph[6] and Staplin[18] as a guide. Certain spectral characteristics are seen that are diagnostic for metal-coordinated fluorophosphine or carbonyl complexes. For example, the ν(PF) of PF_3 is reported to shift to higher frequencies upon coordination to a metal center.[19a] A

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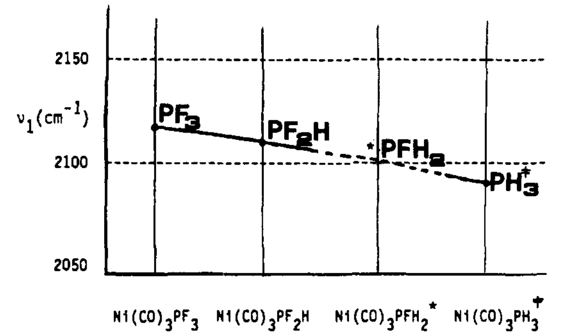

Figure 5. Carbon monoxide symmetric stretching frequencies (A_1 mode) for the series $(CO)_3Ni(PF_{3-x}H_x)$. An asterisk denotes that the compound is still unknown; a double dagger denotes the frequency corrected from hydrocarbon solution to vapor phase empirically. See Table II.

similar ν(PF) shift is seen for the nickel complexes of PF_2H. The ν(PF) stretching frequencies of $(CO)_3NiPF_2H$, $(CO)_2Ni(PF_2H)_2$, and $Ni(PF_2H)_4$ are 883, 853, and 906 cm^{-1}. All are higher than the value of 839 cm^{-1} for the Q branch of PF_2H(g). It is interesting to note, however, that simple trends in ν(PF) are not seen as CO groups are systematically replaced by PF_2H groups, starting with $(CO)_3Ni(PF_2H)$. Similarly, simple systematic trends in ν(PH) were not seen as CO groups were replaced by PF_2H.

In contrast the totally symmetric CO stretching vibrations, ν(CO) A_1, show remarkably consistent change as CO groups are replaced by ligands, L, in the series $Ni(CO)_{(4-n)}L_n$ where L is any ligand. Table II lists the carbonyl stretching frequencies (A_1 mode) for a number of these compounds. Several trends are observable. Consider the sequence $Ni(CO)_4$, ν(CO) 2131 cm^{-1}; $Ni(CO)_3PF_2H$, ν(CO) = 2110 cm^{-1}; and $Ni(CO)_2(PF_2H)_2$, ν(CO) 2087 cm^{-1} for which ν(CO) values are now available. There is an almost linear decrease in ν as each CO is substituted by PF_2H. Exactly the same type of change is observed when PF_3 is substituted for CO in $Ni(CO)_{4-x}L_x$ series except that the change with PF_2H is greater than that with PF_3. See Figure 4. The decrease in the A_1 CO stretching frequency when a CO is replaced by PF_3 is conventionally explained on the assumption that PF_3 is a poorer π-bonding-acceptor ligand than is CO.[29] Because PF_3 is a poorer π acceptor than CO, more negative charge remains on the metal atom when PF_3 replaces one of the CO ligands. This excess electron density is then transferred to the *anti*bonding orbitals of the remaining CO units, pushing the triple CO bond toward a double bond with a lower CO stretching frequency. As Tolman[7] and others have noted, this CO stretching frequency has been used as a parameter to measure the π-acceptor ability of the ligand, which replaces one CO in $Ni(CO)_4$. In Table II selected ligands L are arranged in order of presumed decreasing π-acceptor ability. PF_2H is, as one would expect, a poorer π acid than PF_3 and a slightly poorer π acid than PCl_3. It is, again as one would expect, a better π acid than $(CH_3)_2NPF_2$[22] and a much better π acid than PH_3. Interestingly enough, the CO frequency for $Ni(CO)_3PF_2H$ falls on a line in the sequence $Ni(CO)_3PF_3$, $Ni(CO)_3PF_2H$, $Ni(CO)_3PFH_2$ (unknown), and $Ni(CO)_3PH_3$. (Figure 5). It is quite clear from the data displayed in Figures 4 and 5 that PF_2H is not unusual at all in its effect on the CO stretching frequency. The trend displayed in Figure 5 is amazingly regular. The substitution of an H for an F of PF_3 lowers the ν(CO) of $(CO)_3NiPF_2H$ as expected. One could thus conclude that PF_2H has a lower π-acid capability than PF_3 and perhaps a slightly higher σ-bonding capacity than PF_3, but the latter point relative to σ bonding is not established directly by the data. Tolman examined CO stretching frequencies for 70 compounds of the type $Ni(CO)_3PX^1X^2X^3$ and devised an additivity formula for computing ν(CO) (A_1 mode) for each compound based on the nature of the substituents attached to phosphorus in the ligand $PX^1X^2X^3$. If one uses the data for $Ni(CO)_3PF_3$ to establish additivity values for the fluorines in PF_3 and Tolman's values for the hydrogen atoms to use in PF_2H, it is possible to calcualte the ν(CO) for $Ni(CO)_3PF_2H$ from Tolman's formula:

$$\nu(\mathrm{CO})\ A_1 = 2056.1 + \text{constants for } X^1 + X^2 + X^3 \quad (3)$$

The additivity value for fluorine is 18.2 cm^{-1}; that for hydrogen is 8.3 cm^{-1}. When these values are used to calculate the ν(CO) (A_1 mode) for $Ni(CO)_3PF_2H$ the calculated value is 2100.7 cm^{-1} as compared to an experimental value of 2099 cm^{-1}. Agreement is very good. This additivity relationship is the same as that seen graphically in Figure 5.

Mass Spectral Data. The 70-eV mass spectrum of $(CO)_2Ni(PF_2H)_2$ showed additional peaks resulting from $Ni(CO)(PF_2H)_3$: i.e., $Ni(CO)(PF_2H)_3$, 296 (0.2); $Ni(PF_2H)_3^+$, 268 (0.9). Since the mono- and trisubstituted moieties could not be seen in $(CO)_2Ni(PF_2H)_2$ when sensitive ^{19}F NMR spectra were used as a probe for the system before isolation attempts, it appears that these nickel–PF_2H complexes are quite susceptible to disproportionation in the mass spectrometer and upon handling.[20] This makes the separation process for these studies difficult. Rapid low-temperature separation, followed by immediate freezing of the isolated sample, permitted isolation of the pure species.

Displacement Reactions. The really significant question about PF_2H involves a comparison of the coordinating properties of PF_2H with $-BH_3$ and $-Ni(CO)_3$, or $-Ni(CO)_2L$ used as reference acids. We are concerned with the overall bond strength in each case as measured by ligand displacement. In the case using BH_3 as a reference acid, PF_2H will neatly displace both PF_3 and PH_3 from H_3BPF_3 and H_3BPH_3. The displacement data indicate quite clearly that PF_2H is a significantly stronger base than PF_3 or PH_3 against BH_3 as the reference acid. In contrast PF_2H displacement reactions involving $-Ni(CO)_3$ or $-Ni(CO)_2L$ as the reference acid are far more equivocal. The data argue in favor of a decreasing strength in the Ni–P ligand bond as one goes from $(CO)_2Ni(PF_3)_2$ to $(CO)_2Ni(PF_2H)_2$ to $(CO)_2Ni(PH_3)_2$ but side reactions complicate the issue. No unusual bond strength for Ni-PF_2H is indicated!

The experiments involved displacement of PF_3 in $(CO)_2Ni(PF_3)_2$ by PF_2H and displacement of PF_2H by PF_3 in $(CO)_2Ni(PF_2H)_2$. When $(CO)_2Ni(PF_3)_2$ and PF_2H were mixed in equimolar quantities and held for extended periods at −80 °C, the dominant species in the reaction mixture were the original $Ni(CO)_2(PF_3)_2$ and the product $Ni(CO)_2(PF_2H)_2$. The dominant product ratio in Table III indicates relative displacement of PF_3 by PF_2H and the reverse process as well. The mixed species $Ni(CO)_2(PF_3)(PF_2H)$ was not a dominant species under the conditions used. The equation for the process is

$$Ni(CO)_2(PF_3)_2 + 2PF_2H \xrightleftharpoons[CH_2Cl_2]{1\ mL} Ni(CO)_2(PF_2H)_2 + 2PF_3 \quad (4)$$

Because equimolar quantities of $Ni(CO)_2(PF_3)_2$ and PF_2H were taken at the start, complete displacement of PF_3 by the available PF_2H would give a final $Ni(CO)_2(PF_3)_2/Ni(CO)_2(PF_2H)_2$ ratio of 1.0. The measured ratios shown in Table III, which are much higher than 10, indicate that PF_2H is displacing relatively little PF_3 in the time allowed.

The reverse process, the displacement of PF_2H from $Ni(CO)_2(PF_2H)_2$ by PF_3, was also carried out under conditions identical with those used for displacement of PF_3 by PF_2H. Again, the final ratio of $Ni(CO)_2(PF_3)_2/Ni(CO)_2(PF_2H)_2$ would be 1 if displacement of PF_2H by PF_3 were complete. Measured ratios as high as 1/4 now indicate quite clearly that under the conditions of the reaction PF_3 displaces PF_2H more rapidly than PF_2H displaces PF_3. Because side products began to be of concern after 19 days at −80 °C, the mixtures were not held longer in an attempt to obtain an equilibrium system.

The data suggest quite clearly that under comparable conditions PF_3 displaces PF_2H significantly more rapidly than PF_2H displaces

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(29) One can argue about whether the spectral data for the C≡O stretching frequencies in carbonyl indicate the π component of the bond or the total $\sigma + \pi$ interaction, but this differentiation is not of crucial importance here.

PF_3. Tolman in his study of equilibrium displacement reactions involving NiL_4 species stated: "Generally those ligands seemed to be most rapidly displaced which gave the least stable complexes as judged from the equilibrated ligand exchange solutions." Since the exchange process in closely related species involves ligand dissociation as the first step in the mechanism, this generalization is very reasonable. On the basis of Tolman's observation, PF_3 would appear to give a more stable complex of the form $Ni(CO)_2L_2$ than does PF_2H. The final ratios measured also suggest this point but the ratios do not indicate true equilibrium values. Side reactions involving destruction of PF_2H prevented us from obtaining true equilibrium constants or even final ratios by continuing the experiments for longer times. The true equilibrium relationships have not yet been obtained, but data available as of now indicate that PF_2H is less strongly bound to Ni than is PF_3. PF_2H is more strongly bound than is PH_3. This relationship was supported by ν(CO) data in earlier studies where steric factors (cone angles) were not involved.

Anomalous Base Strength of PF_2H. Much of the past interest in PF_2H as a ligand has focused on its unusual base strength toward boranes as reference acids. As noted earlier, $F_2HP{\cdot}BH_3$ is more stable thermally than either $F_3P{\cdot}BH_3$ or $H_3P{\cdot}BH_3$. Furthermore F_2HP will displace F_3P or H_3P quantitatively from the respective borane adducts. Microwave studies of $F_3P{\cdot}BH_3$ and $F_2HP{\cdot}BH_3$ have been made by Lide and Kuczkowski[26] and by Pasinski and Kuczkowski.[25] An interesting feature of these structural studies is the fact that the P–B distance is identical within the limits of measurement in both gaseous species: $F_3P{\cdot}BH_3$ (1.836 ± 0.012 Å) and F_2HPBH_3 (1.832 ± 0.009 Å). This is true despite the significant difference in the stability of the two compounds. Another significant structural feature is the geometry of F_2HPBH_3. Pasinski and Kuczkowski wrote, "the most unusual structural feature of $F_2HP{\cdot}BH_3$ is the lack of symmetry of the borane group about the P–B bond. ...the PBH angles indicate a pronounced tilt of the borane group *away from* the fluorine atoms, particularly when compared to the PBH angle of $F_3P{\cdot}BH_3$." They further noted that the isoelectronic molecule F_2HSiCH_3, which is quite similar to $F_2HP{\cdot}BH_3$ does not show the tilt of the CH_3 group. A comparison of the barriers to internal rotation of $F_2HP{\cdot}BH_3$[16] (3.6–4.5 kcal/mol) and isoelectronic F_2HSiCH_3 (1.25 kcal/mol) indicates a higher barrier to rotation in the phosphorus compound as compared to the silicon compound. These experimental facts were consistent with a model in which "the negative fluorines and protonic hydrogen bonded to phosphorus could interact with the hydridic hydrogens bonded to boron to tilt the borane group away from the fluorines." See also ref 24.

In a subsequent ab initio analysis of the borane complexes of F_3P, F_2HP, and H_3P Armstrong[5c] concluded that "the greater stability of the difluoro derivative over the trifluorophosphine complex stems from (1) smaller antibonding interactions present in $HPF_2{\cdot}BH_3$, (2) a lower reorganization energy of HPF_2, and (3) more favorable orbital energies of HPF_2." Armstrong's first point, smaller antibonding interactions, is, in its simplest form, comparable to the proposal of Pasinski and Kuczkowski who suggested that replacement of a negatively charged fluorine on phosphorus by a slightly positively charged proton would replace a hydride–fluoride repulsion by a hydride–proton attraction. In a later and related proposal Centofanti[27] considered variations in stability of various difluorophosphine–boranes using difluorophosphines such as HPF_2, FPF_2, $ClPF_2$, $BrPF_2$, etc. by using a model based on the assumption that the parameter limiting the stability of the PB bond is the electrostatic repulsion between the group attached to phosphorus and the borane unit. In HPF_2 the repulsion of F^- is changed into the attraction of a slightly protonic hydrogen atom causing an increase in stability.

Items 2 and 3 of Armstrong are characteristic of only HPF_2 and should make $Ni(HPF_2)_4$ more stable than $Ni(PF_3)_4$. Armstrong noted that the contribution due to differences in the reorganization energy (item 2) must be small—a conclusion that is widely shared. Armstrong's third point, more favorable orbital Centofanti[27] considered HPF_2, was considered in an independent theoretical-photoelectron spectroscopy study by Cowley et al.[28] Although some interpretational difficulties for PE spectra were recognized, it was concluded that the "lone pair stabilization energies, Δa_1" of bases, occurring on coordination, can be taken as a crude indicator of the σ-donor ability of the base. Use of this parameter indicated that the σ-donor ability of PF_2H was higher than that of PF_3 or PH_3. [Δa_1: PH_3, 1.22 eV, PF_2H, 1.6 eV; PF_3, 0.5 eV.] Since it is concluded that σ-donor capability is of major importance in the formation of BH_3 adducts, the energies of the lone pairs suggest that $HPF_2{\cdot}BH_3$ should be the most stable but $H_3P{\cdot}BH_3$ should be much more stable than $H_3B{\cdot}PF_3$. The latter point is contrary to fact.

Data given in this paper indicate that the unusual base strength of PF_2H toward acids is quite specific for borane acids. No evidence of any kind indicates unusual strength for the Ni–PF_2H bond. In fact, quite the opposite is indicated. PF_3 appears to be a stronger base than PF_2H toward Ni(0). Explanations of the anomalous base strength of PF_2H that focus on properties of the ligand itself would appear to be inadequate. In our judgement, bond characteristics involving both the acid and the base must be considered. For example the interaction of the somewhat hydridic hydrogen of the borane with the somewhat protonic hydrogen of the PF_2H would appear to be a specific interaction that can still generate unusual base strength in the unusually stable compounds $F_3HP{\cdot}BH_3$ and $F_2HP{\cdot}B_4H_8$.

Acknowledgment. Major support of this work by the National Science Foundation through Grant No. CHE 7920313 is gratefully acknowledged. Mass spectra were obtained through the University of Utah Mass Spectroscopy Laboratory, which has been funded by NSF Grant Nos. CHE 8100424 and CHE 8310031 and by the University of Utah Institutional Funds Committee. Many of the NMR spectra were obtained on equipment funded by the NSF, the DOD, and the University of Utah. W. E. Buhro and E. J. O'Connor, working in the laboratory of Prof. J. A. Gladysz, graciously ran the FT-IR spectra reported here. Finally, we are most appreciative of the many contributions made to this work by Prof. Goji Kodama. His timely suggestions and criticisms as well as help in obtaining the NMR spectra are much appreciated.