were identified by physical properties, infrared spectra, and NMR spectra.

Acknowledgment. Support of this work by the National Science Foundation under Grant No. 32079 is gratefully acknowledged. Helpful discussions with Professor Goji Kodama are also greatly appreciated.

Registry No. Ni, 7440-02-0; $Ni(PF_3)_4$, 13859-65-9; $Ni(CO)_4$, 13463-39-3; H_3BCO, 13205-44-2; H_3BPF_3, 14931-39-6; B_2H_6, 19287-45-7; PH_3, 7803-51-2; PF_2H, 14984-74-8; PF_3H_2, 13659-65-9.

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Reaction of Difluorophosphine with Nickel and with Palladium in the Metal-Atom Reactor. The Anomalous Base Strength of Difluorophosphine

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Received October 4, 1978

Although $Ni(PF_2H)_4$ could not be made by previously known bulk methods, the substance has been prepared by metal-atom–ligand cocondensation techniques. It is a colorless liquid (fp −50 °C) which decomposes slowly at room temperature. A sample of $Ni(PF_2H)_4$ held 24 h at 25 °C and 8 h at 40 °C decomposed completely. About 80% of the originally coordinated PF_2H could be recovered as PF_2H while about 20% underwent decomposition to give $PF_3(g)$, $PF_3H_2(g)$, and yellow solids of empirical formula $(PH)_n$. The compound was characterized unequivocally by infrared and NMR spectroscopy. Chemical shift values and coupling constants are reported. The decomposition of the complex is disucssed. The ligand PF_2H forms a less stable compound with nickel than does PF_3 but a more stable compound than does PH_3. No $Ni(PH_3)_4$ has yet been identified. On this basis it is concluded that the unusual stability of $F_2HP{\cdot}BH_3$ relative to $F_3P{\cdot}BH_3$ and $H_3P{\cdot}BH_3$ must be attributed to specific hydride–proton interactions involving BH_3 rather than to the unusual base strength of the PF_2H ligand.

In the previous paper[1] it was shown that the reaction of PF_2H with sulfide-activated nickel does not give the tetrakis(difluorophosphine)nickel(0) compound; instead PF_3H_2 and PF_3 were identified as the gaseous products. It was postulated that interaction of metallic nickel and PF_2H did occur, but decomposition of the complex ensued under the conditions used (standing for 46 h at 25 °C). A method for generating very reactive nickel for reaction at very low temperatures would appear to be needed for the synthesis of $Ni(PF_2H)_4$. The cocondensation process or metal-atom reactor, pioneered by Skell and Wescott[2] and developed by Skell, Timms,[3] and Klabunde,[4] seemed to be ideally suited to test this concept. The technique permitted the synthesis of the elusive $Ni(PF_2H)_4$ as a distinct species, but the corresponding palladium complex could not be isolated. Most processes involving the metal-atom reactor have used a ligand available in reasonable quantities. In this process a ligand available in very limited supply was used to prepare a comparatively unstable product which could not be obtained by the conventional bulk methods.

Synthesis of $Ni(PF_2H)_4$. A small sample of PF_2H (about 14–15 mmol) was used in the metal-atom reactor of a type described by Klabunde[4] and by Timms.[3] After all of the PF_2H had been passed into the system, the products were raised to 0 °C and fractionated, and then the recovered PF_2H was used again with more nickel vapor. Three cycles of this type generated a 23% conversion of PF_2H to $Ni(PF_2H)_4$. The equation and conditions are

$$Ni + 4PF_2H \xrightarrow[-196\text{ to }0\ ^\circ C]{\text{metal-atom reactor}} Ni(PF_2H)_4$$

Tetrakis(difluorophosphine)nickel(0) is a white solid which melts at −50 ± 2 °C to give a colorless liquid. Its molecular weight as determined by vapor density at 25 °C was 340 ± 10 (theoretical 338). The vapor pressure of the material was less than 0.05 mm at −45 °C. In the process of formation or handling, a little $Ni(PF_3)_4$ may be formed.

Liquid $Ni(PF_2H)_4$ decomposes only very slowly at room temperature. After 2 h at 25 °C only a slight amount of discoloration of the sample was observed; at 40 °C the compound was sufficiently stable that its NMR spectrum could be obtained. In an IR cell a gaseous sample showed no decrease in peak intensity after 2 h at room temperature. On the other hand, a 0.7-mmol sample held at room temperature for 24 h and then held at 40 °C for 8 h gave black nickel

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Table I. Vibrational Spectra of PF_2H, $Ni(PF_2H)_4$, PF_3, and $Ni(PF_3)_4$ (cm^{-1})

assignt	Raman $PF_2H(s)^a$	IR $PF_2H(g)^b$	IR $PF_2H(s)^c$	IR $PF_2H(l)^c$	gas IR $Ni(PF_2H)_4{}^c$	IR $PF_3(g)^c$	IR $Ni(PF_3)_4{}^d$
ν(PH), str	2318 sh	2257 (R) s	2251 (R) s	2317 vs	2355 vs		
	2311 vs	2242 (Q) s	2240 (Q) vs				
		2228 (P) s	2233 (P) s				
δ(HPF), def	*1008* ms	1030 (R) s	1016 vs	1008 vs	1025 vs		
		1016 (Q) s					
		1008 (P) s					
δ(HPF), def	960 m	959 vvw			939 w		
ν(PF), sym str	845 m	852	851 (R)	825 vs	906 vs	892	903
	810 vs	839 vvs	838 (Q) vvs				
	800 m	826 br	828 (P)				
ν(PF), asym str	*783* vvs			783 vvs	868 vvs	860	866
	772 m						
$\delta(PF_2)$, def	*374* w	367 m	367 w	371 vs	513 m	486	502
		347 m	348 w		348 w	344	383
lattice modes	159 w						
	92 w						

[a] Raman spectrum on solid by Dunning and Taylor.[7] Italic frequencies are the fundamental for the mode assigned. [b] Infrared, gas.[7] [c] This study. [d] This study and ref 6.

powder, some yellow solids above the nickel, and gaseous products consisting of 2.2 mmol of PF_2H, 0.2 mmol of PF_3H_2, and 0.2 mmol of PF_3. Under the conditions used here about 80% of the PF_2H bound in the complex came off as recoverable PF_2H, but about 20% underwent decomposition which can be described by the equation

$$6PF_2H \xrightarrow{Ni} 2PF_3(g) + 2PF_3H_2(g) + (2/n)(PH)_n(s) \atop \text{yellow solids}$$

Infrared Spectrum of $Ni(PF_2H)_4$. The infrared spectrum of $Ni(PF_2H)_4$ is recorded in Table I along with values for PF_2H, PF_3, and $Ni(PF_3)_4$. In order to establish a meaningful base for determining changes which occur when PF_2H coordinates to nickel, we need firm assignments for PF_2H. Very recently Dunning and Taylor[7] have obtained the high-resolution Raman spectrum for PF_2H in both gaseous and solid phases. These data were used as a basis for making small changes in two of the earlier assignments from this laboratory.[8] The values of Dunning and Taylor are compared with spectra from this investigation in Table I. Their modification of earlier assignments is used here. It is also of interest that the values obtained in this study for PF_3 are all within two wavenumbers of those listed by Nakamoto[5a] for PF_3, and our spectrum for $Ni(PF_3)_4$ is in good agreement with that of Loutellier and Bigorgne.[6]

Although a detailed analysis of the spectrum of $Ni(PF_2H)_4$ would be fairly complicated, a very good treatment of the experimental data can be obtained by using a simple 1:1 model (i.e., $Ni(PF_2H)$) analogous to that suggested by Nakamoto[5b] for making an analysis of the spectrum of ammine complexes such as $[Zn(NH_3)_4]^{2+}$ (i.e., $M(NH_3)$). This model can be used to discuss $Ni(PF_3)_4$ in terms of the segment $Ni(PF_3)$ which has C_{3v} symmetry. Nine fundamental modes would be expected for this segment of which three would be doubly degenerate; thus, six infrared frequencies would be anticipated for $Ni(PF_3)_4$. Four are seen in the region examined (Table I) and two would be expected below the range of our instrument. A similar analysis for the subunit $Ni(PF_2H)$ of symmetry C_s indicates that nine fundamental modes would again be expected, but there would be no degeneracies. Six of the expected nine frequencies are seen and three would be expected below the range of our instrument.

Like the infrared spectra of the metal carbonyls, the infrared spectra of the metal PF_3 addition compounds have been quite extensively discussed in terms of their relationship to bonding patterns. In 1967, Kruck[9] noted a small increase in the frequency of the P–F stretching mode when PF_3 is coordinated to a metal atom. The change was rationalized by the suggestion that free PF_3 has a $p\pi$–$d\pi$ component in the P–F bond which is strengthened when the ligand becomes coordinated to a zerovalent metal atom. The strengthening was attributed to an increase in the effective positive charge on the phosphorus when the free electron pair on the PF_3 was donated to form the metal–phosphorus σ bond. The enhanced positive charge on the phosphorus would increase its ability to accept π electrons from the fluorine thus strengthening the P–F π linkage. On the other hand, any electron density transferred to phosphorus from the metal in an M–P π bond would weaken the P–F π bond. Since the P–F π-bond enhancement would be distributed over three P–F linkages and would also be opposed by the M–P π bond, Kruck noted that the change in P–F frequency resulting from ligand coordination should be small. Such is the case; Table I shows shifts of 11 and 6 cm^{-1}. Force constant calculations for the P–F linkage are in agreement with the postulate that the P–F bond is strengthened when PF_3 is coordinated[10,11] [free PF_3, 5.38×10^5 dyn/cm; PF_3 in $Ni(PF_3)_4$, 7.73×10^5 dyn/cm]. Available data on P–F bond distances are somewhat ambiguous but they suggest that for the nickel adduct, P–F distances are insensitive to bond-order changes of this size. On the basis of an electron diffraction study,[12,13] it has been reported that the geometry of PF_3 is essentially unchanged when it is coordinated to Ni to give $Ni(PF_3)_4$, but there is a definite contraction of the P–F linkage when PF_3 is coordinated to Pt to give $Pt(PF_3)_4$.

An application of the foregoing arguments to the coordination of PF_2H would suggest that changes in the P–F stretching frequency resulting from coordination should be significantly greater than those observed for PF_3 since π-bonding effects would be distributed over only two P–F linkages rather than three; the prediction is borne out. If the gas-phase spectrum of PF_2H is used as the reference to give data comparable to that for PF_3, the shift in P–F stretching frequency on coordination of PF_2H is about 50 cm^{-1} (vs. 11 cm^{-1} and 6 cm^{-1}). If the liquid-phase spectrum of PF_2H is used as a reference so that the symmetric and asymmetric P–F stretching modes can be resolved, the changes on coordination would be about 80 cm^{-1} (Table I). As predicted by Kruck's model, the changes for PF_2H are significantly larger than those for PF_3.

Unfortunately, the case for the P–H stretching mode is more difficult to rationalize. The P–H linkage, in contrast to the P–F linkage, should not have a π component; thus coordination of PF_2H to a metal would not be expected to increase the P–H stretching frequency. Quite the opposite effect would be anticipated in non-π-bonding systems. For example in the

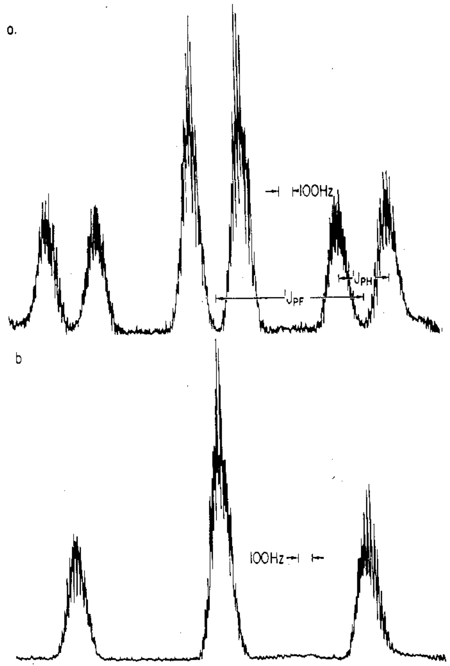

Figure 1. ^{31}P NMR spectra of $Ni(PF_2H)_4$: (a) $T = -35$ °C, CD_2Cl_2 solvent, 40.5 MHz, FT mode; (b) proton-decoupled, $T = -35$ °C, CD_2Cl_2 solvent, 40.5 MHz, FT mode.

non-π-bonding N–H case, the N–H stretching frequency is known to decrease when NH_3 is coordinated to a metal cation[5c] (free NH_3, 3414, 3336 cm^{-1}; $[Co(NH_3)_6](ClO_4)_3$, 3320, 3240 cm^{-1}). Further, the ionization of H^+ from a coordinated NH_3 is significantly easier than the corresponding process from free NH_3. The data of Table I show that shifts in the P–H stretching frequency are in direct conflict with the foregoing expectations. Values for P–H stretching frequencies behave like values for ν(P–F) and go up 115 cm^{-1} when gaseous PF_2H is selected as a reference or 28 cm^{-1} when liquid PF_2H is used. The result can be rationalized by a roundabout argument which postulates that π bonding to phosphorus in PF_2H arises from two fluorines and the metal atom. Presumably this would transfer more charge to the phosphorus atom than is lost through donation of the lone pair in σ-bond formation. The argument is after-the-fact at best;[14] but the ease with which a proton can be removed from $Ni(PF_2H)_4$ becomes of interest. The foregoing arguments suggest that it will be harder to remove an H^+ from $Ni(PF_2H)_4$ than it is to remove the proton from free PF_2H.

NMR Spectra of $Ni(PF_2H)_4$. Phosphorus (Figure 1), fluorine (Figure 2), and proton (Figure 3) NMR spectra were obtained on $Ni(PF_2H)_4$ in CD_2Cl_2 solution and as the neat liquid. No significant differences could be seen as a result of adding solvent. The gross features of the spectra confirm the existence of coordinated PF_2H. For example, the ^{31}P spectrum (Figure 1a) shows the expected triplet resulting from P–F coupling, and each member of the triplet is split into a doublet by P–H coupling. The proton-decoupled ^{31}P spectrum (Figure 1b) confirms the interpretation. Similarly the proton spectrum shows the expected doublet from P–H coupling with each member of the doublet split into a triplet by FPH coupling. The fluorine spectrum (Figure 2) is clearly second order, and resembles in gross form the ^{19}F spectra reported[15] for molecules such as $Ni(PF_3)_4$ and $Ni(PF_2X)_4$.

A complete analysis of spectra of this type is a horrendous task; molecules of this type fall in the class mentioned by Harris[16] which are never first order but which may yield NMR parameters by direct measurement using approximate formulas. An approximate analysis is presented here; the problem is being explored further.

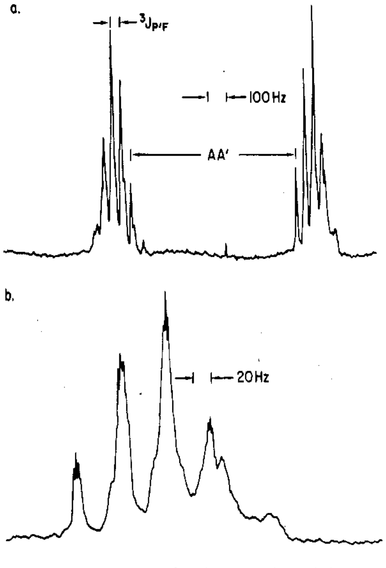

Figure 2. ^{19}F NMR spectra of $Ni(PF_2H)_4$: (a) $T = -35$ °C, 94.1 MHz, FT mode; (b) upfield member of doublet in Figure 2a expanded on the horizontal scale by a factor of 5. $T = -35$ °C, 94.1 MHz, FT mode.

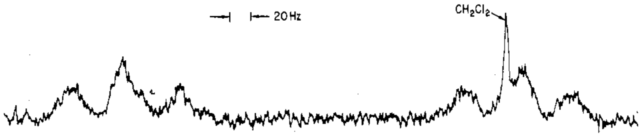

Figure 3. ^1H NMR spectrum of $Ni(PF_2H)_4$. $T = -30$ °C, CD_2Cl_2 solvent, 60 MHz, CW mode.

The ^{19}F NMR Spectrum. The second-order ^{19}F spectrum can be analyzed in approximate terms by using equations of Lynden-Bell[15b] and Harris as described by Nixon and Sexton[15a] for $Ni(ClCH_2PF_2)_4$. The lines $\nu_F \pm {}^1/_2({}^1J_{PF} + {}^3J_{PF})$ are the innermost lines in this system and arise from transitions between states where all the phosphorus nuclear spins are parallel. The separation between other members of the multiplet are taken as $^3J_{PF}$. The spectrum in Figure 2 shows a value of about 48 Hz for $^3J_{PF}$. The separation of the inner lines of the multiplet, measured as 895 Hz, is given[15a] as equal to $^1J_{PF} + 3{}^3J_{PF}$. Since $^1J_{PF}$ is known to be negative for systems of this type[15b] and $^3J_{PF}$ is positive, the value of $^1J_{PF}$ is $-895 - 3 \times 48$ or -1040 Hz. Reddy and Schmutzler[17] found that a plot of $^1J_{PF}$ in complexes of the form $Ni(PF_2X)_4$ is a linear function of the electronegativity of X. When the electronegativity of hydrogen (2.1) is used in this plot, a $^1J_{PF}$ of -1040 Hz is seen to be roughly consistent with this relationship.

The change in fluorine chemical shifts when free PF_2X is coordinated to nickel was also found by Reddy and Schmutzler[17] to be a linear function of the electronegativity of X. An extrapolation of the Reddy and Schmutzler line ($\Delta\delta$(F) vs. electronegativity of X) to the electronegativity value of H gives an expected $\Delta\delta$(F) (change in chemical shift of fluorine on coordination) of about 44 ± 3. This is in good agreement with the experimental value of 44.

The ^{31}P Spectrum. The ^{31}P spectrum is recognized as being very complex and an analysis comparable to that used for fluorine is difficult. In the hydrogen-decoupled ^{31}P spectrum there should also be a pair of inner lines separated by $^1J_{PF} + 3{}^3J_{PF}$. Such lines should arise from transitions between states where all the fluorine nuclear spins are parallel. Such states with eight parallel fluorine spins have very low statistical weight; hence the lines should be very weak. The lines do not appear in our spectra.

On the other hand, the ^{31}P spectrum appears to be first order in its gross features, although elements of complexity are

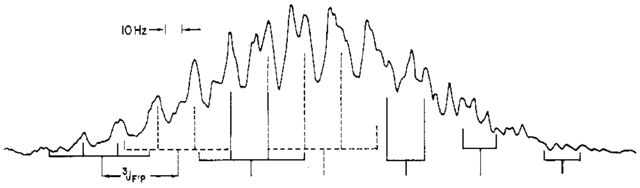

Figure 4. Proton-decoupled ^{31}P NMR spectrum of $Ni(PF_2H)_4$: downfield member of the triplet expanded by a factor of 10. T = −35 °C, CD_2Cl_2 solvent, 40.5 MHz, FT mode.

Table II. Summary of NMR Data

nucleus obsd	δ(d)	$^1J_{FP}$	data for $Ni(PF_2H)_4$ $^3J_{F^1P}$	$^2J_{P^1P}$	$^1J_{HP}$	$^2J_{FH}$
$^{31}P^{a,d}$	−218	1090			375	
$^{31}P^{b,d}$	−218		45	20		
$^{19}F^{c}$	+77.1	1040	48			
$^{1}H^{a}$	−8.30				375	50

[a] Assuming first-order behavior. [b] 10-fold expansion of horizontal scale and first-order behavior. [c] Second-order analysis. [d] ^{31}P chemical shifts use old convention (i.e., downfield from H_3PO_4 is negative).

clearly apparent in the detailed spectra. From the gross features of the spectrum, first-order analysis gives $^1J_{FP}$ as 1090 Hz which compares fairly well with the more reliable value of 1040 Hz from the ^{19}F spectrum. First-order analysis also gives $^1J_{HP}$ as 375 Hz. Figure 4 shows the downfield member of the proton-decoupled ^{31}P triplet with a tenfold horizontal scale expansion. From the six distant fluorines in the three remote PF_2H groups a 1:6:15:20:15:6:1 septet resulting from $^3J_{PF}$ would be expected by first-order rules. As the fork diagram indicates, such a septet can be assigned, but one must, in all honesty, note that the details of the spectrum are not accurately reproduced by this fork diagram. Separation of members of the septet indicates a $^3J_{FP}$ of about 45 Hz. This compares favorably with a $^3J_{PF}$ value of 48 obtained from the ^{19}F spectrum. With some optimism, a crude estimate of $^2J_{PP}$ of about 20 Hz can be made from separations of sublines in any single line of the septet (Figure 4).

The chemical shift value for phosphorus in $Ni(PF_2H)_4$ appears to be anomalous when compared to that of other related molecules in the literature. In general δ(P) for phosphorus in a ligand becomes more negative when the phosphorus-containing ligand is coordinated to a zerovalent metal.[17,18] (The old convention for ^{31}P chemical shift (i.e., downfield from H_3PO_4 is negative) is used here because of the many quantitative comparisons with earlier work, particularly ref 17.) It has been further noted[18] that such a shift is greatest for the lightest transition elements. In the case of $Ni(PF_2H)_4$ the δ(P) value becomes more positive (the above-mentioned convention applies) when PF_2H is coordinated to the light element Ni. The point is worthy of further consideration.

In 1967, Reddy and Schmutzler[17] quantitatively defined ^{31}P chemical shift changes arising from coordination in terms of the parameter Δδ(P), where the quantity is defined as δ(P) for ^{31}P in the complexed ligand minus δ(P) for ^{31}P in the free ligand.[19] They reported that the Δδ(P) values for a group of compounds of empirical formula $Ni(PF_2X)_4$ are a linear function of the electronegativity of the group X. An extrapolation of the Reddy and Schmutzler plot (Figure 5) to permit inclusion of the electronegativity of H (2.1) indicates a value of 6 ± 2 for Δδ(P) of $Ni(PF_2H)_4$. The measured value is very close to 6.

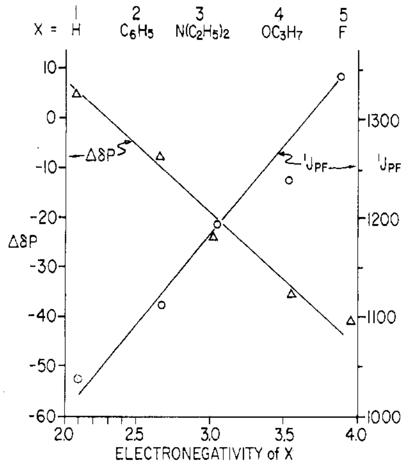

Figure 5. Change of chemical shift values for ^{31}P in $Ni(PF_2X)_4$ and of $^1J_{PF}$ in $Ni(PF_2X)_4$ as a function of electronegativity of X (after Reddy and Schmutzler[17]).

Earlier analysis[17] of these changes in δ(P) have centered on two dominant factors.[19b] The first is an increase in the electron pair accepting ability and π-bonding capability of P which results from increased electronegativity of X in PF_2X and from electron pair donation by phosphorus as it forms a σ bond to the metal. Such an increase in π-bonding capability for P influences the paramagnetic term to make Δδ(P) negative as is usually observed.

An even more significant second factor dominates observations in the present case. As the field around the phosphorus atom becomes more asymmetric, the lone pair is polarized in a manner which generates a large downfield shift of δ(P). The point is illustrated by comparing free PF_3 (−97) to free PF_2H (−224) and free PH_3 (+238). Placement of a metal center in the lone pair region should increase the symmetry of charge vectors around the phosphorus and would be expected to make δ(P) less negative in the coordinated ligand than it was in the free ligand. Thus a positive value of δ(P) for $Ni(PF_2H)_4$ can be rationalized.

The Proton NMR Spectrum in $Ni(PF_2H)_4$. As in the case of the ^{31}P spectrum, the ^1H spectrum can be approximated using first-order behavior. This permits an independent direct estimate of the value of $^1J_{PH}$ (374 Hz) which compares well with the value of 375 Hz obtained from the phosphorus spectrum. It is also possible to estimate the value of $^2J_{FH}$ for PF_2H in $Ni(PF_2H)_4$ as 52 Hz.

Attempted Preparation of $Pd(PF_3)_4$. As is well-known, $Pd(PF_3)_4$ is significantly less stable than is $Ni(PF_3)_4$. The former compound decomposes on melting at −20 °C while $Ni(PF_3)_4$ is a liquid which can be distilled at 71 °C with little decomposition. When Pd vapor and F_2PH were cocondensed,

Table III. Comparative NMR Data

	δ(P)	δ(F)	δ(H)	$^1J_{PF}$	$^1J_{PH}$	$^3J_{PF}$	$^2J_{HF}$	J_{P^1P}
PF_2H	−224	+121.6	−7.64	−1143	182			
$Ni(PF_2H)_4$	−218	+77.1	−8.30	−1040	374	46	50	(20)?
PF_3	−97	36.2		−1400				
$Ni(PF_3)_4$	−138	17		−1347		32		(3)
$PF_2N(CH_3)_2$	−143	65		−1197				
$Ni(PF_2N(CH_3)_2)_4$	-168^a	39		−1125		31		(10)?

[a] Ethyl, not methyl.

a small amount of H_2 was generated. When the system was warmed to −23 °C the entire pump-out train became plated with metal. Significant amounts of F_3PH_2 were also isolated. No evidence for a stable $Pd(PF_2H)_4$ was ever obtained, but the ready transport of Pd in the system and the appearance of F_3PH_2 indicated that the compound or a closely related one formed at low temperature and then decomposed on the walls of the container at 25 °C.

Discussion

The foregoing data establish unambiguously the identity of $Ni(PF_2H)_4$. The compound is more stable than $Ni(PH_3)_4$ which has defied all attempts to make it by the metal-atom or some other technique[3] but is significantly less stable than the well-known $Ni(PF_3)_4$ compound. As a ligand toward nickel, PF_2H lies between PH_3 and PF_3 in coordinating strength. On the other hand, it has been shown[21] that PF_2H adds BH_3 or B_4H_8 to give much more stable adducts than does either PH_3 or PF_3. In view of the data on $Ni(PF_2H)_4$ it would now seem quite clear that the unusual base strength of PF_2H, as displayed in its interactions with borane groups, is a specific interaction, not a general increase in electron donor properties.

The question of the still unique interaction between PH_2H and BH_3 remains. An early proposal from this laboratory[21] suggested that interaction between protons of groups such as amines and hydridic hydrogens of R_2HNBH_3 could correlate vapor pressures of amine–boranes. Relatively recently a structural study of F_2HPBH_3 by Pasinski and Kuczkowski[20] revealed a unique structural feature in this molecule which is closely related to that early suggestion involving interaction between protonic and hydridic hydrogens. The microwave study[20] revealed that the BH_3 group of $F_2HP{\cdot}BH_3$ is tilted away from the fluorines of F_2PH and toward the proton. Pasinski and Kuczkowski were not able to justify this structural feature by a molecular orbital calculation and, in a suggestion closely related to the earlier[21] $\delta(H)^+$–$\delta(H)^-$ interaction concept, proposed "that 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". In our judgement it is this extra interaction between protonic and hydridic hydrogens which generates both the "tilt" and the unusual stability of the borane adducts of PF_2H. Because this feature is lacking in $Ni(PF_2H)_4$, the stability is less than that of $Ni(PF_3)_4$. This concept would also account for the high barrier to internal rotation of $HF_2P{\cdot}BH_3$ (3.6–4.5 kcal/mol) as compared to the very similar molecule HF_2SiCH_3 (1.25 kcal/mol) which has an Si–C bond length comparable to that of the P–B bond in $HF_2P{\cdot}BH_3$.

In 1975, Armstrong[22] reported on ab initio calculations for $HF_2P{\cdot}BH_3$. He concluded that 80% of the bond linking P and B is of σ character but that d-orbital participation is still significant. He also drew several detailed conclusions which are pertinent to the arguments proposed here. The calculations indicated that the hydrogen of BH_3 which is tilted toward the hydrogen of HPF_2 has gained electron density (more hydridic) while the two hydrogens inclined away from the fluorine atoms of HPF_2 have lost electronic charge. Further, the hydrogen on phosphorus is protonic in character and becomes slightly more protonic as a result of the σ bond between P and B (contrast the character of the H in the PF_2H of $Ni(PF_2H)_4$; vide infra). The very specific nature of the interactions between PF_2H and boranes would make it easy to understand the relatively low stability of $F_2PH{\cdot}HI$ and of $Ni(PF_2H)_4$ in contrast to cases where F_2PH displays strong basic properties.

One other feature is worthy of note. $Ni(PF_2H)_4$ has a lower vapor pressure than $Ni(PF_3)_4$. We attribute this lower volatility to weak interactions between protonic hydrogens on the phosphorus and the negative fluorines in an adjacent molecule of $Ni(PF_2H)_4$.

Experimental Section

General Methods. Standard vacuum-line procedures[23] were used in conjunction with a metal-atom reactor of the type used by Klabunde.[4] Infrared spectra were run on gaseous samples at pressures of 3 and 7 torr by using a Beckman IR-12 high-resolution spectrometer. NMR samples were run on the neat liquid and on approximately 1.0 M samples in CD_2Cl_2. In the case of the proton NMR signal of $Ni(PF_2H)_4$ a small amount of CH_2Cl_2 in CD_2Cl_2 can be seen superimposed on one of the upfield peaks. ^{19}F and ^{31}P spectra were run on a Varian XL-100 FT-mode spectrometer, and ^1H spectra were run on a Varian A-56/60A instrument in a CW mode. For ^{19}F the standard was $CFCl_3$ (external), for ^{31}P the standard was H_3PO_4 (external), and for ^1H the standard was $Si(CH_3)_4$ (external). Deuterium was used for the lock for FT spectra.

Materials. PH_2H was prepared by literature methods.[24] Metallic nickel was obtained from Alfa Inorganics as 99.9%+ purity. All other reagents were commercial material of CP grade.

Procedures. In a typical run, PF_2H was purified on the vacuum line just before use. Traps at −126, −140, −160, and −196 °C were used. PF_2H stopped initially in the −126 °C trap. When the trap series was opened to the vacuum pumps, small amounts of $F_2PH{\cdot}HI$ were stopped at −140 °C, pure PF_2H was stopped at −160 °C, and PF_3 was stopped at −196 °C. PF_2H was run through three or four purification cycles just before use.

In a typical cocondensation reaction an Al_2O_3-coated CS-1002A crucible (Sylvania) was baked out at about 1600 °C for 25 min. A 4.15-mmol sample of 99.9% Ni (Alfa Inorganics) was placed in the crucible, and the system was degassed by exposure to the vacuum pumps for 30 min and then by heating the metal to its melting point under a dynamic vacuum. The temperature was then raised by passing a current of 40 A through the crucible while a 13.6-mmol sample of F_2PH was admitted through the gas nozzle from a vessle held at −112 °C. The cocondensation time was 25–30 min. During the entire run the lower part of the reactor was held at −196 °C.

After the reaction was over, the system was raised to 0 °C and volatile components were distilled out into traps held at −196 °C. The material was fractionated through traps at −112 and −196 °C. $Ni(PF_2H)_4$ was retained at −112 °C and unused PF_2H was trapped at −196 °C. The recovered PF_2H was then used again in additional cycles.

In a further fractionation process $Ni(PF_2H)_4$ was passed through traps at −78, −126, and −196 °C. The material retained at −78 °C was transferred into a 5-mm NMR tube for study. $Ni(PF_3)_4$ will slowly pass through a trap at −78 °C while $Ni(PF_2H)_4$ is retained. The small amount of material retained in the −196 °C trap of the above fractionation was mostly F_2PH (about 1% of the original sample) with barely detectable (^{19}F NMR) amounts of PF_3 and SiF_4.

Acknowledgment. This work was supported by the National Science Foundation under Grant CHE77-01013, which is gratefully acknowledged.

Registry No. PF_2H, 14984-74-8; $Ni(PF_2H)_4$, 69814-91-1; PF_3, 7783-55-3; $Ni(PF_3)_4$, 13859-65-9.

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The Remarkable Decarbonylation of Chromium, Molybdenum, and Tungsten Hexacarbonyls Supported on Silica and the Nature of These Materials as Heterogeneous Catalysts

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Received August 11, 1978

The temperature-programmed decomposition (TPDE) of the hexacarbonyls supported on SiO_2 gives rise to a single, narrow peak which is quite uncharacteristic of high surface area supports. Unlike Al_2O_3, SiO_2 does not sufficiently stabilize zerovalent subcarbonyl species during TPDE to allow for their ready isolation. Nonetheless, such species exist during the initial stages of TPDE and at least some of them are reversibly formed as was found for all of the subcarbonyl species identified on alumina. Thus, the hexacarbonyls provide a route to low-valent, supported Cr, Mo, and W which cannot be achieved by the traditional methods of catalyst synthesis. Contrary to published reports, the metals undergo partial oxidation by reaction with the support during TPDE and the complete decompositions are irreversible. The nature of the active sites for the metathesis of propylene is reinterpreted in light of this surface chemistry and it is suggested that the activity is due to both a subcarbonyl species which is formed near 100 °C and mildly oxidized and decarbonylated species which are formed at higher temperatures. It is reported that these materials are also slightly active for propylene hydrogenation, and the surface chemistry and activity of the catalysts are compared to those of the hexacarbonyls supported on Al_2O_3.

Introduction

The chemistry of molecular complexes has been at the forefront of catalytic research during the last decade. Most of this work has been directed at homogeneous catalysts or their close cousins, immobilized homogeneous catalysts. A significant feature of this last class of catalysts is that the active site is known to exist in solution and in grafting the complex to a support, usually a polymer, considerable effort is made to prevent the support from modifying the active site. Relatively few results have been published on another class of catalysts which might be considered to bridge the gap between traditional heterogeneous catalysts of supported metals and homogeneous catalysts: molecular complexes directly deposited on refractory oxides. Such catalysts have the advantages of a large choice of catalyst precursors (as in homogeneous catalysis) and thermal stability of the support (characteristic of traditional heterogeneous catalysts). Since the metal is not shielded from the support by a chain of ligands, it is expected that the activity of these catalysts will be strongly influenced by the nature of the support.

$Mo(CO)_6$ and $W(CO)_6$ supported on Al_2O_3 were among the first catalysts reported for the metathesis of olefins[2] and this prompted detailed studies of $Mo(CO)_6/Al_2O_3$.[3-15] Some salient features of this system are that activation in flowing He near 100 °C gives quantitative formation of $Mo(CO)_3$ads[11] and recent work suggests that this species is probably an active site for the metathesis of propylene.[10] Temperatures above 300 °C are necessary to remove the remaining ligands at a reasonable rate and the complete decarbonylation is accompanied by a reaction of the Mo with the hydroxyl groups of the support (σ-OH) which causes the Mo to become oxidized.[9] Both $Mo(CO)_3$ads and the active site for metathesis of this catalyst are reversibly formed, but the complete decomposition of $Mo(CO)_6/Al_2O_3$ is not reversible.[10] Mild oxidation (to $\sim Mo^{2+}$) also produced an active catalyst.

The hexacarbonyls supported on SiO_2 have been studied by IR[5,15] and in addition $Mo(CO)_6/SiO_2$ has been characterized by ESR[6] and its activity for the metathesis of propylene measured.[7] The primary conclusions of these works are as follows: (1) The hexacarbonyls undergo complete decarbonylation near room temperature to yield zerovalent metals.[15] (2) No subcarbonyl species are formed during the decompositions.[15] (3) The complete decompositions are reversible (by exposure to ≥50 torr of CO at 45 °C).[15] (4) The support can oxidize the hexacarbonyls at temperatures ≥20 °C.[6] (5) The active site of $Mo(CO)_6/SiO_2$ for the metathesis of propylene is a completely decarbonylated species in which the metal is partially oxidized (perhaps Mo^{4+}).[5-7] Most of these conclusions are quite different from what was found in the case of $Mo(CO)_6/Al_2O_3$. In this paper we apply the recently developed technique of temperature programmed decomposition (TPDE)[14] to further examine the surface chemistry of the hexacarbonyls supported on SiO_2. We also introduce the "activity spectrum" as a complementary technique which provides information on the nature of the active sites for a catalytic reaction.

Experimental Section

A 0.500-g sample of SiO_2 (Davison Grade 62, $a_s = 340\ m^2/g$, average pore diameter = 14 nm, and in one experiment Cabot Corporation Grade EH-5 Cab-O-Sil, $a_s = 390\ m^2/g$, nonporous) was