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Reaction of Active Nickel with PF_3, H_3BCO, H_3BPF_3, PH_3, and PF_2H. Preparation of Complexes of the Form $M(L)_4$ and Other Processes

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Gaseous PF_3, initially at 2-atm pressure and *25 °C*, will react with sulfide-activated nickel in 46 h to convert 62% of the original PF_3 to $Ni(PF_3)_4$. Gaseous H_3BCO will react with sulfide-activated nickel to give $Ni(CO)_4$ and B_2H_6 with 87% conversion of H_3BCO under similar conditions. Gaseous F_3PBH_3 (initially at a pressure of 2 atm) will react at 50 °C over 46 h to convert 98% of the original F_3PBH_3 to $Ni(PF_3)_4$ and B_2H_6. When PH_3 was allowed to react with this extremely reactive sulfide-activated nickel, H_2 and unreacted PH_3 were recovered but *no* $Ni(PH_3)_4$ was ever found. Similarly the reaction of PF_2H with sulfide-activated nickel gave *no* tetrakis ligand complex. Rather, only PF_3H_2, PF_3, and unreacted PF_2H were recovered as volatiles. The foregoing observations are interpreted in mechanistic terms involving gas adsorption and hydride and fluoride transfer to the metal. It is postulated that the fluoride coating is removable in the presence of hydrogenic species such as PF_2H, or H_3BPF_3, but is not easily removable when H is not present as in the case of pure PF_3. Reactions of Ni with PF_3 are believed to be inhibited by a nickel fluoride coating. It is suggested that B_2H_6 should promote the formation of PF_3 complexes from PF_3 and active metals.

The molecules of the fluorophosphine series PF_3, PF_2H, PFH_2, PH_3 display interesting stability trends. The second member of the series, PF_2H, known since 1965,[1] is prepared with considerable difficulty while the third member, PFH_2, is still unknown.[2] Base properties of the known members of the series also present some anomalies. For example, PF_3 is fundamentally a π acid, forming stable complexes with transition-metal atoms and their ions.[3–5] The PF_3 complex with BH_3 is of very limited stability[6] while no purely σ complex such as that formed with H^+ is known. In contrast, PH_3 is fundamentally a σ base, forming a stable complex with PH_4^+. The BH_3 complex is roughly comparable in stability to that of F_3PBH_3,[7,8] while no complexes such as $Ni(PH_3)_4$ are known. Timms[9] tried to make $Ni(PH_3)_x$ molecules by the metal-atom technique but obtained only H_2 and undefined solids. He[9] did prepare the mixed complex $Ni(PF_3)_3PH_3$ as a stable compound but $Ni(PF_3)_2(PH_3)_2$ decomposed at room temperature. Another mixed PH_3 complex $Cr(CO)_3(PH_3)_3$ has also been reported.[10]

If PF_2H were to follow smoothly in the series, its BH_3 complex should have a stability comparable to that of PF_3 and to that of PH_3. In actual fact PF_2H forms an unusually stable complex with both BH_3 and B_4H_8.[7,8] Thus PF_2H will displace PF_3 or PH_3 quantitatively from F_3PBH_3 or H_3PBH_3. The reactions of PF_2H with protons and with metal atoms remain largely unexplored. Rudolph found some evidence for the relatively unstable cation $PF_2H_2^+$ and some evidence for $Ni(PF_2H)(CO)_3$, but he was unable to prepare $Ni(PF_2H)_4$ by displacement methods. This paper is concerned with the reactions of active nickel with PF_3, PF_2H, PH_3, F_3PBH_3, and $OCBH_3$. For purposes of comparison the reactions of nickel with CO were examined. The studies were intended to define more precisely the strength of PF_2H as a π-acid ligand. In particular we wanted to know whether PF_2H had anomalously high base strength toward nickel atoms or whether its unusual base strength was limited only to borane acids.

Reactions of CO, PF_3, H_3BCO, and H_3BPF_3 with Bulk Nickel. Although CO reacts readily with active nickel powder at 1 atm of CO pressure and 25 °C, the reaction of PF_3 under comparable conditions is slow and incomplete.[12] Kruck[13] noted that under extreme conditions (pressure 70 atm, $T > 100$ °C) nickel powder could be converted quantitatively to $Ni(PF_3)_4$, but he wrote, "(this) is a further example of the rare direct formation of a nickel(0) complex from metallic nickel and a compound of trivalent phosphorus". Street and Burg[14] using relatively mild conditions and nickel obtained from the pyrolysis of $Ni(CO)_4$ obtained only very small yields of $Ni(PF_3)_4$. Nixon and Sexton[15] were able to get about 38% of the PF_3 in glass tubes (unspecified pressure) to react with active nickel powder at 60 °C. Clearly direct reaction is not usually an effective route for the synthesis of $M(PF_3)_x$ complexes. For purposes of this study it was essential to prepare nickel of unusual activity.

In general, active nickel is produced by the thermal decomposition of nickel oxalate or formate under vacuum.[12,15] In 1946 Gilliland and Blanchard[16b] reported that the activity of such nickel toward CO can be improved by using sulfide activators. In 1963 Heinicke and Harenz[16a] reapplied this

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Table I. Reaction of Sulfide-Activated Nickel with CO, PF_3, H_3BCO, and H_3BPF_3

A. CO and PF_3

	run			
	1	2	3	4
mmol of Ni	0.50	1.08	1.08	1.08
mmol of CO	4.34			
mmol of PF_3		2.25	2.15	2.42
time	30 min	17 h	17 h	46 h
temp,[a] °C	25	25	70	25
mmol of $Ni(PF_3)_4$ recovd		0.18	0.40	0.38
mmol of PF_3 recovd[b]		1.49	0.50	0.83
mmol of $Ni(CO)_4$ recovd	0.48			
% yield of $Ni(X)_4$[c]	96	32	74	62

B. H_3BCO and H_3BPF_3

	run					
	1	2	3	4	5[d]	6[d]
mmol of Ni	0.54	0.54	1.08	1.08	1.08	1.08
mmol of H_3BCO	2.11	1.57	2.17	2.30	1.68	
mmol of H_3BPF_3						1.78
time[d]	30 min	17 h	20 h	46 h	46 h	46 h
mmol of $Ni(PF_3)_4$ recovd						0.43
mmol of $Ni(CO)_4$ recovd	0.05	0.24	0.41	0.50	0.30	
mmol of B_2H_6 recovd[e]	0.12	0.49	0.83	1.02	0.74	0.87
mmol of H_3BCO recovd	0.86	0.47	0.50	0.26	0.20	
% yield of $Ni(X)_4$ based on H_3BX charged	9	61	76	87	71[d]	97[d]
% yield of $Ni(X)_4$ based on H_3BX actually consumed	16	87	98	98	81	98

[a] Initial pressure about 2 atm throughout. [b] Within the limits of experimental error, all PF_3 not used in making $Ni(PF_3)_4$ was recovered. [c] Yield of run 1 based on amount of Ni added; CO was in excess. Yields of runs 2–4 based on PF_3 added; Ni was in excess. [d] All temperatures were 25 °C except for run 5 where the temperature was 45 °C and run 6 where it was 50 °C. Initial pressures were around 2 atm. [e] B_2H_6 recovered in each case essentially quantitative for amount H_3BX used.

Table II. Reaction of Activated Nickel with PF_3 and PF_2H

	run	
	1	2
A. PH_3		
mmol of Ni	1.08	1.08
mmol of PH_3	2.40	2.01
temp,[a] °C	25	50
time, h	15	18
mmol of PH_3 recovd	2.06	1.61
mmol of H_2	0.35	0.51
H_2/PH_3 used	1.0	1.28
B. PF_2H[b]		
mmol of Ni	1.05	1.08
mmol of PF_2H	1.71	3.21
temp, °C	−78	25
time, h	17	18
mmol of PF_2H recovd	1.70	1.65
% added PF_2H not recovd	0.6	49
other products	none	PF_3H_2, PF_3

[a] At pressures of 2 atm at 25 °C. [b] In each case a solid yellow residue remained in the tube.

observation to improve the activity of nickel toward CO. They also found that mechanical working of the nickel was useful. By using sulfide activation techniques in this study we have generated nickel which is more reactive toward PF_3 than any nickel previously used, but it is significant that the reactivity of such nickel toward PF_3 is always very dramatically lower than its activity toward CO.

In our studies sulfide-activated nickel reacted essentially quantitatively with CO (pressure 2–1 atm) in a sealed tube at 25 °C in less than 30 min. By way of contrast, the same nickel reacted with PF_3 under comparable conditions to give a 62% yield of $Ni(PF_3)_4$ over a 46-h period. After 46 h excess nickel remained in the tube (Table I).

The complexes H_3BCO and H_3BPF_3 also react with sulfide-activated nickel under conditions comparable to those used for CO and PF_3. The complex H_3BCO reacts much more slowly and less completely than does pure CO. After 46 h (vs. 30 min for pure CO) an 87% yield of $Ni(CO)_4$ was obtained (based on H_3BCO charged). The equation is

$$Ni(s) + 4H_3BCO(g) \xrightarrow[\substack{25\ ^\circ C \\ 2\ atm \\ P_{init}}]{46\ h} Ni(CO)_4(l) + 2B_2H_6(g)$$

Although H_3BCO was less effective than CO in generating $Ni(CO)_4$, H_3BPF_3 was more effective than PF_3 in forming $Ni(PF_3)_4$. After 46 h at 50 °C 98% of the original H_3BPF_3 was converted to $Ni(PF_3)_4$ and B_2H_6 (yield essentially quantitative). The original H_3BPF_3 pressure was 2 atm. Data are summarized in Table IB.

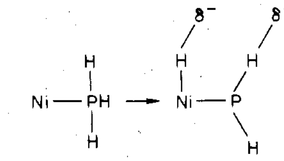
Nickel which had not been sulfide activated gave no reaction with H_3BCO or H_3BPF_3 even with initial pressures of 10 atm. Since the activity of the sulfide-activated nickel was very high, it seemed appropriate to check its reactions with PH_3 and PF_2H.

Reaction of PF_2H and PH_3 with Sulfide-Activated Bulk Nickel. Reaction with PH_3. Data for the reaction of PH_3 and sulfide-activated nickel are shown in Table IIA. No evidence for $Ni(PH_3)_4$ was ever obtained. Products were a solid residue and H_2 gas. The results are comparable to those found by Timms[9] in his cocondensation experiments. The observations suggest formation of a complex followed by its decomposition to give H_2 and a solid.

Reaction with PF_2H. Data for the reactions of PF_2H are shown in Table IIB. The results were rather surprising. No evidence for $Ni(PF_2H)_4$ was ever obtained, but both PF_3H_2 and PF_3 were isolated in low yield, suggesting that some unstable metal adducts might have formed. When excess PF_2H was allowed to react with $Ni(PF_3)_4$ in an attempted displacement reaction, yellow solids, PF_3, and PF_3H_2 were again identified as products.

Discussion

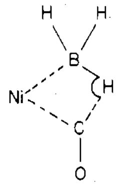
Bulk nickel of very high reactivity has been generated. Such nickel reacted quantitatively with CO at 25 °C and pressures near 1 atm in less than 30 min. Under comparable conditions, and in a separate experiment, only 32% of the PF_3 present in the sealed reaction tube was converted to $Ni(PF_3)_4$ after 17 h. With PH_3 under comparable conditions, 20–25% of the original PH_3 was destroyed after 17 h, but no $Ni(PH_3)_4$ was ever found. The data suggest that a $Ni(PH_3)_n$ complex was formed only slightly less rapidly than was the PF_3 complex but that it decomposed at room temperature to give H_2 and other products. The transfer of a PH_3 hydrogen to a nickel surface would seem to be one of the more probable early steps in the process.



Since 1.0–1.28 H_2 molecules were released for each PH_3 molecule consumed, the black solid would appear to be a $Ni(PH_x)_y$ residue.

In the case of PF_2H, 48% of the original ligand was destroyed by nickel in 18 h at 25 °C, but no $Ni(PF_3H)_4$ was formed. These data suggest that PF_2H reacted *more* rapidly with the active nickel surface than did PF_3 but that the resulting compound decomposed soon after it formed. The appearance of PF_3H_2 in the products suggests that HF was split out of a coordinated PF_2H molecule in a process analogous to that by which H_2 split from PH_3. The resulting HF (coordinated) then added to an incoming PF_2H molecule to give PF_3H_2. One attractive possibility for generating HF involves transfer of F^- to the metal followed by loss of HF from a hydrogen of an adjacent coordinated PF_2H molecule. (These arguments are suggested by the fact that Rudolph found that an unstable species, believed to be $PF_2H{\cdot}HI$, could be formed from a mixture of PF_2H and HI. This compound decomposed to give HF as one of the products. This attacked the glass to give SiF_4, PF_3, and yellow solids.) The appearance of PF_3H_2 is suggestive of the process of reductive fluorophosphination of metal salts[17b] in which $(CH_3)_2NPF_2Cl_2$ is produced in the reaction of R_2NPF_2 and $CuCl_2$.

The reactions involving H_3BCO and H_3BPF_3 with active nickel raise interesting questions relative to mechanisms. At least two relatively distinct possibilities can be visualized. In one process the H_3BX (X = CO or PF_3) molecule would be absorbed on the metal surface to give a multicenter intermediate such as



Decomposition of such an adsorbed species could well lead to the observed B_2H_6 and $Ni(CO)_4$ or $Ni(PF_3)_4$. In the second possibility the active nickel would simply act as a scavenger for CO or PF_3 liberated through decomposition of the borane complex. Because ligand was removed, the reverse reaction would be blocked and decomposition facilitated. This idea suggests that the nickel in such a process would be analogous to the acid used in the acid-assisted base-displacement reactions described earlier from this laboratory.[8] The process involving adsorption of H_3BCO is favored by the data below.

In run number 1 of Table IB it will be noticed that 1.25 mmol of H_3BCO had disappeared from the system but only about 0.24 mmol or 20% of that H_3BCO had been converted to B_2H_6 and $Ni(CO)_4$ after 30 min. On the other hand, after 20 h under comparable conditions all of the H_3BCO which had been adsorbed (1.67 mmol) and was not recoverable was recovered as B_2H_6 and $Ni(CO)_4$. These facts suggest rather strongly that the initial process is a relatively rapid adsorption of H_3BCO on the nickel surface and then a slower nonreversible decomposition of all that was adsorbed to give B_2H_6 and $Ni(CO)_4$. The process would be roughly comparable to that suggested for PH_3 and PF_2H. This process would also account for the fact that Ni(active) reacts more rapidly with CO than with H_3BCO. Although it would be tempting to hypothesize that active nickel would accelerate the decomposition of adsorbed H_3BCO, it is significant to note that after 30 min (run number 1, Table IB) only 9% of the original H_3BCO had been converted to B_2H_6 and $Ni(CO)_4$; yet under comparable conditions, 12–14% of free H_3BCO decomposed to CO and B_2H_6 in the initial decomposition studies of Burg and Schlesinger.[18] While the decomposition of adsorbed H_3BCO may be somewhat slower than that of free H_3BCO, it is clear that the adsorbed borane decomposes more completely (89%) than does free H_3BCO (31%). The formation equilibrium is shifted by CO removal.

One then comes to the question of why PF_3 and metallic nickel react slowly and ineffectively. Since $Ni(PF_3)_4$ is somewhat more stable than $Ni(CO)_4$, the problem would appear to involve a coating on the metal surface. In the reaction with PH_3 and nickel it was suggested that hydride transfer to metal following PH_3 coordination was a first step in the decomposition process. The transfer of a fluoride from PF_3 to an open coordination site on the nickel could give an adherent, relatively nonreactive coating reminiscent of the nickel fluoride coatings which make nickel impervious to fluorine attack. This hypothesis is made more attractive by several observations. First, PCl_3, though a poorer π acid, reacts with Ni more readily than does PF_3. Second, nickel gradually loses its reactivity during exposure to PF_3. Third, hydrogen, present in F_3PBH_3 as a hydride or present in PF_2H, seems to render the coating less stable and less effective. In support of this postulate we note that F_3PBH_3 and nickel were converted in 97% yield to $Ni(PF_3)_4$ and B_2H_6 under conditions where yields with PF_3 were only about 60%. An extrapolation of these arguments suggests that B_2H_6 added to PF_3 in relatively small amounts should effectively promote formation of the $M(PF_3)_n$ compounds.

Finally we note that reaction products with Ni and PF_2H suggest that HF may have been generated. The process would clean the Ni surface of fluoride and make its reaction with PF_2H more rapid than its reaction with PF_3. This postulate is in agreement with fact.

Experimental Section

General Procedures. Standard vacuum-line procedures as described by Shriver[20] were used throughout. In general, products were separated by trap-to-trap distillation. Infrared spectra were taken on a Beckman IR-20, using a 70-cm path-length gas cell with KBr windows. NMR spectra for proton and fluorine were taken on a Varian A56-60A; a Varian XL-100 was used for boron and phosphorus spectra. X-ray powder patterns were taken with a General Electric unit using a Cu target and operating at 35 kV and 25 mA.

Materials. Nickel formate dihydrate was prepared from the reaction of formic acid with either nickel carbonate or nickel hydroxide, both obtained from J. T. Baker Chemical Co. H_2S was obtained from Matheson. H_3BCO was prepared as described by Carter[21] by using CO from Matheson and B_2H_6 from Callery Chemical Co. PF_2H was prepared as described by Rudolph.[22] Phosphine was prepared by the pyrolysis of phosphorous acid[23] obtained from Allied Chemical Co.

Preparation of Sulfide-Activated Nickel. Nickel powder was prepared in a tube with a breakoff tip by heating nickel formate dihydrate to 200 °C under dynamic vacuum. The system was held at temperatures just below 200 °C under dynamic vacuum for about 30 min and then it was allowed to cool. To the freshly prepared nickel (about 1 mmol) cooled to −196 °C was added 1 mmol of H_2S. The system was allowed to warm slowly to room temperature and then the H_2S was condensed back again. This warming and condensing process was repeated three times, after which the H_2S was removed under dynamic vacuum. Within limits of measurement, the H_2S charged was recovered completely. The nickel so prepared was very reactive relative to the initial nickel powder.

Reactions Involving Sulfide-Activated Nickel. On the freshly prepared sulfide-activated nickel, prepared as described above, the appropriate gas was condensed in the quantity indicated. (Since CO could not be condensed, it was just cooled and added at about 1 atm.) The tube was then sealed off, warmed to the desired temperature, and allowed to react for the time indicated. Two modes of reaction were used. In one, the tube was placed in a shaker and agitated during the reaction period. In the second, the tube was placed in an oil bath or allowed to stand at room temperature without agitation. Only trivial differences in yield were observed between agitated and nonagitated tubes.

After reaction was complete the tube was fastened to the vacuum line through its breakoff tip, the tube was opened to the line, the products were fractionated by trap-to-trap distillation, and products were identified by physical properties, infrared spectra, and NMR spectra.

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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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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

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

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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