Table I. Low-Resolution Mass Spectrum of Cl_2BNH_2 at 70 eV

m/e	Rel intens	Ions	*m/e*	Rel intens	Ions
10	11.2	$^{10}B^+$	62	100.0	$^{37}Cl^{10}BNH^+$, $^{37}Cl^{11}BN^+$, $^{35}Cl^{11}BNH_2^+$
11	45.1	$^{11}B^+$	63	15.4	$^{37}Cl^{10}BNH_2^+$, $^{37}Cl^{11}BNH^+$
17.5	1.8	$^{35}Cl^{2+}$	64	31.7	$^{37}Cl^{11}BNH_2^+$
18.5	0.5	$^{37}Cl^{2+}$	80	1.6	$^{10}B^{35}Cl_2^+$
24	0.8	$^{10}BN^+$	81	6.7	$^{11}B^{35}Cl_2^+$
25	8.6	$^{11}BN^+$, $^{10}BNH^+$	82	1.1	$^{10}B^{35}Cl^{37}Cl^+$
26	24.3	$^{11}BNH^+$, $^{10}BNH_2^+$	83	4.1	$^{11}B^{35}Cl^{37}Cl^+$
27	18.6	$^{11}BNH_2^+$	84	0.2	$^{10}B^{37}Cl_2^+$
45	2.8	$^{10}B^{35}Cl^+$	85	0.7	$^{11}B^{37}Cl_2^+$
46	12.9	$^{11}B^{35}Cl^+$	96	8.2	$^{35}Cl_2{}^{10}BNH_2^+$
47	1.0	$^{10}B^{37}Cl^+$	97	33.2	$^{35}Cl_2{}^{11}BNH_2^+$
48	4.2	$^{11}B^{37}Cl^+$	98	6.0	$^{35}Cl^{37}Cl^{10}BNH_2^+$
59	1.2	$^{35}Cl^{10}BN^+$	99	21.0	$^{35}Cl^{37}Cl^{11}BNH_2^+$
60	9.7	$^{35}Cl^{11}BN^+$, $^{35}Cl^{10}BNH^+$	100	1.2	$^{37}Cl_2{}^{10}BNH_2^+$
61	43.8	$^{37}Cl^{10}BN^+$, $^{35}Cl^{10}BNH_2^+$, $^{35}Cl^{11}BNH^+$	101	3.3	$^{37}Cl_2{}^{11}BNH_2^+$

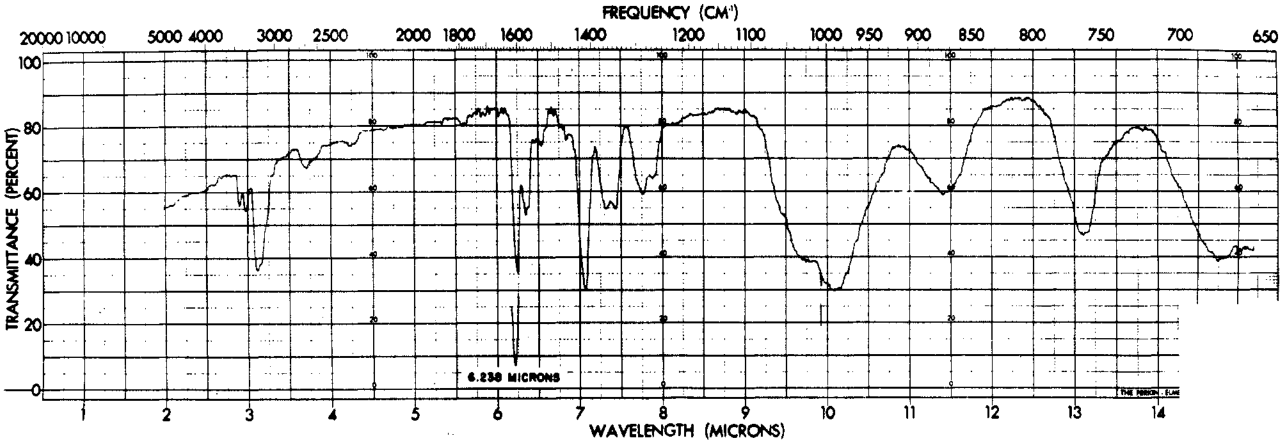

Figure 1. Infrared spectrum of condensed Cl_2BNH_2 at −196°.

room temperature. Evidently Cl_2BNH_2 reacted upon condensation to form all nonvolatile products. This colorless, transparent (almost invisible) condensate rapidly became white upon opening the trap to the atmosphere, and hence great care was exercised to exclude moisture from the system. The hydrolysis of condensed Cl_2BNH_2 with water in excess yielded HCl as the only volatile gaseous product as determined by mass spectrometric analysis. After complete evaporation of the water, a white residue of boric acid and NH_4Cl remained in accord with the equation

$$(Cl_2BNH_2)_n + 3nH_2O \rightarrow nNH_4Cl + nB(OH)_3 + nHCl$$

The infrared spectrum of condensed Cl_2BNH_2 was observed as a function of temperature, and a spectrum recorded at −196° after deposition at that temperature appears in Figure 1. With minor and smooth changes of relative intensities, the spectra were equivalent at a series of temperatures up to 25° as were those observed during warming a sample deposited at −100°. These data were completely reproducible. The only substantive change during warming was the disappearance of the band between 1330 and 1380 cm^{-1}. This band was not observed in samples deposited at −100°.

The isoelectronic equivalent of vinylidene chloride can be prepared as a reasonably stable gas, but it is immediately lost upon condensation even at −196°. If the resulting solid is a polymer, it is an uninteresting one due to its immediate reaction with H_2O.

Registry No. NH_3, 7664-41-7; BCl_3, 10294-34-5; Cl_2BNH_2, 37805-57-5.

Acknowledgment. We are grateful to two coworkers, Dr. W. Lutzhoft and Mr. R. M. Parikh, who conducted a number of preliminary experiments.

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Ligand Action of Trifluoromethylphosphine and Bis(trifluoromethyl)phosphine toward Nickel Carbonyl and Nitrosylcobalt Carbonyl

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Received July 28, 1972

The displacement of one or two CO's from $Ni(CO)_4$ or one CO from $NOCo(CO)_3$ by CF_3PH_2 or $(CF_3)_2PH$ occurs quantitatively in sealed tubes in the absence of sunlight, at temperatures below 55°. The present study, taken with earlier experience,[1-3] indicates a considerable increase in bonding power when CF_3 replaces one H in phosphine and a far more moderate increase with further substitution of CF_3 for H. Moreover, there is no more than a very small increase in the

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C-O stretching frequencies for the L-Ni-CO and L-CoNO-CO compounds, for ligands in the series CF_3PH_2, $(CF_3)_2PH$, $(CF_3)_3P$, which seem to compete almost equally well with CO for bonding by metal 3d electrons. It appears that substitution of one or two H's (or even one CH_3 group[3]) for CF_3 in $(CF_3)_3P$ causes little change in the electron-acceptor strength of phosphorus.

Syntheses. Equations 1-6, with reaction conditions and millimolar stoichiometry (negative quantities for recovered excess reactants), summarize our experiments on the synthesis of new complexes by substitution.

$$\begin{array}{lclclcl} \mathrm{Ni(CO)_4} & + & \mathrm{CF_3PH_2} & \rightarrow & \mathrm{CF_3PH_2Ni(CO)_3} & + & \mathrm{CO} \\ 3.80 & & 4.21 & & 3.79 & & 3.81 \\ & & \underline{-0.39} & & & & \\ & & 3.82 & & (8\text{-}10\ \mathrm{hr}, 40^\circ) & & \end{array} \tag{1}$$

$$\begin{array}{lclclcl} \mathrm{Ni(CO)_4} & + & \mathrm{2CF_3PH_2} & \rightarrow & \mathrm{(CF_3PH_2)_2Ni(CO)_2} & + & \mathrm{2CO} \\ 2.60 & & 6.78 & & 2.57 & & 5.20 \\ & & \underline{-1.56} & & & & \\ & & 5.22 & & (8\ \mathrm{hr}, 40^\circ; 3\ \mathrm{hr}, 50^\circ) & & \end{array} \tag{2}$$

$$\begin{array}{lclclcl} \mathrm{NOCo(CO)_3} & + & \mathrm{CF_3PH_2} & \rightarrow & \mathrm{CF_3PH_2CoNO(CO)_2} & + & \mathrm{CO} \\ 2.63 & & 4.43 & & 2.62 & & 2.64 \\ & & \underline{-1.82} & & & & \\ & & 2.61 & & (14\text{-}16\ \mathrm{hr}, 55^\circ) & & \end{array} \tag{3}$$

$$\begin{array}{lclclcl} \mathrm{Ni(CO)_4} & + & \mathrm{(CF_3)_2PH} & \rightarrow & \mathrm{(CF_3)_2PHNi(CO)_3} & + & \mathrm{CO} \\ 3.76 & & 4.60 & & 3.76 & & 3.74 \\ & & \underline{-0.84} & & & & \\ & & 3.76 & & (8\text{-}10\ \mathrm{hr}, 36^\circ) & & \end{array} \tag{4}$$

$$\begin{array}{lclclcl} \mathrm{Ni(CO)_4} & + & \mathrm{2(CF_3)_2PH} & \rightarrow & \mathrm{[(CF_3)_2PH]_2Ni(CO)_2} & + & \mathrm{2CO} \\ 2.58 & & 6.80 & & 2.55 & & 5.18 \\ & & \underline{-1.60} & & & & \\ & & 5.20 & & (8\ \mathrm{hr}, 36^\circ; 2\ \mathrm{hr}, 50^\circ) & & \end{array} \tag{5}$$

$$\begin{array}{lclclcl} \mathrm{NOCo(CO)_3} & + & \mathrm{(CF_3)_2PH} & \rightarrow & \mathrm{(CF_3)_2PHCoNO(CO)_2} & + & \mathrm{CO} \\ 2.65 & & 4.51 & & 2.65 & & 2.67 \\ & & \underline{-1.86} & & & & \\ & & 2.65 & & (16\ \mathrm{hr}, 55^\circ) & & \end{array} \tag{6}$$

For each of these experiments, the volatile reactants were controlled and measured in a Stock-type high-vacuum system. At the end of each process, the CO was drawn off through a −196° trap by means of an automatic Sprengel pump[4] and collected for measurement; then the excess phosphine ligand was separated from the complex and measured; finally, the remaining complex was weighed. The cobalt complexes could be distilled without loss under high vacuum, whereas the nickel complexes partially decomposed during such distillations. For experiments 1 and 4 single heatings were sufficient; for each of the others it was necessary to remove the evolved CO in midcourse in order to complete the reaction.

Nmr Spectra. The purity of the new complexes was shown by the absence or minimal presence of impurity peaks in their nmr spectra. The nmr parameters (Varian T-60 or HA-100 instrument with "neat" samples) are compared with earlier data, in Table I.

For the proton spectra, τ has the usual definition: the distance (ppm) upfield from a point 10 ppm downfield of TMS. The coupling constants J_{PCF} and J_{HPCF} represent agreement of measurements from both nuclei, except that J_{PCF} for the cobalt complexes could not be measured from the phosphorus side because the cobalt quadrupole prevented observation of their phosphorus spectra. The δ standards for phosphorus and fluorine were H_3PO_4 and Cl_3CF, respectively, with upfield measurements positive.

It is interesting that both the P-H and the P-C-F coupling constants are larger for the complexes than for the free ligands, as expected when lone-pair electrons (having mostly P_{3s} character) increase their p character for dative bonding, so that other bonds to phosphorus use more s character. Such an increase of s character decidedly strengthens the P-H bond in $(CH_3)_2PH\cdot BH_3$,[5] whereas the following infrared evidence indicates little such P-H bond enhancement for the present complexes.

Table I. Nmr Spectra of the Phosphine Complexes

	τ	J_{PH}	δ_P	δ_F	J_{PCF}	J_{HPCF}
L = PH_3[1]	8.9	183	238			
$LNi(CO)_3$	7.17	302	177			
$LCoNO(CO)_3$	7.33	326				
L = CF_3PH_2	7.02	200	127	43.7	49	12.0
$LNi(CO)_3$	5.71	313	68	52.8	63	9.0
$L_2Ni(CO)_2$	5.62	309	65	53.6	60	8.8
$LCoNO(CO)_2$	5.64	327		52.9	64	8.5
L = $(CF_3)_2PH$	5.98	214	50	49.2	68	9.6
$LNi(CO)_3$	4.88	326	−4.6	56.2	77	7.3
$L_2Ni(CO)_2$	4.79	320	−5.0	57.5	75	7.1
$LCoNO(CO)_2$	4.7	331		56.3	80	6.9

Infrared Spectra. The frequencies (cm^{-1}) in Table II were recorded for vapor-phase samples, stabilized by CO where necessary. The instrument was the Perkin-Elmer 457, calibrated to ±2 cm^{-1}. In this table, the letter c designates the major peak of a complex band.

Instability of the Nickel Complexes. The decomposition of the reaction 4 product evidently involved processes 7 and 8. The forward progress of (7) would be aided by the decomposition of $Ni(CO)_4$ (reversibly forming CO); thus both processes were favored by low CO pressures in relatively large containers; small volumes worked against CO formation. Process 7 was demonstrated by the appearance of the C-O stretching frequencies of both disproportionation products in the vapor-phase infrared spectrum.

$$\mathrm{2(CF_3)_2PHNi(CO)_3} \rightleftarrows \mathrm{[(CF_3)_2PH]_2Ni(CO)_2} + \mathrm{Ni(CO)_4} \tag{7}$$

$$n\mathrm{(CF_3)_2PHNi(CO)_3} \rightarrow \mathrm{[(CF_3)_2PHNi(CO)_2]}_n + n\mathrm{CO} \tag{8}$$

The nonvolatile brown product of process 8 evidently was a Ni(CO)Ni bridge-bonded polymer, for the infrared spectrum of its CCl_4 solution (simple enough to indicate a single kind of polymer) included a CO-bridge stretching frequency at 1712 cm^{-1}, as well as C-O terminal stretching at 2070 cm^{-1}. This infrared spectrum also indicated intact $(CF_3)_2PH$ ligand, showing P-H stretching and bending modes at 2352 and 856, 810 cm^{-1}. An osmometric molecular weight determination for this polymer (in CCl_4 solution) indicated n to be no less than 4.

The complex $[(CF_3)_2PH]_2Ni(CO)_2$ also decomposed partially under low pressures, but far less extensively than $(CF_3)_2PHNi(CO)_3$; for the study of reaction 8, its products evidently were not present in such amounts as to cause confusion. The instability of the CF_3PH_2-Ni complexes was only qualitatively observed.

A Photochemical Side Reaction. With early exposure to sunlight, the reaction 4 experiment develops the purple-red color due to the compound long ago designated as "NiPPNi."[6] This result is explained by the separate processes

$$\mathrm{2(CF_3)_2PH} \rightarrow \mathrm{P_2(CF_3)_4} + \mathrm{H_2} \tag{9}$$

$$\mathrm{P_2(CF_3)_4} + \mathrm{2Ni(CO)_4} \rightarrow \underset{\text{"NiPPNi"}}{\mathrm{P_2(CF_3)_4[Ni(CO)_3]_2}} + \mathrm{2CO} \tag{10}$$

Reaction 9 was indicated by the presence of H_2 in the CO

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Table II. Significant Infrared Peaks

	P-H str	C-O str	N-O str	P-H bend
CF_3PH_2	2348 2337			841 sh 830 821 sh
$(CF_3)_2PH$	2353			856 810
$CF_3PH_2Ni(CO)_3$	2352	2103 2058		856 c
$(CF_3PH_2)_2Ni(CO)_2$	2350	2102 2052		852 c
$(CF_3)_2PHNi(CO)_3$	2360	2105 2060		852
$[(CF_3)_2PH]_2Ni(CO)_2$	2359	2102 2058		850
$CF_3PH_2CoNO(CO)_2$	2350	2073 2027	1820	863 c
$(CF_3)_2PHCoNO(CO)_2$	2355	2083 2040	1820	865

coming from reaction 4: CuO-combustion analysis gave water in appropriate yield. Reaction 10 was proved by finding in the ^{19}F nmr spectrum a pattern exactly matching that of an authentic sample of "NiPPNi"—a second-order spectrum centered at 52.2 ppm upfield of Cl_3CF and with main outer peaks 99 cps apart. The central complex of peaks is somewhat more cleanly resolved than in the very similar spectrum of $P_2(CF_3)_4$ (δ 46.9 ppm; outer-peak separation, 85 cps). The infrared spectrum also identified "NiPPNi": C-O stretching at 2092 and 2075 cm^{-1}; C-F stretching at 1174, 1148, 1132, and 1119 cm^{-1}. It is estimated that reactions 9 and 10 accounted for no more than a 10% loss of yield in reaction 4.

It is interesting that the pure product $(CF_3)_2PHNi(CO)_3$ from the dark reaction 4 failed to develop the "NiPPNi" color in sunlight. Reaction 9 probably requires free $(CF_3)_2PH$ as well as catalysts not easily specified.

A separate experiment showed that "NiPPNi" is destroyed, with liberation of $P_2(CF_3)_4$, by action of $(CF_3)_2PH$ in great excess. This result explains why the color, appearing early in reaction 4 in sunlight, fades out when the tube is kept for some hours in the dark. Thus the very early formation of "NiPPNi" suggests a nonequilibrium steady state. However, when the photochemical process has gone so far as to give 3-4 mole % concentrations of "NiPPNi," the color will not fade out in the dark because the available $(CF_3)_2PH$ is not enough to destroy much of the "NiPPNi."

No such photochemical process was found in relation to processes other than 4 (or incipient 5) nor in the action of PH_3 on $Ni(CO)_4$.[1] Most probably the diphosphines P_2H_4 and $(CF_3PH)_2$ were not formed in appreciable proportions and would not have competed with the monophosphines as ligands.

Registry No. $Ni(CO)_4$, 13463-39-3; CF_3PH_2, 420-52-0; $NOCo(CO)_3$, 14096-82-3; $(CF_3)_2PH$, 460-96-8; $CF_3PH_2Ni(CO)_3$, 37478-09-4; $(CF_3PH_2)_2Ni(CO)_2$, 37478-10-7; $CF_3PH_2CoNO(CO)_2$, 37478-11-8; $(CF_3)_2PHNi(CO)_3$, 37478-12-9; $[(CF_3)_2PH]_2Ni(CO)_2$, 37478-13-0; $(CF_3)_2PHCoNO(CO)_2$, 37534-36-4.

Acknowledgment. The generous support of this research by the National Science Foundation (Grant GP-17472) is gratefully acknowledged.

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Fluorine-19 Nuclear Magnetic Resonance Studies on Fluoroborate Species in Aqueous Solution[1]

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Received August 4, 1972

The behavior of fluoroborates in water has been recently studied potentiometrically[3] to determine the composition of species which are present in metastable amounts with respect to equilibrium with BF_4^-. Because the BF_4^- ion is kinetically slow to form except in highly acidic media, only the species BF_3OH^-, $BF_2(OH)_2^-$, and $BF(OH)_3^-$ are present after short times. The dissociation quotient for $HBF_3(OH)$ is estimated at >0.2 and the quotient for $HBF_2(OH)_2$ is estimated to be $>10^{-4}$.

The properties of BF_4^- in water have been known for some time and the physical evidence for the tetrahedral structure was reviewed previously.[1] The kinetics of the equilibrium reaction

$$H_2O + BF_4^- = BF_3OH^- + HF \tag{1}$$

has been studied by Wamser[4] and by Anbar and Gutman.[5] The latter authors studied the kinetics and the rate law in detail for both the forward reaction above and the exchange reaction for BF_4^- with fluoride ion. The reaction parameters for the hydrolysis and exchange reaction show that these two processes occur through the same rate-determining step. From the potentiometric measurements it is apparent that the fluoroborate species, other than BF_4^-, exchange or equilibrate with boric acid much more rapidly although the exchange mechanisms are not known.

Kuhlmann and Grant[6] have shown that the ^{19}F resonance of BF_4^- produces a quartet of equivalent lines with a coupling constant for the B-F interactions of 1-4 Hz depending on the concentration and nature of the cations. Also, the ^{11}B spectra for 7 *M* $NaBF_4$ solutions exhibit the sharp 1:4:6:4:1 quintet expected for the ^{11}B coupled to four equivalent F nuclei with a coupling constant of 4.6 Hz. By boiling solutions containing $NaBF_4$ in the presence of calcium carbonate a small amount of hydrolysis was effected and the ^{19}F and ^{11}B spectra were observed for what was believed to be BF_3OH^-. A weak ^{19}F quartet was observed 6.2 ppm downfield from the BF_4^- quartet. The ^{11}B resonance spectrum consisted of a partially resolved quartet with a coupling constant of 12.7 Hz. The wider resonance lines of BF_3OH^- compared with BF_4^- are attributed to the quadrupolar broadening in the unsymmetrical BF_3OH^-.

We have examined the ^{19}F spectra of solutions expected to contain BF_3OH^-, $BF_2(OH)_2^-$, and $BF(OH)_3^-$ in different amounts. Estimates of equilibrium quotients were made from these data along with potentiometric measurements of hydrogen ion and fluoride ion concentrations.

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(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(2) (a) Reactor Chemistry Division, Oak Ridge National Laboratory. (b) Product Certification Division, Oak Ridge National Laboratory.

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