at room temperature. The product mixture was passed through traps held at -10 and -50 °C. The product was retained in the trap at -50 °C in 30% yield. It was further purified by gas chromatography using a 4-ft column packed with 25% Kel-F No. 3 oil on Chromosorb-P. Two isomers II and III were isolated in equal amounts. The infrared spectrum of II consists of bands at 1290 m, 1250 vs, 1200 w, 1150 vs, 1090 m, 1025 w, 980 s, 890 w, 830 vs, 730 vs, 660 vs, 620 vs, 570 w, 550 m, and 485 m, cm^{-1}. The ^{19}F NMR spectrum consists of a multiplet at ϕ 46.10 (SF_4), a pentet at ϕ -64.11 (CF_3S), and a pentet at ϕ -63.07 (CF_3C). The ^1H NMR spectrum consists of a multiplet at δ 6.94. The infrared spectrum of III consists of bands at 1280 m, 1250 vs, 1210 m, 1285 vs, 1150 vs, 1090 m, 1025 s, 980 vs, 890 m, 840 vs, 730 vs, 690 m, 650 vs, 620 vs, 550 m, and 485 w cm^{-1}. The ^{19}F NMR spectrum consists of a multiplet at ϕ 42.97 (SF_4), a pentet at ϕ -64.39 (CF_3S), and a singlet at ϕ -69.20 (CF_3C). The ^1H NMR spectrum consists of a multiplet at δ 7.35. The EI mass spectrum contains a molecular ion at m/e 306 [$CF_3C(CF_3SF_4)CHCl^+$, 0.8%] with other fragments at m/e 239 ($CF_3SF_4C_2H^{37}Cl^+$, 1.37%), 235 ($CF_3SF_4C_2H^{35}Cl^+$, 3.82%), 199 ($CF_3SF_2CHCCl^+$, 13.35%), 139 ($CF_3SF_2^+$, 2.70%), 131 ($SF_2CC^{37}Cl^+$, 4.30%), 129 ($SF_2C_2^{35}Cl^+$, 13%), 89 (SF_3^+, 21.3%), and 69 (CF_3^+, 100%).

Anal. Calcd for $C_4HF_{10}SCl$: S, 10.45. Found: S, 9.43.

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Preparation of New Bis(dialkylamino)phosphine Species via Reduction of Bis(dialkylamino)halophosphines[1a]

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Four new bis(dialkylamino)phosphine species, $(Me_2N)_2PH$, $CH_3\overline{NCH_2CH_2N(CH_3)}PH$, $(CO)_3Ni[(Me_2N)_2PH]$, and $(CO)_3Ni[CH_3\overline{NCH_2CH_2N(CH_3)}PH]$, have easily been prepared in good yields through reduction of corresponding bis(dialkylamino)halophosphines by lithium tri-*sec*-butylborohydride. The preparation and characterization of these compounds are discussed. An improved synthesis for obtaining quantitative yields of $(CO)_3NiL$ [L = Me_2NPF_2, $(Me_2N)_2PF$, $CH_3\overline{NCH_2CH_2N(CH_3)}PF$] is also described.

Introduction

Secondary phosphines can now be prepared quite easily by a number of methods, the most common being the reduction of halophosphine derivatives or the alkylation of phosphine species.[2] In contrast, previous attempts to prepare the secondary aminophosphine $(Me_2N)_2PH$ have been unsuccessful. Recently the syntheses of $(i\text{-}Pr_2N)_2PH$, and $(Et_2N)_2PH$ were reported by King, Sadanani, and Sundaram.[3,4] The compounds were prepared by the reaction of the corresponding $(R_2N)_2PCl$ precursor with $LiAlH_4$ in diethyl ether. An analogous reaction of $(Me_2N)_2PCl$, however, did not produce any evidence of $(Me_2N)_2PH$ formation.[3,4] Nöth and Vetter monitored the reaction of $LiBH_4$ with $(Me_2N)_2PCl$ and were able to obtain the borane adduct of bis(dimethylamino)phosphine, $(Me_2N)_2PH{\cdot}BH_3$, but not the free phosphine itself.[5] The use of $LiAlH[OC(CH_3)_3]_3$ as a reducing agent on $(Me_2N)_2PCl$ was also unsuccessful as a method for preparing $(Me_2N)_2PH$.[6]

The only other examples of trivalent phosphorus derivatives of the type $(R_2N)_2PH$ are silylphosphines, $(Me_3Si)_2NP(R)H$,[7] and heterocycles of the type $R\overline{NCH_2CH_2CHR'N(R)}PH$ or $R\overline{NCH_2CH_2N(R)}PH$, where R groups are usually large alkyl structures and R' is H or an alkyl group.[4]

These results suggest interesting possibilities relative to the mechanism of the process. A number of dicoordinated phosphorus cations of the type $(R_2N)_2P^+$ are known.[9] These cations are strong Lewis acids,[10] and the ring structures are particularly stable. If they were to form, even briefly, in solution due to the precipitation of lithium halide, one would expect rapid reaction with any hydride to produce bis(dialkylamino)phosphines. The reported results show that this description is too simplistic. The data now available show that the reactions are very sensitive to the reducing agent chosen and to the type of organic group attached to the nitrogen.

In this study the reactivity of a number of bis(dialkylamino)halophosphines with hindered borohydride reducing agents such as the commercial "Selectrides" (lithium, sodium, or potassium tri-*sec*-butylborohydride) has been examined. The general equation for the reduction process is

$$(R_2N)_2PX + M[HBR_3] \rightarrow (R_2N)_2PH + MX + BR_3 \quad (1)$$

By use of this method it has been possible to synthesize easily and in high yield the elusive $(Me_2N)_2PH$, along with the new cyclic bis(methylamino)phosphine $CH_3\overline{NCH_2CH_2N(CH_3)}PH$.

We were also interested in the coordination chemistry of these new phosphine species. The coordination chemistry of aminohalophosphines is quite rich and has been extensively studied,[11] and the coordination chemistry of the phosphenium cation species is an area of current interest.[12] By use of the L-Selectride

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reductive method, two new nickel complexes have been synthesized from their bis(dialkylamino)halophosphine derivatives. Both $(CO)_3Ni[(Me_2N)_2PH]$ and $(CO)_3Ni[CH_3NCH_2CH_2N(CH_3)PH]$ have been prepared and characterized by ^{31}P NMR spectroscopy.

The preparation and characterization of these four new compounds is discussed below, and their NMR data are compared to those of similar compounds in the literature.

Prior to this study, labile compounds of the form $(CO)_3NiL$ (L = PF_3, Me_2NPF_2, Et_2NPF_2, $C_5H_{10}NPF_2$) have been prepared only as part of $(CO)_xNiL_{4-x}$ mixtures.[13-15] Isolation of $(CO)_3NiL$ (L = PF_3, Me_2NPF_2) from the mixture involves tedious and difficult separations.[13,16] These mixtures have been prepared by ligand-exchange reactions involving $Ni(CO)_4/NiL_4$ or $Ni(CO)_4/L$ systems or by the disproportionation of room-temperature $(CO)_2NiL_2$ species. In contrast, a number of disubstituted compounds have been characterized,[17] including $(CO)_2Ni(Me_2NPF_2)_2$ and $(CO)_2Ni[(Me_2N)_2PF]_2$. These can be preferentially prepared by controlling the ratio of the reactants and the reaction conditions used.[11a]

In this paper we present a procedure for the direct quantitative preparation and isolation of $(CO)_3NiL$ (L = Me_2NPF_2, $(Me_2N)_2PF$, $CH_3NCH_2CH_2N(CH_3)PF$). A controlled substitution process is the method of choice. The product can be used in situ or it can be isolated by trap-to-trap distillation. The equation for the process is

$$Ni(CO)_4 \text{ (excess)} + L \xrightarrow[-30°C]{CH_2Cl_2} (CO)_3NiL + CO \qquad (2)$$

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. Mass spectral data were obtained by using a VG micromass 7070 double-focusing high-resolution mass spectrometer with a VG Data System 2000 instrument with electron-impact ionization at either 70 or 20 eV. NMR spectra were obtained on Varian XL-100 FT mode or FT-80A spectrometers. External standards were used for all spectra: 85% H_3PO_4 for ^{31}P NMR, $CFCl_3$ for ^{19}F NMR, and $Si(CH_3)_4$ for ^1H NMR. Downfield shifts have positive values.

Materials. $(Me_2N)_2PF$ can be prepared by the method of Fleming[18] or of Reddy and Schmutzler.[19] Cyclic $CH_3NCH_2CH_2N(CH_3)PF$ can be prepared by the method of Fleming, Lupton, and Jekot[9a] or by the fluorination of the corresponding chloro compound.[12b] Me_2NPF_2 was prepared and characterized as reported by Morse et al.[20] CH_2Cl_2 was distilled, dried, and degassed before use. $Ni(CO)_4$ was obtained from Pfaltz & Bauer, Inc., and was fractionated before use. "Selectride" reducing agents (Li, Na, K) are commercially available in 1 M THF solutions from Aldrich Chemical Co., Inc.

Preparation of Free Phosphine Ligands. (a) Preparation of $(Me_2N)_2PH$. In a typical reaction 1 mmol of $(Me_2N)_2PF$ or $(Me_2N)_2PCl$ was condensed into the bottom of a 9-mm-o.d. NMR/reaction tube equipped with a gas-expansion bulb, a capped side arm, and a connecting joint with a stopcock, which was used to attach the system to the vacuum line. Then, with nitrogen gas flushing the system, the side arm was uncapped and 1 mL (1 mmol) of L-Selectride was syringed onto the frozen $(Me_2N)_2PX$. The reaction sample was then removed from the vacuum line and allowed to warm to −23 °C. Reaction progress was monitored by occasional ^{31}P NMR spectra. In about 15–30 min, a 77% yield of $(Me_2N)_2PH$ was observed by NMR. The only other products observed were the unreacted $(Me_2N)_2PF$ and a slight amount of $(Me_2N)_3P$ in some of the samples. The amount of $(Me_2N)_3P$ increases, and the solution slowly turns yellowish, if the sample is held at room temperature for even 0.5 h. This decomposition can be prevented by holding the sample at −23 °C. The ^{31}P NMR spectrum shows a distinctive P–H doublet at 95 ppm with a coupling constant, J_{PH}, of 250 Hz. The ^1H NMR spectrum of the reaction solution is complicated, but a clear P–H doublet is seen at 5.43 ppm with a 250 Hz coupling constant. The ^{11}B NMR spectrum shows a broad absorption for BR_3. The infrared spectrum shows a strong P–H stretching band at 2280 cm^{-1}, which is also consistent with the above assignment (see Table I). The volatile materials were fractionated from a trap held at −31 °C (bromobenzene

Table I. Comparison of IR and NMR Data for Bis(dialkylamino)phosphines

compd	IR (PH), cm^{-1}	^{31}P NMR, ppm	J_{PH}, Hz	^1H NMR, ppm
$(Me_2N)_2PH$	2280	95	250	5.43
$(Et_2N)_2PH$[4]	2272	76.3	259	
$(i\text{-}Pr_2N)_2PH$[3,4]	2225	42.1	254	5.8
$CH_3NCH_2CH_2N(CH_3)PH$		97.4	150	
$(CH_3)_3CNCH_2CH_2N[C(CH_3)_3]PH$[4]				
$RNCH_2CH_2CHR'N(R)PH$[5]				
R = t-Bu, R' = H		49.6	214	5.7
R = t-Bu, R' = Me		12.7	229	6.0
R = Me, R' = Me (81% A isomer)		82.2	192	
R = Me, R' = Me (19% B isomer)		47.3	202.5	

Table II. Mass Spectral Data[a,b]

m/z	ion	rel intens[c]
	$[(CH_3)_2N]_2PH$ (20 eV)	
120	$[(CH_3)_2N]_2PH^+$	3
119	$[(CH_3)_2N]_2P^+$	9
76	$(CH_3)_2NPH^+$	14
45	$N\text{–}P^+$	>100
44	$(CH_3)_2N^+$	>100
43	$(CH_3)_2N^+ - H$	>100
42	$(CH_3)_2N^+ - 2H$	>100
	$(CO)_3Ni[[(CH_3)_2N]_2PF]$ (70 eV)	
280	$(CO)_3Ni[[(CH_3)_2N]_2PF]^+$	0.4
252	$(CO)_2Ni[[(CH_3)_2N]_2PF]^+$	2
224	$(CO)Ni[[(CH_3)_2N]_2PF]^+$	7
196	$Ni[[(CH_3)_2N]_2PF]^+$	5
138	$[(CH_3)_2N]_2PF^+$	24
119	$[(CH_3)_2N]_2P^+$	21
94	$(CH_3)_2NPF^+$	100
45	$N\text{–}P^+$	16
44	$(CH_3)_2N^+$	70
43	$(CH_3)_2N^+ - H$	41
42	$(CH_3)_2N^+ - 2H$	93
	$(CO)_3Ni[CH_3NCH_2CH_2(CH_3)NPF]$ (70 eV)	
278	$(CO)_3Ni[CH_3NCH_2CH_2(CH_3)NPF]^+$	0.7
250	$(CO)_2Ni[CH_3NCH_2CH_2(CH_3)NPF]^+$	7
222	$(CO)Ni[CH_3NCH_2CH_2(CH_3)NPF]^+$	12
194	$Ni[CH_3NCH_2CH_2(CH_3)NPF]^+$	0.9
136	$CH_3NCH_2CH_2(CH_3)NPF^+$	44
117	$CH_3NCH_2CH_2(CH_3)NP^+$	100
93	$CH_2(CH_3)NPF^+$	93
78	CH_2NPF^+	34
57	$C\text{–}N\text{–}P^+$	12
42	$(CH_3)_2N^+ - 2H$	29

[a] Listing of parent peaks and structurally significant fragments. [b] Peaks correlating to masses less than 35 are omitted due to ambiguity of small fragments. [c] Samples normalized to most abundant peak above mass 35.

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Table III. Summary of NMR Data[a]

L	L chem shift, ppm	L coupling const, Hz	$(CO)_3NiL$ chem shift, ppm	$(CO)_3NiL$ coupling const, Hz
		^{31}P NMR		
Me_2NPF_2	143	$J_{PF} = 1197$	169	$J_{PF} = 1160$
$(Me_2N)_2PF$	151	$J_{PF} = 1046$	178	$J_{PF} = 1060$
$CH_3\overline{NCH_2CH_2N(CH_3)}PF$	138	$J_{PF} = 1047$	161.5	$J_{PF} = 1100$
$(Me_2N)_2PH$	95	$J_{PH} = 250$	112.6	$J_{PH} = 380$
$CH_3\overline{NCH_2CH_2N(CH_3)}PH$	97.4	$J_{PH} = 150$	118.5	$J_{PH} = 280$
		^{19}F NMR		
Me_2NPF_2	−65.3	$J_{PF} = 1197$	−44.3[b]	$J_{PF} = 1160$[b]
$(Me_2N)_2PF$	−100.6	$J_{PF} = 1046$	−68.9	$J_{PF} = 1068$
$CH_3\overline{NCH_2CH_2N(CH_3)}PF$	−63.2	$J_{PF} = 1055$	−31.5	$J_{PF} = 1025$

[a] ^{31}P, ^{19}F, and J_{PF} NMR data for Me_2NPF_2, $(Me_2N)_2PF$, and $CH_3\overline{NCH_2CH_2N(CH_3)}PF$ are from ref 19 and 9a and have been verified by this laboratory. [b] Compares well with the reported ^{19}F NMR values of −44.8 ppm and J_{PF} = 1157 Hz for $(CO)_3Ni(Me_2NPF_2)$.[14]

slush) and through traps held at −63 °C (chloroform slush) and at −196 °C. After about 3 h the product was isolated in the −63 °C trap as clear crystals that melted evenly upon warming to room temperature to give a clear liquid that decomposes at room temperature. Mass spectral data for this product are consistent with the formation of $(Me_2N)_2PH$. Electron-impact mass spectra were obtained at both 70 and 20 eV. The parent peak and the $M^{+\cdot} - 1$ peak are only seen in the 20 eV spectra due to the extreme sensitivity of $(Me_2N)_2PH$ to electron impact. The most abundant ions in the mass spectra are the same for both voltages and are those expected for the breakdown of the aminophosphine species (see Table II). In Table II, the relative intensity of the fragments were normalized for convenience to the most abundant peak above m/z 35. In the case of $(Me_2N)_2PH$, the parent peak is present in such low abundance that the smaller molecular weight peaks appear off scale on the 20-eV spectra.

(b) Preparation of $CH_3\overline{NCH_2CH_2N(CH_3)}PH$. The cyclic bis(alkylamino)phosphine was prepared in a similar fashion by the 1:1 reaction of $CH_3\overline{NCH_2CH_2N(CH_3)}PF$ with L-Selectride at −23 °C. A 91% yield was indicated by ^{31}P NMR spectroscopy. This cyclic phosphine has a characteristic P–H doublet at 97.4 ppm with J_{PH} = 150 Hz.

Preparation of Monosubstituted Nickel Carbonyl Complexes. (a) Preparation of $(CO)_3NiL$ (L = Me_2NPF_2, $(Me_2N)_2PF$, $CH_3\overline{NCH_2CH_2N(CH_3)}PF$). In a typical reaction, a 0.34-mmol sample of the fluorophosphine ligand was condensed into a sample tube along with dried, degassed, and distilled CH_2Cl_2. The sample was warmed and mixed so that a homogeneous solution was obtained; it was frozen to −196 °C, and a 2.61-mmol sample of $Ni(CO)_4$ was then condensed onto the frozen ligand/solvent system. At least a 2:1 excess of $Ni(CO)_4$ is needed. The reaction time was usually 2–3 h at −30 °C. At 0 °C or room temperature the reaction was much faster, but then disproportionation became more of a problem. The reactions were all quantitative on the basis of the consumption of the phosphine ligand as monitored by ^{31}P NMR spectroscopy. The liberated CO, as measured in the Toepler pump system, indicated loss of one CO for each phosphine ligand incorporated into the complex. The pure compounds can be isolated by holding the solution at −23 °C and distilling the excess $Ni(CO)_4$ and CH_2Cl_2 into a trap at −196 °C. In each case the resulting monosubstituted compound was pure as monitored by ^{31}P NMR spectroscopy at −30 °C. ^{31}P and ^{19}F NMR data are as follows:

	ppm ^{31}P	ppm ^{19}F	J_{PF}, Hz
$(CO)_3Ni(Me_2NPF_2)$	169	−44.3	1160
$(CO)_3Ni[(Me_2N)_2PF]$	178	−68.9	1060
$(CO)_3Ni[CH_3\overline{NCH_2CH_2N(CH_3)}PF]$	161.5	−31.5	1100

The mass spectrum for the compound $(CO)_3Ni[(Me_2N)_2PF]$ shows peaks corresponding to the following ions: $(CO)_3NiL^{+\cdot}$, m/z 280; $(CO)_2NiL^+$, m/z 252; $(CO)NiL^+$, m/z 224; NiL^+, m/z 196. The peaks of greatest intensity were fragments resulting from the breakdown of the ligand $(Me_2N)_2PF$. For the cyclic compound, $(CO)_3Ni[CH_3\overline{NCH_2CH_2N(CH_3)}PF]$, the data are similar (see Table II). For both of these monosubstituted nickel carbonyl compounds the mass spectra were obtained at 70 and 20 eV. The high-intensity peaks are similar for both voltages. The expected isotopic pattern due to the five isotopes of nickel is seen for each of these species. Only the most intense peak in each isotopic group is listed in Table II. Detailed data are available for both compounds.[21]

(b) Preparation of $(CO)_3NiL'$ (L' = $(Me_2N)_2PH$, $CH_3\overline{NCH_2CH_2N(CH_3)}PH$). A sample of $(CO)_3Ni[(Me_2N)_2PF]$ was prepared. Volatile components were removed from the system at −23 °C, and then an equimolar amount of L-Selectride was syringed onto the *frozen* fluorophosphine. The reaction was monitored by ^{31}P NMR spectroscopy while it was allowed to warm to −23 °C. This reaction was slower than the comparable reduction of the free ligand (60% after 10 h), and it is more complicated. Both the reactant and product disproportionate into their di- and trisubstituted nickel complexes upon standing at −23 °C. The addition of CO pressure to the system minimizes the disproportionation of the product phosphine to yield 73% of the monosubstituted phosphine $(CO)_3Ni[(Me_2N)_2PH]$, as evidenced by ^{31}P NMR spectroscopy. This result can be rationalized by the fact that numerous ligand-exchange reactions of tetracoordinated nickel complexes have been shown to be initiated by a first-order dissociative process.[22] For this particular case loss of a ligand would produce a highly reactive, 16-electron intermediate.[23] An increase in CO pressure increases the probability that CO will be incorporated back into the system as opposed to incorporation of L'. The incorporation of another L' causes contamination of the product. ^{31}P NMR data for the new nickel phosphine complex, $(CO)_3Ni[(Me_2N)_2PH]$: doublet, 112.6 ppm, J_{PH} = 380 Hz (see Table III).

In an analogous manner the monosubstituted cyclic phosphine $(CO)_3Ni[CH_3\overline{NCH_2CH_2N(CH_3)}PH]$ was prepared by the 1:1 reaction of L-Selectride and the monosubstituted fluorophosphine at −23 °C. Unlike the previous reaction, this reaction is clean and shows no disproportionation. NMR spectra show that a P–H product is obtained in a 49% yield after 4 h at −23 °C and the yield increases to 71% after 22 h at −23 °C. The ^{31}P NMR chemical shift is 118.5 ppm with a coupling constant, J_{PH}, of 280 Hz.

(c) Other Reactions with Selectrides. (i) PCl_3, PF_3, and PH_3 Reactions. In each case a 1:3 ratio of trihalophosphine (or phosphine) to "Selectride" in THF solvent was used, and the reactions were monitored by ^{31}P NMR spectroscopy. Temperatures could be varied from −100 to +25 °C. The reaction of PCl_3 or PF_3 with "Selectride" yielded PH_3 even at temperatures as low as −100 °C. The product PH_3 will react *very slowly* with "Selectride" at −80 °C. Several hours were required. Products of the PH_3 reaction are not yet defined.

(ii) Reaction of PF_2Cl with "Selectrides". In a typical reaction 1 mmol of PF_2Cl was allowed to react with 1 mmol of L-, N-, or K-Selectride in THF at temperatures ranging from −100 to −90 °C. In all cases PF_3 and PH_3 were the major products under these conditions. Other yet unidentified PF_2-containing species were also formed, as evidenced by P–F coupling seen on the ^{31}P NMR spectra obtained. No evidence of PF_2H formation was seen in these reactions.

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Table IV. Summary of L-Selectride Reactions

L	reacn with L (products)	reacn with $Ni(CO)_3L$ (products)	reacn with NiL_4 (products)
$(Me_2N)_2PF$	clean reacn ($(Me_2N)_2PH$)	clean reacn ($(CO)_3Ni[(Me_2N)_2PH]$)	
$CH_3\overline{NCH_2CH_2N(CH_3)}PF$	clean reacn ($CH_3\overline{NCH_2CH_2N(CH_3)}PH$)	clean reacn ($(CO)_3Ni[CH_3\overline{NCH_2CH_2N(CH_3)}PH]$)	
PF_2Cl	redn occurs ($PF_3 + PH_3$ + others)		redn occurs ($Ni(PF_3)_4$) + others
PCl_3	clean reacn (PH_3)		clean reacn (PH_3 + Ni)
PF_3	clean reacn (PH_3)		

Results and Discussion

(1) Synthesis of $(R_2N)_2PH$, $CH_3\overline{NCH_2CH_2N(CH_3)}PH$, and Related Species. The work of King and co-workers[3,4] has shown conclusively that steric factors are of importance in the reduction of $(R_2N)_2PCl$ by $LiAlH_4$. If the R groups are large and bulky such as isopropyl or *tert*-butyl, the phosphine, $(R_2N)_2PH$, can be obtained in good yields. If R is methyl, the reaction is more complicated and $(Me_2N)_3P$ rather than $(Me_2N)_2PH$ is the major product. The results reported from this study show clearly that steric inhibition of side reactions that generate $(Me_2N)_3P$ can also be achieved by using a sterically hindered hydride source such as a "Selectride". An analysis of steric factors that are important in obtaining $(Me_2N)_2PH$ is in progress. The pertinent available data on halophosphine reduction can be summarized by the equations

$$(Me_2N)_2PCl + LiAlH_4 \rightarrow (Me_2N)_3P \text{ (nearly quantitative yield) + other products} \quad (3a)^{3,4}$$

$$CH_3\overline{NCH_2CH_2N(CH_3)}PCl + LiAlH_4 \rightarrow ? \text{ (no P–H by } ^{31}P \text{ NMR)} \quad (3b)^{3,4}$$

$$(Me_2N)_2PCl + Li[AlH(OC(CH_3)_3)_3] \rightarrow (Me_2N)_2POC(CH_3)_3 + \text{other products} \quad (4)^{6}$$

$$(Me_2N)_2PCl + LiBH_4 \rightarrow (Me_2N)_2PH{\cdot}BH_3 + LiCl \quad (5)^{5}$$

$$(Me_2N)_2PX + LiBH[CH(CH_3)C_2H_5]_3 \rightarrow (Me_2N)_2PH + LiX + B[CH(CH_3)C_2H_5]_3$$

$$X = Cl, F \quad (6a)^{25}$$

$$CH_3\overline{NCH_2CH_2N(CH_3)}PF + LiBH[CH(CH_3)C_2H_5] \rightarrow CH_3\overline{NCH_2CH_2N(CH_3)}PH + LiF + B[CH(CH_3)C_2H_5]_3 \quad (6b)^{25}$$

Clearly the tendency to form an acid–base BH_3 adduct as seen in reaction 5 is minimized by use of the "Selectride" where the sterically hindered weak acid BR_3 is formed in the solution in place of BH_3. Details accounting for differences in the reducing behavior of the $LiAlHR_3$ compounds are still being studied. As reactions 3 and 4 show clearly, the nature of the three R groups attached to Al is important. The "Selectrides" have a number of advantages in the synthesis of these $(R_2N)_2PH$ compounds. L-Selectride is a more moderate reducing agent compared with $LiAlH_4$; it does not contain groups such as $-OC(CH_3)_3$, which can themselves attack the P–X bond, and it releases a comparatively weak Lewis acid ($BR_3 < BH_3$), which shows no tendency to complex to the desired aminophosphine product. L-Selectride is convenient to use; solubility problems are minimal even at low temperature, and simple syringe techniques can be applied.

(2) Reactions of "Selectrides" with PX_3, $Ni(PX_3)_4$, PX_2Y, and $Ni(PX_2Y)_4$ Where X and Y Are Halogens. This study focused on an identification of products formed when PCl_3, PF_3, $Ni(PCl_3)_4$, PF_2Cl, and $Ni(PF_2Cl)_4$ were allowed to react with "Selectrides" as limited-strength reducing agents. It was hoped that, through selective reduction of PF_2Cl or $Ni(PF_2Cl)_4$, PF_2H or $Ni(PF_2H)_4$ might be prepared. Current routes to PF_2H and its compounds involve the unstable and experimentally difficult compound PF_2I. All attempts to prepare PF_2H and compounds of PF_2H by reduction of PF_2Cl have been unsuccessful up to this point.

As indicated in Table IV both free PCl_3 and coordinated PCl_3 in $Ni(PCl_3)_4$ are reduced to PH_3 by L-Selectride in THF. PF_3 will also react with L-Selectride to form PH_3. The reaction of PF_2Cl with L-, N-, or K-Selectride in THF gave PH_3 and PF_3 as major products at temperatures of −90 to −100 °C. The test reaction of $Ni(PF_2Cl)_4$ with L-Selectride produced $Ni(PF_3)_4$ and other unidentified products. The data indicate quite clearly that although "Selectrides" will reduce P–F bonds, P–Cl bonds will be reduced preferentially by *limited amounts* of "Selectride" acting on PF_2Cl or $Ni(PF_2Cl)_4$.

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Registry No. $(Me_2N)_2PH$, 20502-83-4; $(Me_2N)_2PF$, 1735-82-6; $(Me_2N)_2PCl$, 3348-44-5; $CH_3\overline{NCH_2CH_2N(CH_3)}PH$, 95616-77-6; $CH_3\overline{NCH_2CH_2N(CH_3)}PF$, 33672-91-2; Me_2NPF_2, 814-97-1; $(CO)_3Ni(Me_2NPF_2)$, 37410-10-9; $(CO)_3Ni[(Me_2N)_2PF]$, 95616-79-8; $(CO)_3Ni[CH_3\overline{NCH_2CH_2N(CH_3)}PF]$, 95616-80-1; $(CO)_3Ni[(Me_2N)_2PH]$, 95616-81-2; $(CO)_3Ni[CH_3\overline{NCH_2CH_2N(CH_3)}PH]$, 95616-78-7; PCl_3, 7719-12-2; PF_3, 7783-55-3; PH_3, 7803-51-2; PF_2Cl, 14335-40-1; L-Selectride, 38721-52-7; N-Selectride, 67276-04-4; K-Selectride, 54575-49-4.

(25) This work.