Preparation and Characterization of Di(tertiary phosphines) with Electronegative Substituents. 2. Unsymmetrical Derivatives

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The o-carborane phosphino derivatives $R_2P[B_{10}H_{10}C_2]PR'R''$ ($R = C_6H_5$, $R' = R'' = NMe_2$, F; $R = C_6H_5$, $R' = F$, R'' $= NMe_2$; $R = R' = NMe_2$, $R'' = F$) have been prepared and characterized by mass spectrometry and infrared and ^1H, ^{19}F, and ^{31}P NMR spectroscopy.

Introduction

Recently we have prepared and characterized symmetrically substituted diphosphino derivatives of o-carborane of the type $RR'P[B_{10}H_{10}C_2]PRR'$ ($R = R' = NMe_2$; $R = NMe_2$, $R' =$ F) and the cyclic $FP[B_{10}H_{10}C_2]_2PF$.[1] The unsymmetrical di(tertiary phosphines) are of special interest since they offer, as ligands, the possibility of observing the effects of two differently substituted coordinating phosphorus atoms. A series of phosphines of the formula $(C_6H_5)_2P(CH_2)_2P(C_6H_5)R$ (R = Me, Et, i-Pr) have been prepared.[2] However, unsymmetrical di(tertiary phosphines) with highly electronegative substituents are rather rare. Recently, Sharp et al. synthesized and characterized $(C_6H_5)_2P(CH_2)_2PR_2$ ($R = CF_3$, C_6F_5).[3,4] Morse et al. have reported the interesting compound $Me_2N(F)P-(CH_2)_2PF_2$, but it is not particularly stable.[5]

We report here the unsymmetrical di(tertiary phosphines) with the electronegative substituents $N(CH_3)_2$ and F containing o-carborane as a backbone.

Results and Discussion

Synthesis. The lithium carborane derivatives provide a convenient precursor for reaction with halophosphines.[6] Lithium o-carborane reacts with $(C_6H_5)_2PCl$ in benzene to give the mono(tertiary phosphine) I. Compound I has been
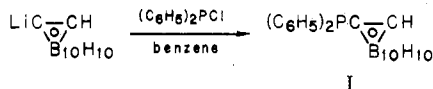

previously reported in 1972 but was not fully characterized.[7] A modified procedure for its preparation is given in the Experimental Section, and a complete spectroscopic characterization has been made in this work.

Compound I reacts smoothly with n-BuLi in ethyl ether to give the lithium derivative which reacts with $ClP(NMe_2)_2$ to form $(C_6H_5)_2P[B_{10}H_{10}C_2]P(NMe_2)_2$ (II) in 54% yield.
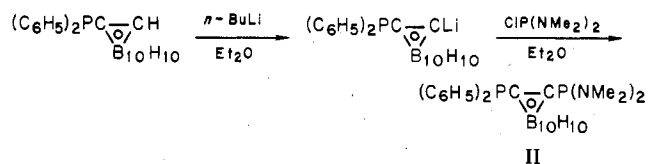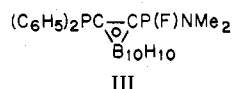

When compound II is mixed with PF_5 in hexane, a white solid is formed. Pressure measurements show that 2 mol of PF_5/mol of substrate is used up. This solid is probably an adduct of the type
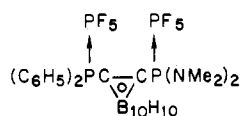

analogous to the adduct observed between some other dialkylaminophosphines and PF_5.[1,8] The adduct decomposes at

90 °C to give $(C_6H_5)_2P[B_{10}H_{10}C_2]P(F)NMe_2$ (III) in 60%

yield. Attempts to substitute F for both NMe_2 groups by the reaction with large excesses of PF_5 were unsuccessful. The suggested adduct implies the reactants are bound at the site of reaction making the exchange a rather specific process. No C_6H_5–P cleavage is observed upon the decomposition of the adduct. Compound III is also produced by heating a mixture of II and an excess of PF_3 in hexane–benzene for 6 days at 120 °C. However the yield is considerably lower than in the reaction with PF_5.

The lithium derivative of I reacts with PF_2Br in ethyl ether to form $(C_6H_5)_2P[B_{10}H_{10}C_2]PF_2$ (IV) in 38% yield. If the
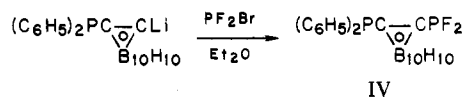
reaction is run in benzene, considerably lower yields (~25%) are observed, and color changes from blue to red to pink to yellow indicate that a competing reaction may be proceeding via a radical mechanism. The nucleophilic displacement of Br leading to the desired product is favored in the more polar ether solvent system.

Other attempts to prepare IV by treating II with reagents such as AsF_3, SbF_5, C_6H_5COF, or HCl followed by SbF_3 were unsuccessful or gave IV in very low yield. Considerable C–P cleavage was observed in most of the cases.

The previously prepared symmetrical derivative[1] $(Me_2N)_2P[B_{10}H_{10}C_2]P(NMe_2)_2$ reacts with an excess of PF_3 in benzene forming $(Me_2N)_2P[B_{10}H_{10}C_2]P(F)NMe_2$ (V). The

reaction does not go beyond one NMe_2–F exchange regardless of the amount of PF_3 present, even at temperatures as high as 120 °C. The highest yield (57%) is reached after 4 days at 90–100 °C.

All the phosphines except compound IV are remarkably stable to air and humidity; I and II are not affected by protic solvents at room temperature. The fluorinated phosphines III and V hydrolyze slowly. Compound IV is considerably more susceptible to hydrolysis in solution.

Mass Spectra. Table I lists the mass spectral data for the new phosphines. In all cases the parent molecular ion is clearly observed and the m/e ratio is in agreement with the calculated molecular weight. In the spectra of II and V the base peak is m/e 119, $P(NMe_2)_2^+$, and that in the spectrum of III is m/e 94, $FPNMe_2^+$, indicating that P–C bond cleavage is facile. Peaks at m/e 120, $HP(F)NMe_2^+$, are observed as is a peak at m/e 186, $HP(C_6H_5)_2^+$, for II, III, and V. These ions are

Table I. Mass Spectral Data[a]

	intensity[b]				
m/e	II	III	IV	V	assignment[c]
446	20				$(C_6H_5)_2P[B_{10}H_{10}C_2]P(NMe_2)_2$
421		20			$(C_6H_5)_2P[B_{10}H_{10}C_2]P(F)NMe_2$
402	90				$(C_6H_5)_2P[B_{10}H_{10}C_2]PNMe_2$
396				32	$(C_6H_5)_2P[B_{10}H_{10}C_2]PF_2$
378		80			$(C_6H_5)_2P[B_{10}H_{10}C_2]P(H)F$
359	70				$(C_6H_5)_2P[B_{10}H_{10}C_2]PH$
355				10	$(Me_2N)_2P[B_{10}H_{10}C_2]P(F)NMe_2$
336				37	$(Me_2N)_2P[B_{10}H_{10}C_2]PNMe_2$
328	16				$(C_6H_5)_2P[B_{10}H_{10}C_2]H$
327		30	100		$(C_6H_5)_2P[B_{10}H_{10}C_2]$
311				53	$Me_2NP[B_{10}H_{10}C_2]P(F)NMe_2$
280	13				$C_6H_5P[B_{10}H_{10}C_2]P$
268				22	$HP[B_{10}H_{10}C_2]P(F)NMe_2$
249			24		$C_6H_5P(B_{10}H_{10}C_2)$
186	6	35	16		$HP(C_6H_5)_2$
185	13	30	74		$P(C_6H_5)_2$
184	9	30	22		$HPC_{12}H_8$
183	31	45	86		$PC_{12}H_8$
161			17		$[B_{10}H_{10}C_2]F$
152	16	20	16		$C_{12}H_8$
120	37			31	$HP(NMe_2)_2$
119	100			100	$P(NMe_2)_2$
109	13		6		HPC_6H_5
108	9	18	21		PC_6H_5
107	9	28	22		PC_6H_4
95				7	$HP(F)NMe_2$
94		100		51	$FPNMe_2$
76	96			71	$HPNMe_2$
60	21			19	$HPNCH_2$

[a] Isotopic patterns for a ten-boron cage were observed for all B_{10}-containing ions. These are not listed in the table. Ions with $m/e < 60$ are also not listed. [b] Relative to the most intense peak in the spectrum. Relative intensity < 6 not listed. [c] Formulas are written suggesting probable ion structure.
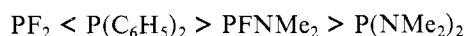
Table II. Infrared Spectral Data[a]

	$(P)C_6H_5$[b]	N–C str	P–C str	P–N str	P–F str
I	1433 vs		1090 s		
II	1432 vs	1265 ms	1090 ms	973 ms	
		1180 ms		960 s	
		1155 ms			
III	1430 vs	1290 s	1083 s	982 vs	830 m
		1255 s			
		1183 s			
IV	1436 vs		1091 s		830 vs
					810 vs
V		(1290 ms)[c]		(989 vs)	825 w
		(1280 ms)		974 vs	
		1270 ms		963 vs	
		1178 s			

[a] In cm^{-1}. Nujol mulls. Abbreviations: str, stretching; v, very; s, strong; m, medium; w, weak. [b] Planar ring deformation. [c] Values in the P(F)NMe$_2$ group are in parentheses.

probably formed by ion–molecule reactions due to the high concentration of ions formed in the source upon volatilization of the solid. The high abundance of disubstituted phosphorus ions and ions such as NMe$_2$$^+$, CH$_2NMe^+$, and CH$_2NCH_2$$^+$ suggests that d-shell participation stabilizes the electron deficiency of the phosphorus atom.[9] The normal fragmentation path of the P(C$_6$H$_5$)$_2$$^+$ is clearly observable in the fragmentation of II, III, and V.[10]

The relative intensities of the fragment ions PR(R′)$^+$ (R = R′ = R, NMe$_2$, C$_6$H$_5$; R = NMe$_2$, R′ = F) in each spectrum suggest the order of P–C bond cleavage under electron impact is

$$PF_2 < P(C_6H_5)_2 > PFNMe_2 > P(NMe_2)_2$$

Infrared Spectra. Table II lists the frequencies tentatively assigned to the N–C, P–C$_6$H$_5$, P–N, and P–F stretchings and

Table III. ^{1}H NMR Data[a]

	$\delta_{C_6H_5}$	δ_{Me}	$^3J_{PH}$	$^4J_{FH}$
I	7.33 m			
	7.45 m			
II	7.75 m	2.79 d	9.0	
	7.40 m			
III	7.80 m	2.75 dd	9.6	4.5
	7.37 m			
IV	7.70 m			
	7.25 m			
V		2.72 d	9.7	~2.8
		(~2.72 dd)[b]	(~9.0)[b]	

[a] Chemical shifts in ppm downfield from Me$_4$Si. Coupling constants in hertz. Solvent: CDCl$_3$. [b] In P(F)NMe$_2$ group.

Table IV. ^{19}F NMR Data[a]

	δ_F	$^1J_{PF}$	$^4J_{PF}$
III	118.4 dd	1009.5	21.2
IV	83.5 dd	1249.0	44.8
V	117.9 dd	1006.7	19.7

[a] Chemical shifts in ppm upfield from CFCl$_3$. Coupling constants in hertz. Solvent: CDCl$_3$.

Table V. ^{31}P NMR Data[a]

	$\delta_{P(C_6H_5)_2}$	$\delta_{P(NMe_2)_2}$	$\delta_{P(F)NMe_2}$	δ_{PF_2}	$^3J_{PP}$
I	25.2 s				
II	17.3 d	104.0 d			120.0
III	10.4 dd		157.2 dd		151.2
IV	11.1 dt			139.4 td	177.8
V		96.6 dd	145.5 dd		157.5

[a] Chemical shifts in ppm downfield from H$_3$PO$_4$ (85%). Coupling constants in hertz. Solvent: CDCl$_3$.

the planar ring-deformation mode in the P(C$_6$H$_5$)$_2$ group. The assignments have been made by analogy with related systems.[11-17] The typical absorption bands of the carborane cage are observed as follows: several strong bands in the 2540–2630-cm^{-1} range (B–H stretching), a strong band in the 720–725-cm^{-1} range (cage deformation), and two or three bands of variable intensity in the 995–1080-cm^{-1} range (tentatively assigned to B–H deformation modes).

Compound I shows the expected absorption due to the C–H stretching (3045 cm^{-1}) and two bands that can be assigned to the C–H deformation modes (1165 and 1120 cm^{-1}).

The N–C stretching assignments are highly tentative since coupling with the methyl deformation modes is likely. This frequency is higher in the fluorinated moiety. The increased electronegativity of nitrogen due to the electron drift caused by fluorine will lower the bonding orbitals strengthening the N–C bond. The same situation was observed in the previously prepared phosphino derivatives.[1]

The P–N stretching frequencies fall in the upper limit of the suggested region (940–980 cm^{-1}) for P(NMe$_2$)$_2$-containing compounds.[11] This indicates a rather strong p$_\pi \rightarrow$ d$_\pi$ interaction from N $\rightarrow$ P as observed[1] in (Me$_2$N)$_2$P[B$_{10}$H$_{10}$C$_2$]P-(NMe$_2$)$_2$ (977 and 965 cm^{-1}), Me$_2$N(F)P[B$_{10}$H$_{10}$C$_2$]P(NMe$_2$)$_2$ (988 cm^{-1}), and other analogous systems.[11,12] Such interaction is favored by the electron-withdrawing power of the carborane cage.[6] Substitution of NMe$_2$ by fluorine shifts the P–N stretching frequency to higher energy. The more electronegative fluorine strengthens the p$_\pi \rightarrow$ d$_\pi$ interaction by pulling electron density away from phosphorus and lowering the energy of the phosphorus d orbitals.

The compounds containing the P(NMe$_2$)$_2$ moiety (II and V), including the symmetrical one previously indicated, show two P–N stretching bands which are assigned to the expected symmetrical and asymmetrical vibrations.[12]

The enhanced basicity of the phosphorus atom and reduced basicity of the nitrogen atom due to the N → P π interaction may account for the considerable P–C bond cleavage observed by acidic attack on the moiety C–P(NMe$_2$)$_2$ rather than a P–N cleavage.

Nuclear Magnetic Resonance. Tables III, IV and V list the ^{1}H, ^{19}F, and ^{31}P NMR parameters, respectively, of the new phosphino derivatives.

The phenyl protons show their characteristic resonance as two multiplets in the 7.25–7.80 ppm range. The chemical shifts of the methyl protons fall in the expected region for similar systems.[18,19,20] No coupling is observed between the methyl groups and the far phosphorus atom, and all the methyls appear to be equivalent in a given moiety. The $^3J_{PH}$ and the $^4J_{FH}$ values are in the range observed for numerous compounds of the same type.[18,19,21] In compound V the doublet of doublets due to the methyl protons in the P(F)NMe$_2$ moiety is not well resolved but is discernible on a vastly expanded trace.

The ^{19}F chemical shifts fall in the lower limit of the region observed for similar systems, and the $^1J_{PF}$ values are typical for such systems.[18,21-23] The large magnitude of $^4J_{PF}$ is unusual and probably reflects the electron delocalizing ability of the carborane cage. The fine structure on the ^{19}F resonances due to the F–H interaction is more clearly observed in III ($^4J_{FH}$ = 4.5 Hz) than in V ($^4J_{FH} \approx 2.8$ Hz).

The ^{31}P chemical shifts are in agreement with those of compounds with similar phosphine moieties.[23] The chemical shifts move downfield as the electronegativity of the substituents increases. However, the chemical shift of the fluorinated phosphorus in compound IV appears at a higher field than expected. The increased lone-pair–substituent angle in IV increases the s character of the electron lone-pair shielding the phosphorus nucleus.[24] Thus, this stereochemical effect here outweighs the opposite effect of the highly electronegative fluorine atom. The ^{31}P chemical shift in the P(C$_6$H$_5$)$_2$ group falls in the lower limit of the range of known similar compounds. This effect is not so noticeable in the other moieties since concomitantly the N → P π interaction is enhanced which has a shielding effect on the P nucleus. Only a few long-range PCCP couplings have been measured and the factors affecting these couplings are not well understood. For example, PCCP coupling in di(tertiary phosphines) such as (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$ is ~0. The presence of a π-bonding system seems to enhance the P–P coupling. Thus, in *cis*-(C$_6$H$_5$)$_2$PCH=CHP(C$_6$H$_5$)$_2$ and (C$_6$H$_5$)$_2$PC≡C-P(C$_6$H$_5$)$_2$ the $^3J_{PP}$ values are 18.7 and 6.8 Hz, respectively.[25-27] In Me$_2$N(F)PCH$_2$CH$_2$PF$_2$ no P–P coupling was reported[5] while for (C$_6$H$_5$)$_2$PCH$_2$CH$_2$PR$_2$ the P–P couplings are 42.0 Hz (R = CF$_3$) and 42.2 Hz (R = C$_6$F$_5$).[3,4] The $^3J_{PP}$ values reported here are rather large. Stepwise substitution of NMe$_2$ groups by F atoms in II increases the $^3J_{PP}$ value from 120.0 Hz (II) to 151.2 Hz (III) to 177.8 Hz (IV). The increasing electronegativity of the substituents on the P atom increases the s character of the phosphorus orbitals which contributes to the magnitude of the coupling.[28] The $^3J_{PP}$ value for V fits well in the trend indicated above. In addition to the electronegativity factor, the electron-delocalizing ability of the carborane cage[6] also contributes to the large magnitude of the P–P couplings reported here.

Experimental Section

Mass spectra were obtained on a du Pont Model 21-491B spectrometer. Infrared spectra were recorded on a Perkin-Elmer 621 spectrophotometer. Proton and fluorine NMR spectra were obtained on a Varian EM-390 spectrometer at 90 and 84.6 MHz, respectively. Phosphorus NMR spectra were obtained at 32.1 MHz on a Varian CFT-20 spectrometer.

o-Carborane and the lithium derivatives were prepared by methods described in the literature.[7,29] The method used to prepare ClP(NMe$_2$)$_2$

was that of Noeth and Vetter,[30] and PF$_2$Br was prepared as described by Cavell.[31] Solvents were dried over sodium, and ClP(C$_6$H$_5$)$_2$ was distilled at 174 °C (5 mm). All other chemicals were used as received.

All the glassware was dried in an oven overnight and treated with a flame when assembled, and the system purged with dry nitrogen for at least 2 h before charging the chemicals.

(C$_6$H$_5$)$_2$P[B$_{10}$H$_{10}$C$_2$]H (I). Chlorodiphenylphosphine (244 mmol) was added slowly, under nitrogen, to an ice-bath-cooled slurry of lithium *o*-carborane (243 mmol) in benzene. After the solution had been refluxed for 30 h, the benzene was removed in vacuo and the residue extracted with ethyl ether. Evaporation of the filtrate gave a white solid which was recrystallized from *n*-hexane (57.6% yield). Anal. Calcd: C, 51.2; H, 6.4. Found: C, 50.9; H, 6.5.

(C$_6$H$_5$)$_2$P[B$_{10}$H$_{10}$C$_2$]P(NMe$_2$)$_2$ (II). *n*-Butyllithium (31 mmol) in hexane was added dropwise to compound I (30 mmol) in benzene at 0 °C, and bis(dimethylamino)chlorophosphine (31 mmol) was slowly added under nitrogen with vigorous stirring. After the addition was completed the mixture was refluxed for 20 h. Evaporation of the solvents gave a residue which was heated with an excess of *n*-hexane and filtered hot. Partial evaporation of filtrate and cooling gave the product in a 54% yield as a white crystalline solid. Anal. Calcd: C, 48.4; H, 7.2; N, 6.3. Found: C, 48.6; H, 7.4; N, 6.1.

(C$_6$H$_5$)$_2$P[B$_{10}$H$_{10}$C$_2$]P(F)NMe$_2$ (III). In a Fischer-Porter tube a solution of 4.5 mmol of II in *n*-hexane was condensed with 40 mmol of PF$_5$, and then the mixture was allowed to warm to room temperature. A white solid was formed. After elimination of the excess of PF$_5$, the mixture was heated to 90 °C and kept at this temperature for 1 h (at 65 °C the solid disappears). The reactor was allowed to cool to room temperature, and the solvents were removed in vacuo. The residue was extracted with benzene and filtered. Evaporation of the benzene gave a tan solid which was extracted with *n*-pentane. A white, cloudy solution was obtained, which upon evaporation gave the product in a 60% yield. Anal. Calcd: C, 45.6; H, 6.2; N, 3.3. Found: C, 45.3; H, 6.3; N, 3.2.

(C$_6$H$_5$)P[B$_{10}$H$_{10}$C$_2$]PF$_2$ (IV). A slurry of (C$_6$H$_5$)$_2$P[B$_{10}$H$_{10}$C$_2$]Li (prepared from 20 mmol of I and 20 mmol of *n*-BuLi in ether) and 32 mmol of PF$_2$Br was condensed in a Fischer-Porter tube. The tube was allowed to warm to room temperature and to remain at that temperature for 18 h. During this period the reactor was periodically shaken. The volatiles were removed in vacuo, and the residue was extracted with *n*-pentane. The white, cloudy solution was separated and evaporated giving the product in a 38% yield. Anal. Calcd: C, 42.4; H, 5.1. Found: C, 42.0; H, 5.2.

(Me$_2$N)$_2$P[B$_{10}$H$_{10}$C$_2$]P(F)NMe$_2$ (V). In a Fischer-Porter tube a solution of 6.6 mmol of (Me$_2$N)$_2$P[B$_{10}$H$_{10}$C$_2$]P(NMe$_2$)$_2$ in benzene and 70 mmol of PF$_3$ was condensed. The mixture was heated at 90–100 °C for 5 days. Occasionally the reactor was shaken during the heating period. After removal of the volatiles, the solution was filtered and the residue from the filtrate was shaken with *n*-pentane. The white, cloudy solution was separated and evaporated. Recrystallization from *n*-hexane gave the product in a 57% yield. Anal. Calcd: C, 27.0; H, 7.9; N, 11.8. Found: C, 26.8; H, 8.0; N, 11.6.

Registry No. I, 36988-93-9; II, 68200-99-7; III, 68201-00-3; IV, 68201-01-4; V, 68201-02-5; lithium *o*-carborane, 23841-96-5; (C$_6$H$_5$)$_2$PCl, 1079-66-9; ClP(NMe$_2$)$_2$, 3348-44-5; PF$_5$, 7647-19-0; PF$_2$Br, 15597-40-7; PF$_3$, 7783-55-3; (Me$_2$N)$_2$P[B$_{10}$H$_{10}$C$_2$]P(NMe$_2$)$_2$, 66842-19-1.

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Metal Complexes of Fluorophosphines. 7. Cocondensations of Some First-Row Transition-Metal Vapors with (Dimethylamino)difluorophosphine and (Methylamino)bis(difluorophosphine)[1,2]

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Cocondensations of $(CH_3)_2NPF_2$ with Cr, Fe, and Ni vapors give the corresponding $M[PF_2N(CH_3)_2]_n$ complexes (M = Cr, n = 6; M = Fe, n = 5; M = Ni, n = 4). Cocondensations of $CH_3N(PF_2)_2$ with Cr, Fe, Co, and Ni vapors give $Cr[(PF_2)_2NCH_3]_3$, $Fe[(PF_2)_2NCH_3]_4$, $Co_2[(PF_2)_2NCH_3]_5$, and $\{Ni[(PF_2)_2NCH_3]_2\}_n$, respectively. Cocondensations of a 4:1 mixture of $(CH_3)_2NPF_2$ and $CH_3N(PF_2)_2$, respectively, with Cr, Fe, Co, and Ni vapors give white $Cr[PF_2N(CH_3)_2]_4[(PF_2)_2NCH_3]$, red-yellow $Fe[PF_2N(CH_3)_2]_3[(PF_2)_2NCH_3]$, purple $Co_2[PF_2N(CH_3)_2]_2[(PF_2)_2NCH_3]_3$, and a mixture of white $Ni[PF_2N(CH_3)_2]_3[(PF_2)_2NCH_3]$ and light yellow $Ni_2[PF_2N(CH_3)_2]_2[(PF_2)_2NCH_3]_3$, respectively. No products could be obtained by the cocondensation of Mn vapor with either $(CH_3)_2NPF_2$ or $CH_3N(PF_2)_2$.

Introduction

In recent years aminodifluorophosphines of the type R_2NPF_2 have been shown to be good π-acceptor ligands capable of stabilizing low oxidation states of transition metals. The first such observation was the report by Schmutzler[3] that $Ni(CO)_4$ reacts with the (dialkylamino)difluorophosphines R_2NPF_2 (R = CH_3 or 2R = $-(CH_2)_5-$) to give homoleptic[4] zerovalent nickel(0) complexes $Ni(PF_2NR_2)_4$ exhibiting relatively high thermal and oxidative stabilities. Subsequent work in our laboratory has shown that the chelating aminodifluorophosphine $CH_3N(PF_2)_2$ is even more effective at stabilizing low oxidation states: for example, the zerovalent derivatives $M[(PF_2)_2NCH_3]_3$ (M = Cr, Mo, W) exhibit impressive thermal and oxidative stabilities.[5,6]

Up to the present time the chemistry of derivatives of the types $M(PF_2NR_2)_m$ and $M[(PF_2)_2NR]_n$ has been limited to compounds accessible through complete displacement of CO groups from the corresponding metal carbonyls. Syntheses of such compounds by reaction of derivatives containing the metal in a positive formal oxidation state (e.g., a metal halide) with excess aminodifluorophosphine in the presence of strong reducing agents are unattractive because of the potential sensitivity of the P–N and P–F bonds in the ligands toward reductive and/or solvolytic cleavage. A more promising technique for the synthesis of new homoleptic derivatives $M(PF_2NR_2)_m$ and $M[(PF_2)_2NR]_n$ is metal-vapor synthesis.[7,8] Metal-vapor synthesis has already been shown to be a useful method for the synthesis of trifluorophosphine derivatives of the type $M_m(PF_3)_n$: e.g., cocondensation of PF_3 with Cr, Fe, and Ni vapors has been reported to give the complexes $Cr(PF_3)_6$, $Fe(PF_3)_5$, and $Ni(PF_3)_4$, respectively.[9] However, until the work reported here, aminodifluorophosphines of the types R_2NPF_2 and $RN(PF_2)_2$ have never been used as ligands in metal-vapor syntheses.

This paper describes the details of our studies on the cocondensations of $(CH_3)_2NPF_2$ and $CH_3N(PF_2)_2$ with the first-row transition-metal vapors Cr through Ni, inclusive. These particular aminodifluorophosphines were selected because of their volatility and ease of preparation in the relatively large quantities required for metal-vapor synthesis. The particular metals used were selected on the basis of their ease of evaporation in a simple resistive heating apparatus.

Experimental Section

Microanalyses were performed by Atlantic Microanalytical Laboratory, Atlanta, Ga. Proton NMR spectra were run on a Varian T-60 spectrometer at 60 MHz. Carbon-13 NMR spectra were recorded at 25.0336 MHz on a Jeolco PFT-100 spectrometer operating in the pulsed Fourier transform mode with proton decoupling and a deuterium lock. Melting points were taken in capillaries and are uncorrected.

The ligands $(CH_3)_2NPF_2$[10] and $CH_3N(PF_2)_2$[6,11] were prepared by the cited published methods.

The Metal-Vapor Reactor. The metal-vapor reactions were run in equipment described below constructed in the shops at the University of Georgia according to previously reported[8,12] general designs.

The metals were evaporated from commercially available 0.5-mL alumina crucibles (Sylvania Emissive Products, Exeter, N.H.) made from a conical spiral of 1-mm diameter tungsten wire coated with alumina cement. This crucible was mounted between two electrodes inside a 130-mm diameter, 280-mm high, and 4-mm thick Pyrex cylindrical vessel. The electrodes consisted of concentric copper tubes of 4.8 and 13-mm diameters sealed appropriately with silver solder so that they could be cooled by continuously running cold water during an experiment. The electrodes were sealed to the glass top of the reaction vessel by a low vapor pressure resin ("Torr Seal" from Varian Associates, Palo Alto, Calif.). Ligand vapor was admitted to the reaction vessel through a central sample inlet tube so positioned that the vapors from the ligand emerge through numerous small holes 5–15 cm above the crucible of evaporating metal. For easy demountability the electrodes and the ligand inlet tube were attached to a cover which