3 H); ^{13}C NMR (Me_2SO-d_6) 191.0 (acyl CO), 159.8 (enolic C), 135.0, 128.3, 116.1 (imidazole ring C's), 82.8 (vinylic C), 29.5 (CH_3); IR (Nujol) 1670 (s), 1660 (s, acyl C=O), 1230 cm^{-1} (s, C=C). Anal. Calcd for $C_7H_7N_2NaO_2$: C, 48.27; H, 4.06; N, 16.09. Found: C, 48.11; H, 4.14; N, 16.09. The filtrate was analyzed by ^1H NMR and found to contain imidazole.

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Phosphine-Functionalized Phosphazene Precursors: Synthesis and Metal Carbonyl Complexes[1]

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Direct bromination of the benzyl- and allyl-substituted (silylamino)phosphines $(Me_3Si)_2NPRR'$ (**1a**, R = Ph, R' = CH_2Ph; **1b**, R = R' = CH_2Ph; **1c**, R = Ph, R' = $CH_2CH{=}CH_2$; **1d**, R = R' = $CH_2CH{=}CH_2$) affords the *P*-bromophosphoranimines $Me_3SiN{=}P(Br)RR'$ (**2a–d**) which, upon treatment with CF_3CH_2OH/Et_3N or $LiOCH_2CF_3$, are easily converted to the *N*-silyl-*P*-(trifluoroethoxy)phosphoranimines $Me_3SiN{=}P(OCH_2CF_3)RR'$ (**3a–d**). The latter compounds, as well as the simpler analogues $Me_3SiN{=}P(OCH_2CF_3)(R)Me$ (**4**, R = Me; **5**, R = Ph), are smoothly deprotonated by *n*-BuLi in ether solution at −78 °C. Quenching of the resulting anions with Ph_2PCl or $(Me_2N)_2PCl$ yields the title compounds $Me_3SiN{=}P(OCH_2CF_3)(R)CH(R')PPh_2$ (**6**, R = Me, R' = H; **7**, R = Ph, R' = H; **8a**, R = R' = Ph; **8b**, R = CH_2Ph, R' = Ph), $Me_3SiN{=}P(OCH_2CF_3)(R)CH{=}CHCH_2PPh_2$ (**8c**, R = Ph; **8d**, R = $CH_2CH{=}CH_2$), and $Me_3SiN{=}P(OCh_2CF_3)(Me)CH_2P(NMe_2)_2$ (**9**). The phosphine derivatives **6–9** as well as their new precursors **3a–d** are obtained as distillable liquids, fully characterized by NMR spectroscopy (^1H, ^{13}C, and ^{31}P) and elemental analyses. Some rearrangements involving the C=C double bonds are noted for the allyl-substituted phosphoranimines **3c,d** and their Ph_2P derivatives **8c,d**. The phosphine ligands **6**, **7**, **8a**, **8b**, and **9** all react quantitatively with $Fe_2(CO)_9$ at room temperature to give the corresonding (phosphine)$Fe(CO)_4$ complexes **10–12**, **14**, and **15** as viscous liquids, characterized by NMR spectroscopy. Likewise, treatment of ligand **6** with $Cr(CO)_6$ in refluxing diglyme affords the chromium pentacarbonyl complex **13**. These complexation reactions, which proceed cleanly without affecting the $Me_3SiN{=}POCH_2CF_3$ framework of the precursors, are viewed as model reactions for possible derivative chemistry of the poly(alkyl/arylphosphazenes).

Introduction

The synthesis of poly(alkyl/arylphosphazenes), $[NPRR']_n$, has been accomplished by the thermal condensation polymerization of appropriate *N*-silyl-*P*-(trifluoroethoxy)phosphoranimines, $Me_3SiN{=}P(OCH_2CF_3)RR'$, where R = R' = Me, Et, and Ph.[3] Having characterized these simple polymers,[4] we are currently investigating synthetic approaches to related systems with more diverse substituents attached to the backbone via phosphorus–carbon bonds. These new polymers could possess many useful characteristics including higher thermal stability and improved mechanical properties and, with the introduction of suitable ligating sites (e.g., $-CH_2PPh_2$) might also serve as supports for transition-metal catalysts.[5]

Toward these goals, we are studying three general methods of altering the substituents at phosphorus: (1) the synthesis of new (silylamino)phosphines, $(Me_3Si)_2NPRR'$, and *N*-silylphosphoranimines, $Me_3SiN{=}P(X)RR'$, containing more complex alkyl and/or aryl groups, (2) the functionalization of the substituents (R, R') in the phosphazene precursors $Me_3SiN{=}P(OCH_2CF_3)RR'$ via deprotonation/substitution reactions,[6] and (3) the application of similar derivative chemistry to the preformed poly(alkyl/arylphosphazenes). We have recently reported the preparation of a series of silylated derivatives of the poly(alkyl/arylphosphazenes) by the latter approach.[7]

This paper is based on our initial results related to the first two of the above methods. Sepcifically, we report here: (a) the synthesis of several new *N*-silylphosphoranimines containing various combinations of phenyl, benzyl, and allyl substituents on phosphorus; (b) the incorporation of phosphine substituents [Ph_2P or $(Me_2N)_2P$] into the *N*-silyl-*P*-(trifluoroethoxy)-phosphoranimines by the second method; and (c) the coordination of the phosphine sites to simple metal carbonyls.

Results and Discussion

***N*-Silylphosphoranimines.** The (silylamino)phosphines **1a–d** used in this study were prepared as described

(1) Taken in part from: Roy, A. K. Ph.D. Dissertation, Texas Christian University, Fort Worth, TX, 1984.

(2) (a) Present address: Michigan Molecular Institute, Midland, MI. (b) Southern Methodist University.

(3) (a) Wisian-Neilson, P.; Neilson, R. H. *Inorg. Chem.* **1980**, *19*, 1875. (b) Wisian-Neilson, P.; Neilson, R. H. *Inorg. Synth.*, in press. (c) Wisian-Neilson, P.; Neilson, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 2848. (d) Neilson, R. H.; Wisian-Neilson, P. *J. Macromol. Sci., Chem.* **1981**, *A16*, 425.

(4) Neilson, R. H.; Hani, R.; Wisian-Neilson, P.; Meister, J. J.; Roy, A. K.; Hagnauer, G. L. *Macromolecules*, in press.

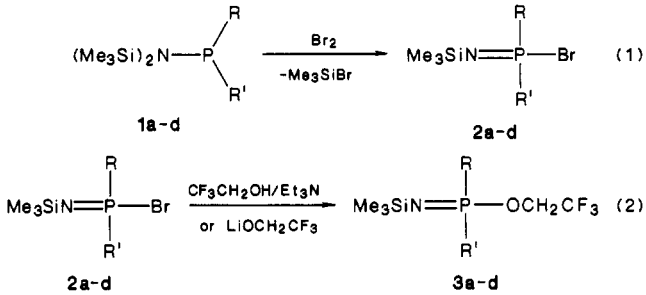
(5) Transition-metal derivatives of aryloxy- and amino-substituted poly(phosphazenes) have been studied. See, for example: Allcock, H. R. *ACS Symp. Ser.* **1983**, *No. 232*, 49.

(6) (a) Wettermark, U.G. Ph.D. Dissertation, Texas Christian University, Fort Worth, TX, 1986. (b) Wettermark, U. G.; Wisian-Neilson, P.; Scheide, G. M.; Neilson, R. H. *Organometallics*, in press.

(7) Wisian-Neilson, P.; Ford, R. R.; Neilson, R. H.; Roy, A. K. *Macromolecules* **1986**, *19*, 2089.

0276-7333/87/2306-0378$01.50/0

earlier[8] according to the Wilburn method[9] in which the chlorophosphines $(Me_3Si)_2NP(R)Cl$ (R = Ph, Cl), prepared from $(Me_3Si)_2NLi$ and $RPCl_2$, are treated with either allyl or benzyl Grignard reagent. As in the case for other (silylamino)phosphines,[3a] compounds **1a–d** undergo a smooth and essentially quantitative oxidation reaction with bromine to yield the *N*-silyl-*P*-bromophosphoranimines **2a–d** (eq 1). Subsequent treatment of **2** with CF_3CH_2OH/Et_3N (**2a–c**) or $LiOCH_2CF_3$ (**2d**) affords the corresponding *N*-silyl-*P*-(trifluoroethoxy)phosphoranimines **3a–d** (eq 2) in ca. 50–75% yields.



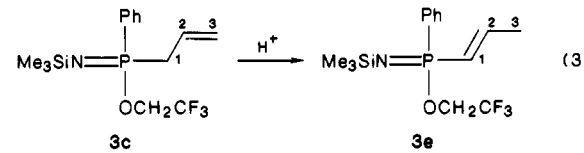
a, R = Ph, R' = CH_2Ph; **b**, R = R' = CH_2Ph; **c**, R = Ph, R' = $CH_2CH{=}CH_2$; **d**, R = R' = $CH_2CH{=}CH_2$

Previous studies involving *N*-silyl-*P*-bromophosphoranimines[3a] have shown that, besides being extremely moisture-sensitive, these compounds are thermally unstable, with the degree of instability increasing with the bulk of the substituents on phosphorus. Thus, the bromophosphoranimines prepared in this study were not purified by distillation; instead, they were characterized by NMR (^1H, ^{13}C, and ^{31}P) spectroscopy (Table I) and used without further purification for the preparation of the *N*-silyl-*P*-(trifluoroethoxy)phosphoranimines **3a–d**. In all cases, complete conversion of the phosphine **1** to the bromophosphoramine **2** was observed by ^{31}P NMR spectroscopy. In the synthesis of the allyl derivatives **2c,d**, it is interesting to note that, when a 1:1 stoichiometry is used, the bromination occurs exclusively at the phosphorus center, leaving the C=C bond intact. This selectivity is important because it makes possible the preparation of poly(alkyl/arylphosphazenes) that contain allyl or vinyl[10] side groups for cross-linking purposes.

The bromophosphoranimines **2a–c** reacted smoothly with CF_3CH_2OH/Et_3N to provide the trifluoroethoxy derivatives **3a–c** in good yields (eq 2). Under the same conditions, however, **3d** was formed in low and inconsistent yields and often decomposed to unidentified substances upon attempted distillation. For **2d**, therefore, $LiOCH_2CF_3$ was used, and the (trifluoroethoxy)phosphoranimine **3d** could then be isolated in 50% yield with no decomposition problems.

The *N*-silyl-*P*-(trifluoroethoxy)phosphoranimines **3a–d** are all colorless, distillable liquids that gave satisfactory microanalytical data (Table II). These compounds are also moisture-sensitive, although much less so than their bromo precursors. They can be stored for long periods of time under an inert atmosphere. The phosphoranimines **3a–d** were characterized by NMR (^1H, ^{13}C, and ^{31}P) spectroscopy, with all of the chemical shifts and coupling constants being in accord with the proposed structures. Because of the general complexity of the phenyl and vinyl regions of the ^1H and ^{13}C NMR spectra, only the data most useful for characterization purposes is listed in Table I. By recording spectra on a high-field instrument (300-MHz ^1H) and by using heteronuclear $^1H/^{13}C$ chemical shift correlation experiments, it is possible to completely assign both the ^1H and ^{13}C NMR spectra. Such data, for example, are summarized in Table III for compound **3c**.

An interesting observation was made with the allyl-substituted compounds **3c** and **3d**. The ^{31}P NMR spectra of both the crude and distilled product **3c** indicate the presence of a small amount of a second compound with a chemical shift close to that of the major product. The ^1H and ^{13}C NMR spectra exhibit minor resonances in regions expected for a terminal CH_3 group of an allyl substituent (ca. 2.0 and 20.0 ppm, respectively). Since a good elemental analysis was obtained for the distilled product, it is reasonable to assign these minor NMR signals to an isomer (**3e**) of the major product in which the terminal 2–3 C=C bond rearranges to the 1–2 position (eq 3). Such



rearrangements of allylphosphoranimines have been observed before[11] and are thought to be acid catalyzed (e.g., by HBr or Et_3NHBr). We noted that the relative amount of the 1–2 isomer **3e** increased on prolonged storage of the sample, especially when the container was occasionally opened to the atmosphere. The acid-catalyzed nature of this rearrangement was confirmed by an NMR tube experiment in which a small crystal of Me_3NHCl was added to a solution of **3c**. After the solution was left standing for 20 h at room temperature, the ^1H NMR integration showed that the **3c**:**3e** ratio decreased from ca. 25:1 to ca. 3:1.

Phosphine Derivatives. The chemistry in this phase of our study is based on an earlier report by Schmidbaur[12] in which the permethylated *N*-silylphosphoranimine (eq 4) was deprotonated by treatment with *n*-BuLi. The re-

sulting carbanion could then be quenched, for example, by Me_3SiCl. Similar deprotonation/substitution reactions have been carried out on methyl-substituted cyclic phosphazenes (e.g., $[Me_2PN]_3$) by Paddock and co-workers.[13] On the other hand, Allcock[14] has reported that phosphazenes bearing *trifluoroethoxy* groups react with *n*-BuLi and various electrophiles (RX) to form vinyl derivatives (i.e., P—O—CR=CF_2). It seemed likely, therefore, that this type of deprotonation/substitution chemistry could lead to some complicated product mixtures when applied to *trifluoroethoxy-substituted* phosphoranimines such as **3a–d**.

In addition to **3a–d**, two other *N*-silyl-*P*-(trifluoroethoxy)phosphoranimines, $Me_3SiN{=}P(OCH_2CF_3)(R)Me$ (**4**, R = Me; **5**, R = Ph), with simpler substituents on phosphorus, were utilized in this work. Upon treatment with

(8) Ford, R. R.; Goodman, M. L.; Neilson, R. H.; Roy, A. K.; Wettermark, U. G.; Wisian-Neilson, P. *Inorg. Chem.* **1984**, *23*, 2063.
(9) Neilson, R. H.; Wisian-Neilson, P. *Inorg. Chem.* **1982**, *21*, 3568.
(10) Neilson, R. H.; Waters, K., unpublished results.
(11) Morton, D. W.; Neilson, R. H. *Organometallics* **1982**, *1*, 623.
(12) Schmidbaur, H.; Jonas, G. *Chem. Ber.* **1967**, *100*, 1120.
(13) Gallicano, K. D.; Oakley, R. T.; Paddock, N. L.; Sharma, R. D. *Can. J. Chem.* **1981**, *59*, 2654.
(14) Allcock, H. R.; Suszko, P. R.; Evans, T. L. *Organometallics* **1982**, *1*, 1443.

Table I. Selected NMR Spectroscopic Data[a]

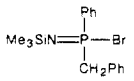
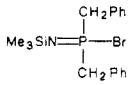
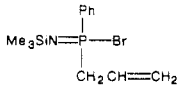
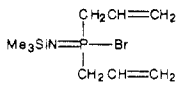
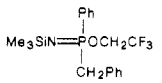
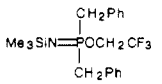
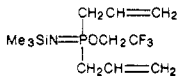
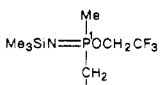
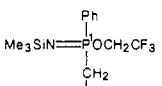
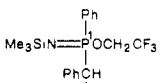
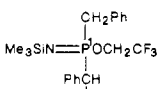
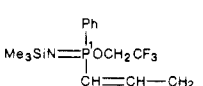
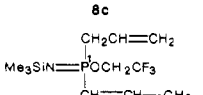
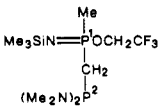
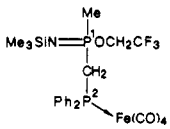
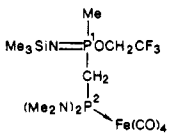
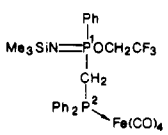
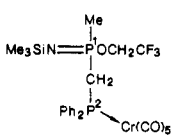
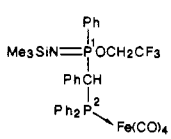
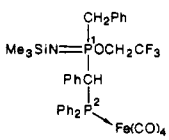
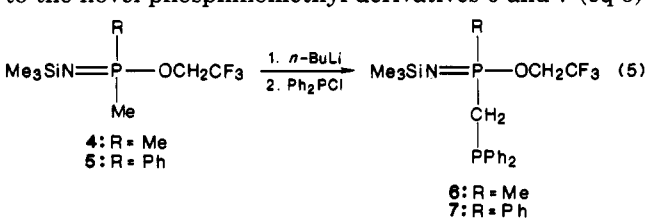
compd	signal	^{1}H NMR δ	^{1}H NMR J_{PH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
 **2a**	Me_3Si	0.35	0.6	2.72	4.9	7.34
	CH_2	3.86	15.3	49.02	75.7	
 **2b**	Me_3Si	0.02		2.50	5.5	9.02[b]
	CH_2	3.58	12.6	46.64	70.2	
 **2c**	Me_3Si	0.15	0.6	2.70	5.5	5.22
	PCH_2	3.23	15.6 (7.2)[c]	47.07	76.9	
	CH=CH_2	5.6–6.1[d]		*e*		
	CH=CH_2	4.8–5.2[d]		121.20	15.3	
 **2d**	Me_3Si	0.37	0.6	2.72	6.1	14.81
	PCH_2	2.72	15.0 (7.2, 1.2)[c]	44.04	72.6	
	CH=CH_2	5.6–6.1[d]		127.98	10.4	
	CH=CH_2	4.9–5.3		121.13	14.6	
 **3a**	Me_3Si	0.08	0.6	3.68	3.1	18.17
	PCH_2	3.31	17.4	40.94	92.8	
 **3b**	Me_3Si	−0.02		3.60	3.1	23.40
	PCH_2	3.08	15.6	39.13	87.3	
 **3d**[b]	Me_3Si	0.27		3.59	3.1	27.85
	PCH_2	2.40	17.4 (7.2, 1.2)[c]	36.57	88.5	
	CH=CH_2	5.5–6.0[d]		128.71	9.2	
	CH=CH_2	4.9–5.2[d]		119.92	13.4	
 **6**	Me_3Si	0.05		3.60	3.1	30.38 (P^1) −26.26 (P^2) (55.5)[f]
	PMe	1.44	14.4 (P^1) 1.2 (P^2)	18.44	90.9 (P^1) 3.0 (P^2)	
	PCH_2	2.59	15.6 (P^1)	33.46	93.4 (P^1) 30.5 (P^2)	
 **7**	Me_3Si	0.12		3.74	2.4	17.67 (P^1) −27.88 (P^2) (57.4)[f]
	PCH_2	2.82	15.3 (P^1)	33.62	95.8 (P^1) 31.1 (P^2)	
 **8a**	Me_3Si	0.38		3.70	2.4	14.91 (P^1) −9.95 (P^2) (65.0)[f] 18.54 (P^1) −8.49 (P^2) (52.3)[f]
	CH	3.2–3.8[d]		49.93	94.6 (P^1) 29.3 (P^2)	
 **8b**	Me_3Si	0.12		3.53	2.4	20.04 (P^1) −9.74 (P^2) (62.3)[f] 24.05 (P^1) −7.44 (P^2) (53.1)[f]
	PCH_2	2.1–3.4[d]		39.88	86.7 (P^1)	
	CH	2.1–3.4[d]		49.08	88.5 (P^1) 28.7 (P^2)	
 **8c**	Me_3Si	0.25		3.6	3.1	11.45 (P^1) −15.70 (P^2) (4.9)[f]
	P^2CH_2	3.13	7.8 (P^2) (1.2, 1.2)[c]	34.25	20.1 (P^1) 18.3 (P^2)	
 **8d**	Me_3Si	0.27		3.64	3.1	17.83 (P^1) −15.56 (P^2) (4.3)[f]
	P^1CH_2	2.1–2.8[d]		38.03	93.4 (P^1)	
	P^2CH_2	2.1–2.8[d]		34.19	18.3 (P^1) 18.3 (P^2)	

Table I (Continued)

compd	signal	^{1}H NMR δ	^{1}H NMR J_{PH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
 9	Me_3Si	−0.10		3.37	3.7	31.34 (P^1) 82.69 (P^2) (74.2)[f]
	P^1Me	1.50	13.5 (P^1)	17.87	91.6 (P^1) 4.9 (P^2)	
	P^1CH_2	2.1–2.4[d]		32.85	90.3 (P^1) 25.6 (P^2)	
	Me_2N	2.69	15.5 (P^2)	38.39	15.3 (P^2)	
 10	Me_3Si	−0.05		3.02	2.9	20.97 (P^1) 60.44 (P^2) (14.6)[f]
	PMe	1.43	14.4 (P^1)	20.11	88.9 (P^1)	
	CH_2	3.12	15.6 (P^1) 10.8 (P^2)	36.55	92.8 (P^1) 17.6 (P^2)	
	CO			213.14	18.6 (P^2)	
 11	Me_3Si	0.01		3.29	3.1	21.41 (P^1) 149.74 (P^2) (6.1)[f]
	PMe	1.63	14.2 (P^1)	19.62	88.7 (P^1)	
	PCH_2	[g]		39.92	93.8 (P^1) 27.5 (P^2)	
	NMe_2	2.65	10.7 (P^1) 20.5 (P^2)	38.58	4.6 (P^1) 18.9 (P^2)	
	CO			213.6	20.4	
 12	Me_3Si	−0.20		3.24		8.16 (P^1) 60.71 (P^2) (14.6)[f]
	PCH_2	3.3[d]		36.45	101.5 (P^1) 17.5 (P^2)	
	CO			213.26	18.7 (P^2)	
 13	Me_2Si	−0.16		3.18	3.9	22.97 (P^1) 41.92 (P^2) (17.1)[f]
	Me	0.95	13.8 (P^1)	19.89	87.8 (P^1)	
	PCH_2	2.91	15.0 (P^1) 6.6 (P^2)	35.63	91.8 (P^1) 8.8 (P^2)	
	CO			216.49	13.7 (P^2)	
 14	Me_3Si	0.14		2.93	2.0	11.71 (P^1) 81.64 (P^2) (26.9)[f] 17.21 (P^1) 84.94 (P^2) (22.5)[f]
	CH	3.3–4.5[f]		53.05	96.7 (P^1) 7.8 (P^2)	
	CO			212.69	16.6 (P^2)	
 15	Me_3Si	−0.23		2.83	2.9	17.50 (P^1) 82.98 (P^2) (1.91)[f] 24.97 (P^1) 86.64 (P^2) (28.3)[f]
	P^1CH_2	2.5–3.8[d]		40.87	85.9 (P^1)	
	CH	2.5–3.8[d]		54.42	82.0 (P^1) 8.8 (P^2)	
	CO			212.66	17.6 (P^2)	

[a] Chemical shifts relative to Me_4Si for ^{1}H and ^{13}C spectra and to H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvents: ^{1}H, CH_2Cl_2; ^{13}C and ^{31}P, $CDCl_3$, unless otherwise noted. [b] Benzene solution. [c] J_{HH} values in parentheses. [d] Complex multiplet. [e] Obscured by phenyl signal. [f] J_{PP} values in parentheses. [g] Obscured by Me_2N signal.

1 equiv of *n*-BuLi at −78 °C in ether solution, followed by the addition of Ph_2PCl, compounds **4** and **5** were converted to the novel phosphinomethyl derivatives **6** and **7** (eq 5)

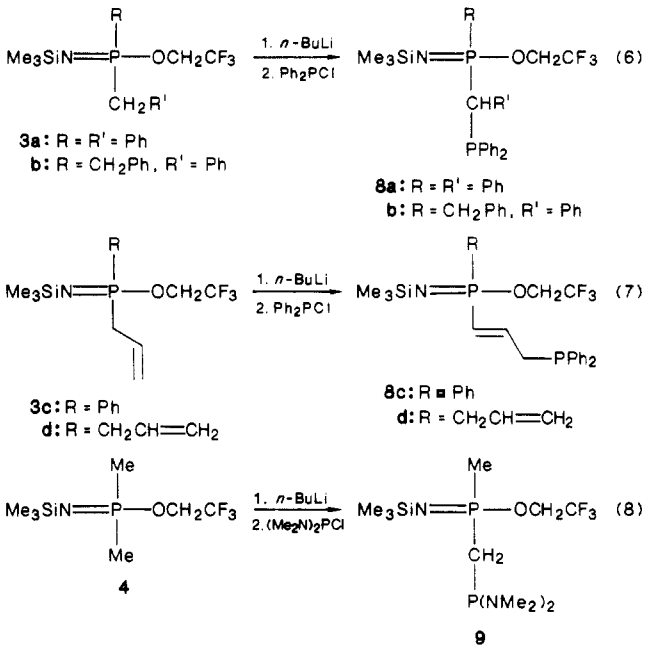


(5)

in 60 and 46% yields, respectively. Thus, in this system, *deprotonation of the P-Me rather than the P-OCH$_2$CF$_3$ substituent is the preferred mode of reactivity*. This observation has significant implications because it makes possible the synthesis of an extremely broad spectrum of functionalized precursors to new poly(alkyl/arylphosphazenes).

In order to complete the series of Ph_2P-substituted phosphoranimines, the trifluoroethoxy compounds **3a–d** were also allowed to react with *n*-BuLi and Ph_2PCl (eq 6 and 7). The phosphinomethyl derivatives **8a–d** were thus obtained in ca. 70–80% yields. By means of a similar procedure, the bis(dimethylamino)phosphine derivative **9** was prepared from the dimethylphosphoranimine **4** (eq 8).

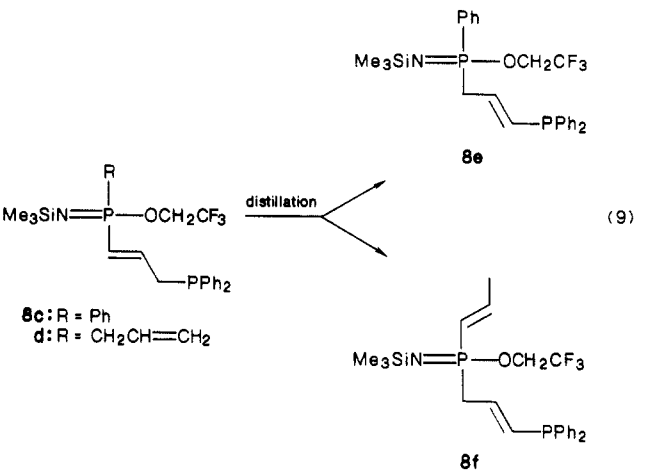
The syntheses of these phosphine derivatives **6–9** were generally routine, but a few special comments should be made. First, although many of them are extremely high boiling liquids (ca. 130–200 °C (0.05 mm), sometimes with wide bp ranges, they all are remarkably stable to distillation and afford satisfactory elemental analyses (Table II).



Second, the NMR spectral data (Table I) provide confirmation of the proposed structures. For example, the ^{31}P NMR spectrum of **6** consists of a doublet at −26.3 ppm, attributed to the Ph_2P– phosphorus and another doublet at 30.3 ppm for the central P(V) phosphorus (J_{pp} = 55.5 Hz). Surprisingly, the Ph_2P– phosphorus does not show a two-bond coupling to the CH_2 protons, although a four-bond coupling (1.2 Hz) to the CH_3 protons is observed in the ^1H NMR spectrum of **6**. Moreover, the central CH_2 group appears as a doublet of doublets in the ^{13}C NMR spectrum with one large (93.4 Hz) and one small (30.5 Hz) coupling to the P(V) and P(III) centers, respectively. Many of these spectral features are consistently found throughout the series of compounds **6–9**.

Third, as might have been expected, the benzyl-substituted derivatives **8a,b** were obtained as mixtures of diastereomers due to the presence of chiral centers at both the P(V) phosphorus and the adjacent $CH(Ph)PPh_2$ carbon. This is confirmed by the presence of two pairs of doublets in the ^{31}P NMR spectra (Figure 1a) of these compounds.

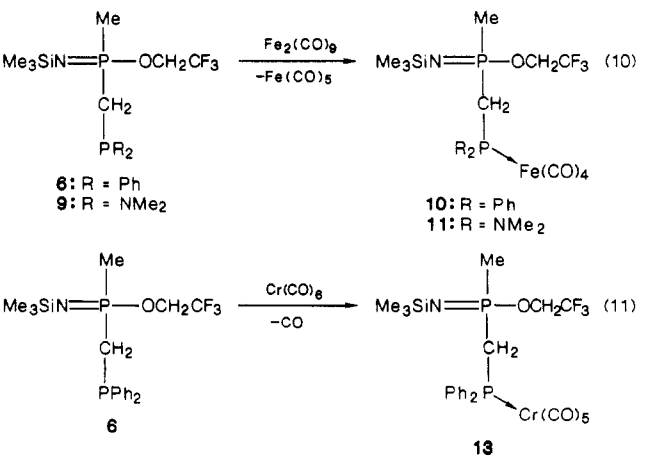
Fourth, the ambident anions generated from the allyl-substituted phosphoranimines **3c,d** react with Ph_2PCl to form derivatives **8c,d** in which the Ph_2P group is attached to the terminal carbon of the allylic side chain. This is inferred mainly from the observation of much smaller four-bond coupling constants (ca. 5 Hz) between the phosphorus nuclei. No indication of the formation of the isomeric P(V)–C–P(III) compounds, with their predictably larger two-bond P–P couplings, was obtained. There was, however, clear evidence of partial rearrangement of the C=C double bonds (eq 9) when these products were distilled. These rearrangements become quite evident when the ^{31}P and ^{13}C NMR spectra of the crude and the distilled products are compared. The distilled products, while yielding satisfactory elemental analyses, each exhibit a second pair of doublets in the ^{31}P NMR spectra which are attributed to the isomers **8e** and **8f**, respectively. Furthermore, while the Ph_2PCH_2 allylic carbon in **8c** shows almost equal couplings to both the P(III) and P(V) phosphorus centers, the P^VCH_2 allylic carbon in **8e** shows a characteristically large (ca. 90 Hz) one-bond coupling to P(V) and a small (ca. 11 Hz) three-bond coupling to P(III). A similar rearrangement for the diallyl derivative **8d,f** is observed. The fact that a doublet (at 19.9 ppm, J_{pc} = 20.8 Hz) for a terminal CH_3 group appears in the ^{13}C NMR spectrum of the distilled product indicates that both C=C double bonds have shifted in this case.



Unlike the rearrangement of their allylic precursors **3c** and **3d**, the double bond shifts in these PPh_2 derivatives are probably not acid catalyzed. Instead, we speculate that traces of LiCl or perhaps *n*-BuLi might be responsible for the partial isomerization which occurred at the very high distillation temperatures.

Metal Carbonyl Complexes. In order to assess the potential of these phosphine-functionalized phosphazene precursors as ligands for transition metals, we have carried out a preliminary study of the reactivity of compounds **6–9** with $Fe_2(CO)_9$ and, in one case, with $Cr(CO)_6$. In addition to being interesting ligands themselves, these "monomers" can serve as models for poly(alkyl/arylphosphazenes) bearing pendant phosphine substituents. The iron and chromium carbonyls were chosen because of their availability and because their structural simplicity should facilitate the characterization of these model complexes by NMR spectroscopy.

When the phosphine derivatives **6** and **9** of the dimethyl precursor **4** were treated with 1 equiv of $Fe_2(CO)_9$ in either hexane or benzene solution at room temperature (eq 10), the corresponding $Fe(CO)_4$ complexes **10** and **11** were formed quantitatively. The *P*-phenyl analogue **7** reacted in a similar fashion to afford the $Fe(CO)_4$ derivative **12**. Also, the chromium pentacarbonyl complex **13** was prepared by the reaction (eq 11) of **6** and $Cr(CO)_6$ in refluxing diglyme.



Upon removal of solvents and unreacted metal carbonyls, these complexes were isolated as orange/brown (**10–12**) or red/brown (**13**) oils that resisted all attempts at crystallization from a variety of solvents. Attempted

Table II. Preparative and Analytical Data

compd	yield, %	bp, °C (*p*, mmHg)	anal.[a] C	H
3a	70	92–112 (0.05)	56.27 (56.09)	6.25 (6.02)
3b	57	102–104 (0.04)	57.40 (57.13)	6.32 (6.31)
3c	75	56–60 (0.05)	49.57 (50.14)	6.23 (6.31)
3d	50	52–55 (1.3)	43.94 (44.14)	7.36 (7.07)
6	60	100–130 (0.05)	52.58 (52.89)	6.24 (6.07)
7	46	164–178 (0.4)	59.58 (58.41)	6.03 (5.72)
8a	80	175–185 (0.05)	63.33 (63.26)	5.48 (5.66)
8b	79	175–195 (0.05)	64.09 (63.80)	5.88 (5.87)
8c	71	158–172 (0.05)	60.26 (60.11)	5.83 (5.82)
8d	73	134–147 (0.02)	57.30 (57.13)	6.42 (6.25)
9	64	89–95 (0.6)	35.73 (36.16)	7.92 (7.72)
10	*b*		44.84 (46.09)	4.23 (4.37)
11	*b*		34.11 (33.78)	5.49 (5.29)

[a] Calculated values in parentheses. [b] Ca. 100% yield of unpurified product.

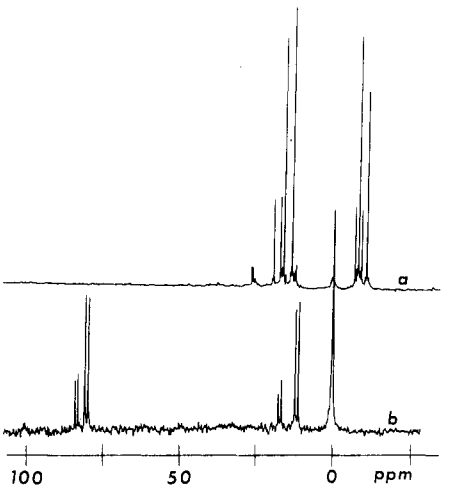
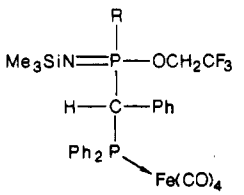


Figure 1. Phosphorus-31 NMR spectra: (a) ligand **8a**; (b) $Fe(CO)_4$ complex **14**.

purification of **10** by distillation led to decomposition of the complex, with a small amount of the free ligand **6** being the only distillable product. Nevertheless, the "crude" complexes were readily characterized by NMR spectroscopy (Table I) and, in the case of **10** and **11**, by reasonably good elemental analyses.

The reactions of the benzyl- and allyl-substituted analogues **8a–d** with $Fe_2(CO)_9$ were also studied. With the diastereomeric phenyl/benzyl (**8a**) and dibenzyl (**8b**) ligands, the expected diastereomeric $Fe(CO)_4$ complexes **14** and **15** were obtained. These derivatives also could not



14: R = Ph
15: R = CH_2Ph

be crystallized, but their structures are readily assigned on the basis of NMR spectral data (Table I). The phenyl/allyl (**8c**) and diallyl (**8d**) ligands, on the other hand, provided mixtures of what are suspected to be isomeric $Fe(CO)_4$ complexes (derived from **8c/8e** and **8d/8f**, respectively) even when the crude unrearranged ligands were used.

All of the metal complexes prepared in this study showed the characteristic downfield shift (ca. 50–90 ppm) of the ^{31}P NMR signal of the phosphine ($-PR_2$) ligand upon coordination to the metal center.[15] The ^{31}P NMR spectra of the free ligand and the metal complex are well-illustrated by those of the phenyl/benzyl compounds **8a** and **14**, shown in Figure 1. In this case, the diastereomeric nature of both the ligand and the complex are readily apparent. The ^{13}C NMR spectra of the metal complexes **10–15** are generally quite similar to those of the uncomplexed ligands except for the appearance of a doublet in the carbonyl region (ca. 212–216 ppm). These data clearly confirm coordination of the metal carbonyl moiety to the pendant phosphine site with no significant interference with the $Me_3SiN{=}P{-}OCH_2CF_3$ backbone of the molecule.

Conclusion. This study has resulted in three major findings. First, the range of new precursors to poly(alkyl/arylphosphazenes) has been broadened to include benzyl- and, more importantly for future studies, *allyl-substituted* phosphoranimines. Second, the facile deprotonation/substitution reactions of the *N*-silyl-*P*-(trifluoroethoxy)phosphoranimines, shown here leading to the phosphine-functionalized derivatives, promises to extend even further the synthetic potential of the condensation route to poly(phosphazenes). Third, the preparation of several metal carbonyl complexes of these "monomer" ligands indicates that similar coordination chemistry should be possible on the preformed poly(alkyl/arylphosphazenes). Investigations of the scope of this type of derivative chemistry and its application to the polymeric analogues are currently in progress in our laboratories.

Experimental Section

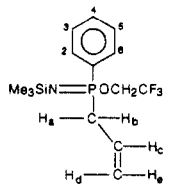
Materials and General Procedures. The following reagents were obtained from commercial sources and used without further purification: bromine, CF_3CH_2OH, *n*-BuLi (hexane solution), PCl_3, Ph_2PCl, Me_3SiNMe_2, $Cr(CO)_6$, and $Fe_2(CO)_9$. Ether, hexane, benzene, diglyme, and Et_3N were distilled from CaH_2 and stored over molecular sieves prior to use. The (silylamino)phosphines[8] **1a–d** and the *N*-silyl-*P*-(trifluoroethoxy)phosphoranimines[3a,b] **4** and **5** were prepared according to the published procedures. The chlorophosphine $(Me_2N)_2PCl$ was prepared in ca. 90% yield by treating PCl_3 with 2 equiv of Me_3SiNMe_2 in ether solution at 0 °C and was characterized by NMR spectroscopy. Proton NMR spectra were recorded on a Varian EM-390 spectrometer; ^{13}C and ^{31}P NMR spectra, with ^1H decoupling, were obtained in the FT mode on a JEOL FX-60 instrument. Some high-field ^1H and ^{13}C NMR spectra (e.g., Table III), including the two-dimensional spectra (see text), were recorded on a Varian XL-300 spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. The following procedures are typical of those used for the preparation of the new compounds in this study. All reactions and other manupulations were carried out under an atmosphere of dry nitrogen or under vacuum.

Preparation of $Me_3SiN{=}P(Br)(CH_2Ph)Ph$ (2a). A 500-mL, 2-necked flask, equipped with a N_2 inlet, magnetic stirrer, and an addition funnel, was charged with the phosphine **1a** (typically 0.15–0.25 mol) and benzene (100–150 mL). The solution was cooled to 0 °C, and an equimolar amount of bromine in benzene (100–150 mL) was added dropwise to the stirred reaction mixture. After the mixture was allowed to warm to room temperature and was stirred for 1 h, the solvent and Me_3SiBr were removed under reduced pressure. The liquid product was characterized by NMR spectroscopy (Table II), showing it to be free of Me_3SiBr, and then used without further purification to prepare **3a**. Compounds **2b–d** were prepared in a similar fashion.

Preparation of $Me_3SiN{=}P(OCH_2CF_3)(CH_2Ph)Ph$ (3a). A 2-L, 3-necked flask, equipped with a N_2 inlet, an addition funnel, and a mechanical stirrer, was charged with the *P*-bromophosphoranimine **2a** (typically, 0.20 mol), benzene (350 mL), and Et_3N (0.20 mol). The solution was cooled to 0 °C, and CF_3CH_2OH (0.20 mol) was added slowly from the addition funnel to the stirred

(15) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

Table III. Complete NMR Spectroscopic Data[a,b] for Phosphoranimine 3c

	signal	^{1}H NMR δ	^{1}H NMR J_{PH}	^{1}H NMR J_{HH}	^{13}C NMR δ	^{13}C NMR J_{PC}
 3c	Me_3Si	0.08			3.76	2.9
	$PCH_{a,b}$	2.80	18.4	7.6 (H_a/H_c) 1.4 ($H_a/H_{d,e}$)	38.76	92.4
	OCH_2	4.00 4.35	8.8 8.8	12.0 (8.8)[c] 12.0 (8.8)[c]	60.35	5.6 (37.8)[d]
	$=CH_c$	5.70	6.0	16.6 (H_c/H_d) 10.3 (H_c/H_e) 7.6 (H_c/H_a)	128.13	9.3
	$=CH_2$: H_d	5.02	5.3	17.0 (H_d/H_c) 1.4 ($H_d/H_{a,e}$)	120.08	12.4
	H_e	5.11	4.2	10.3 (H_e/H_c) 1.4 ($H_e/H_{a,d}$)		
	Ph: H_{3-5}	7.5 (m)			C_1 132.36	128.5
	$H_{2,6}$	7.8 (m)			$C_{2,6}$ 131.86	9.9
					C_4 131.83	1.8
					$C_{3,5}$ 128.48	12.8
	CF_3				123.83	9.6 (277.8)[d]

[a] See footnote *a*, Table I. [b] ^{31}P NMR: δ 19.38. [c] J_{FH} values in parentheses. [d] J_{FC} values in parentheses.

reaction mixture. After the mixture was stirred for ca. 4 h at room temperature, hexane (200 mL) was added and the solids were allowed to settle. The mixture was filtered under N_2, and the solids were washed with several 50-mL portions of hexane. Solvent removal followed by distillation through a 10-cm column afforded **3a** as a colorless liquid. Compounds **3b** and **3c** were prepared by a similar procedure.

Preparation of $Me_3SiN{=}P(OCH_2CF_3)(CH_2CH{=}CH_2)_2$ (3d). In a 500-mL, 3-necked flask, equipped with a N_2 inlet, a magnetic stirrer, and an addition funnel, $LiOCH_2CF_3$ was prepared by the slow addition of *n*-BuLi (0.20 mol, 2.6 M in hexane) to CF_3CH_2OH (0.20 mol, 16.3 mL) in ether (250 mL) at 0 °C. After being stirred for ca. 30 min at room temperature, the solution was transferred slowly via a double-ended needle to a 1-L flask containing a magnetically stirred solution of the *P*-bromophosphoranimine **2d** (0.20 mol) in ether (150 mL) at 0 °C. The reaction mixture was stirred at room temperature overnight, hexane (100 mL) was added, and the mixture was filtered. The solids were washed with hexane, and the solvents were removed under reduced pressure. Distillation through a 10-cm column afforded **3d** as a colorless liquid.

Preparation of $Me_3SiN{=}P(OCH_2CF_3)(Ph)CH(Ph)PPh_2$ (8a). A 250-mL, 3-necked flask, equipped with a N_2 inlet, a magnetic stirrer, and a septum, was charged with the *N*-silyl-*P*-(trifluoroethoxy)phosphoranimine **3a** (typically, 25 mmol) and ether (60 mL). The solution was cooled to −78 °C, and an equimolar quantity of *n*-BuLi was added via syringe. After the mixture was stirred for ca. 30 min, Ph_2PCl (25 mmol) was added and the mixture was allowed to warm to room temperature and was stirred overnight. After the addition of hexane (ca. 50 mL), the mixture was filtered and the solids were washed with hexane. Following solvent removal, distillation through a short-path apparatus gave **8a** as a viscous, pale yellow liquid. The other diphenylphosphine derivatives **6**, **7**, and **8b–d** were prepared from the appropriate precursors by similar procedures. In the preparation of **9**, $(Me_2N)_2PCl$ was used in place of Ph_2PCl; otherwise the procedure was unchanged.

Preparation of $[Me_3SiN{=}P(OCH_2CF_3)(Me)CH_2PPh_2]Fe(CO)_4$ (10). A 50-mL flask, equipped with a N_2 inlet and a magnetic stirrer, was charged with the ligand **6** (2.16 g, 5.00 mmol), $Fe_2(CO)_9$ (1.84 g, 5.05 mmol), and hexane (20 mL). The mixture was stirred overnight at room temperature and then filtered under N_2. Hexane and $Fe(CO)_5$ were removed from the filtrate under reduced pressure and moderate heat (ca. 50 °C). The remaining orange/brown oil was identified as **10** by NMR spectroscopy and elemental analysis (Tables I and II). The other $Fe(CO)_4$ complexes **11**, **12**, **14**, and **15** were prepared by similar procedures.

Preparation of $[Me_3SiN{=}P(OCH_2CF_3)(Me)CH_2PPh_2]Cr(CO)_5$ (13). A 50-mL flask, equipped with a N_2 inlet, a reflux condenser, and a magnetic stirrer, was charged with the ligand **6** (1.72 g, 4.00 mmol), $Cr(CO)_6$ (1.76 g, 8.00 mmol), and diglyme (15 mL). The mixture was heated at reflux for 2 h, during which time some $Cr(CO)_6$ that accumulated in the condenser was washed down with ca. 5 mL of diglyme. After being cooled to room temperature, the flask was placed in a −78 °C bath in order to precipitate the excess $Cr(CO)_6$. The mixture was filtered while cold, and the solid was washed with cold diglyme (20 mL) in two portions. The solvent and a small amount of residual $Cr(CO)_6$ were removed under high vacuum. The remaining red/brown oil was identified as **13** by NMR spectroscopy (Table I).

Acknowledgment. We thank the U. S. Army Research Office and the Robert A. Welch Foundation for generous financial support of this research.