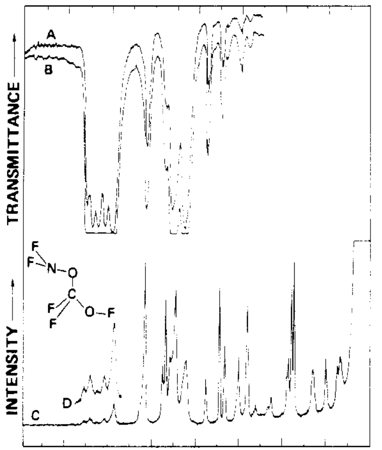
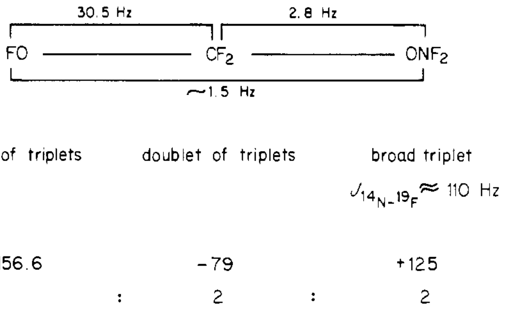


Figure 3. Vibrational spectra of $CF_2(OF)ONF_2$: traces A and B, infrared spectra of the gas recorded in a 5-cm path length cell with AgCl windows at pressures of 42 and 15 torr, respectively; traces C and D, Raman spectra of liquid $CF_2(OF)ONF_2$ at −100 °C recorded at two different sensitivities.

cal mol^{-1}. The Trouton constant (20.3) and the molecular weight of the gas M_r found 153, calcd 153) indicate little or no association in both the liquid and the gas phases.

The structure of the compound was established by vibrational (see Figure 3, Table VI) and ^{19}F NMR spectroscopy:



The compound is stable at ambient temperature and liberates iodine from KI solution.

Conclusion. Complexing of HNF_2 with alkali-metal fluoride has successfully been used to moderate the otherwise explosive reaction of HNF_2 with hypofluorites. The general applicability of this method for the syntheses of *N*,*N*-difluoro-*O*-perfluoroalkylhydroxylamines has been demonstrated, and $CF_2(ONF_2)_2$, the first known example of a geminal-disubstituted $-ONF_2$ compound, has been prepared by this method.

Acknowledgment. The authors are grateful to Dr. C. J. Schack for helpful discussions and to the Air Force Rocket Propulsion Laboratory, the Office of Naval Research, and the Army Research Office for financial support of this work.

Registry No. CF_3OF, 373-91-1; $(CF_3)_2CFOF$, 3848-93-9; $CF_2(OF)_2$, 16282-67-0; $CF_2(OF)ONF_2$, 36781-60-9; HNF_2, 10405-27-3; CF_3ONF_2, 4217-93-0; $(CF_3)_2CFONF_2$, 84194-25-2; $CF_2(ONF_2)_2$, 36781-59-6; KF, 7789-23-3.

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Synthesis of (Silylamino)phosphines with P–H Bonds[1]

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The reactions of several [bis(trimethylsilyl)amino]chlorophosphines, $(Me_3Si)_2NP(R)Cl$, with *i*-PrMgCl generally yield mixtures of the isopropyl substitution products $(Me_3Si)_2NP(R)(i\text{-}Pr)$ and the unexpected reduction products $(Me_3Si)_2NP(R)H$ (R = *i*-Pr, *t*-Bu, CH_2SiMe_3, $N(SiMe_3)_2$, and Ph). The P–H phosphines appear to be formed by a process in which *i*-PrMgCl acts as a reducing agent with elimination of propylene. The reaction is catalyzed by magnesium salts, and the relative yield of reduced product increases with the steric bulk of the phosphorus substituents. In a more direct synthesis, these P–H substituted phosphines are prepared by the reduction of the chlorophosphines with $LiAlH_4$ in ether. Proton, ^{13}C, and ^{31}P NMR data are reported for both series of new phosphines.

Introduction

Silicon–nitrogen–phosphorus compounds, especially the (silylamino)phosphines such as $(Me_3Si)_2NPMe_2$, are becoming increasingly important as synthetic reagents. Areas of active investigation include their use as precursors to new classes of phosphazene polymers[2,3] as well as novel organic[4–6] and organometallic[7–10] phosphorus compounds. Many of the most useful (silylamino)phosphines are prepared from commercially available reagents by a simple "one-pot" synthesis (eq 1) first utilized by Wilburn.[11,12] The complete preparative details of this process have recently been reported.[13]

$$(Me_3Si)_2NH \xrightarrow[(2)\ PCl_3]{(1)\ n\text{-}BuLi} \{(Me_3Si)_2NPCl_2\} \xrightarrow{2RMgX} (Me_3Si)_2NPR_2 \quad (1)$$

In attempting to further generalize this useful synthetic method, however, we find that reduced (P–H) or coupled (P–P) products are sometimes obtained. We report here the isolation and characterization of several new (silylamino)phosphines containing P–H bonds from such reactions. An independent, high-yield synthesis of the same series of compounds is also described.

Results and Discussion

Initially, we were interested in using the Wilburn method (eq 1) to prepare (silylamino)phosphines containing bulky alkyl

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(1) Presented in part at the International Conference on Phosphorus Chemistry, Durham, NC, June 1981, Abstr. 177, and at the 183rd National Meeting of the American Chemical Society, Las Vegas, NV, March 1982, INOR 146.

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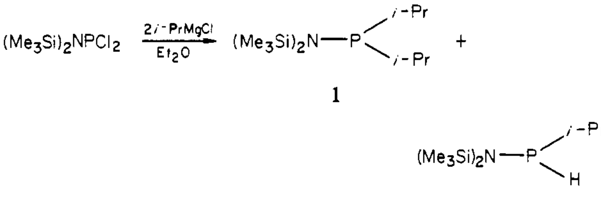
groups on phosphorus. Typically, in this procedure, the unstable dichlorophosphine $(Me_3Si)_2NPCl_2$ is not isolated; rather, the Grignard reagent is simply added directly to the reaction mixture containing $(Me_3Si)_2NPCl_2$. The use of $PhPCl_2$ in place of PCl_3 affords $(Me_3Si)_2NP(Ph)Cl$ as a similarly reactive intermediate species. These chlorophosphines usually react smoothly with Grignard reagents RMgX (R = Me, Et, CH_2SiMe_3, CH_2Ph) to form the corresponding alkylphosphines in high yields.[12,13]

Considerably different results are obtained, however, when *i*-PrMgCl is used. For example, when a solution of the dichlorophosphine is treated with 2 equiv of *i*-PrMgCl in Et_2O at 0 °C (eq 2), the desired diisopropylphosphine **1** is produced



1

(2)

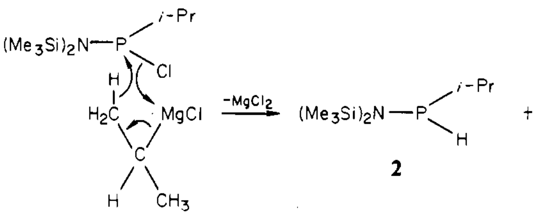
2

but only in low yield (18–27%). Invariably, distillation of the product mixture also affords a more volatile fraction (25–42%), subsequently identified as [bis(trimethylsilyl)amino]isopropylphosphine (**2**).

These compounds are both colorless liquids, which were separated by fractional distillation and fully characterized by NMR (^1H, ^{13}C, and ^{31}P) spectroscopy and elemental analysis (Tables I and II). For compound **2**, the large $^1J_{PH}$ value of 206 Hz is especially indicative of the P–H bond as is the IR stretching frequency ν_{PH} at 2260 cm^{-1}. The synthesis of **2** and other P–H compounds by an alternative route (see below) provides further support for its structural assignment.

The formation of the P–H phosphine **2** is significant for at least two reasons. First, aminophosphines bearing P–H bonds are relatively rare compounds, being thermally unstable in most cases. Until recently, the only such (*silyl*amino)phosphine was $(Me_3Si)_2N–P(H)–N(H)SiMe_3$ reported by Niecke.[14] While our work was in progress, Niecke also published the synthesis of a few other examples including two cyclic compounds[15] and the primary aminophosphine $(Me_3Si)_2NPH_2$.[16] These results, together with those reported here, clearly show that a wide variety of P–H functionalized phosphines can be prepared when the stabilizing bis(trimethylsilyl)amino group is present.

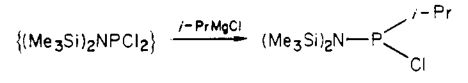
A second point of interest concerns the possible mode of formation of phosphine **2**. Although no detailed mechanistic studies have been attempted, the data obtained thus far are consistent with a process (eq 3, for example) in which the second equivalent of *i*-PrMgCl acts as a reducing agent.



2

$CH_2{=}CHCH_3$ (3)

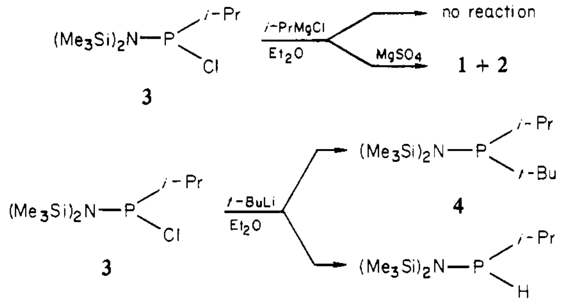
In this context, the important observations are the following. (1) Propylene can be trapped at −78 °C and identified by ^1H NMR as a byproduct of the reaction. This result and the fact that the entire reaction and product workup are done under completely anhydrous conditions eliminate the possibility of the P–H bond resulting from hydrolysis. (2) When just 1 equiv of *i*-PrMgCl is used (eq 4) the monoalkylated chlorophosphine



(4)

3

3 is isolated in good yield as a stable, distillable liquid. The reduction step, therefore, must occur during the reaction with the second equivalent of *i*-PrMgCl. (3) The reaction is catalyzed by magnesium salts; the type of product isolated sometimes depends on whether or not the $MgCl_2$ byproduct is present. The reactions shown in eq 5 and 6 are illustrative



(5a)

(5b)

3

(6a)

4

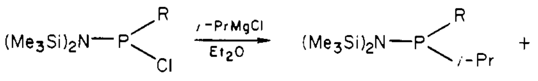
3

(6b)

2

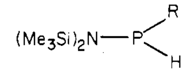
of this point. When the purified chlorophosphine is treated with *i*-PrMgCl in Et_2O, no reaction takes place during 2h at room temperature (eq 5a). Addition of a catalytic amount of anhydrous $MgSO_4$ to the mixture, however, causes a rapid exothermic reaction (eq 5b) leading to a mixture of the substitution (**1**) and reduction (**2**) products. The course of the reaction of **3** with *t*-BuLi also depends on the conditions employed. With prepurified **3**, only the *tert*-butyl substitution product **4** is obtained (eq 6a). On the other hand, when the reaction mixture containing unpurified **3** (and the $MgCl_2$ from its formation) is treated with *t*-BuLi, the only product obtained is the reduced P–H phosphine **2** (eq 6b). (4) The successful isolation and characterization of **1**, **4** and other substitution products (see below) as thermally stable compounds demonstrates that P–H bond formation does not result merely from the instability of such sterically congested molecules.

Steric factors, however, do play a role in determining the type of product(s) formed in such reactions of chlorophosphines with *i*-PrMgCl. We find that the reactions (eq 7) with a variety of [bis(trimethylsilyl)amino]chlorophosphines normally yield a mixture of substitution (P–*i*-Pr) and reduction (P–H) products. Separation is readily accomplished by fractional distillation, and the isolated yields of the two products are shown in eq 7.



3, R = *i*-Pr
5, R = *t*-Bu
6, R = CH_2SiMe_3
7, R = $N(SiMe_3)_2$
8, R = Ph

1, R = *i*-Pr (19%)
4, R = *t*-Bu (0)
9, R = CH_2SiMe_3 (11%)
10, R = $N(SiMe_3)_2$ (3%)
11, R = Ph (40%)



(7)

2, R = *i*-Pr (25%)
12, R = *t*-Bu (52%)
13, R = CH_2SiMe_3 (41%)
14, R = $N(SiMe_3)_2$ (63%)
15, R = Ph (0)

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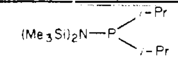
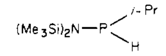
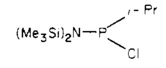
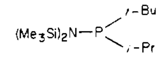
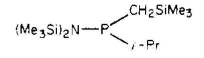
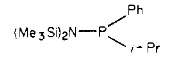
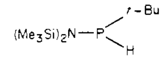
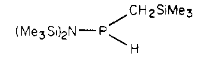
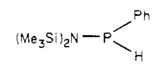
(15) Niecke, E.; Nickleweit-Lüke, A.; Rüger, R. *Phosphorus Sulfur* **1982**, *12*, 213.
(16) Niecke, E.; Rüger, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 62.

Table I. NMR Spectroscopic Data[a]

no.	compd	signal	^{1}H NMR δ	^{1}H NMR J_{PH}	^{1}H NMR J_{HH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
1		$\mathrm{Me_3Si}$[b]	0.20	0.9		4.32	12.7	79.3
			0.20					
		$\mathit{Me}_2\mathrm{CH}$[c]	0.90	2.4	6.6	21.42	14.0	
			1.10	6.9	6.6	20.89	29.9	
		$\mathrm{Me}_2\mathit{CH}$	2.0[d]			28.56	20.5	
2		$\mathrm{Me_3Si}$	0.19	1.0		3.43	5.5	17.6
		$\mathit{Me}_2\mathrm{CH}$[c]	0.90	16.2	7.2	17.08	22.6	
			1.10	14.4	7.2	19.27	22.6	
		$\mathrm{Me}_2\mathit{CH}$	2.00	2.4	7.2	26.60	14.7	
					4.5			
		PH	5.20	206	4.5			
3		$\mathrm{Me_3Si}$	0.30	2.4		4.47	8.6	162.6
		$\mathit{Me}_2\mathrm{CH}$[c]	0.90	16.8	7.2	17.85	23.8	
			1.10	19.8	6.6	18.13	32.3	
		$\mathrm{Me}_2\mathit{CH}$	2.35	2.4	7.2	34.86	37.2	
					6.6			
4		$\mathrm{Me_3Si}$[b]	0.30			6.24		87.2
			0.35	2.4		4.81	13.7	
		$\mathit{Me}_3\mathrm{C}$	1.10	10.8		29.89	15.6	
		$\mathrm{Me}_3\mathit{C}$				31.68	32.2	
		$\mathit{Me}_2\mathrm{CH}$[c]	1.00[d]		6.9	21.64	13.5	
			1.20[d]		6.9	21.02	32.2	
		$\mathrm{Me}_2\mathit{CH}$	2.10[d]		6.9	24.82	23.3	
9		$\mathrm{Me_3SiN}$	0.30	2.4		5.64		59.8
		$\mathrm{Me_3SiC}$	0.15	1.5		0.53	4.9	
		$\mathrm{PCH_2}$	1.2[d]			20.18	44.0	
		$\mathit{Me}_2\mathrm{CH}$[c]	0.90	17.4	6.6	20.54	14.7	
			1.10	14.4	7.2	18.90	27.5	
		$\mathrm{Me}_2\mathit{CH}$	2.0[d]			31.47	19.5	
10	$[(\mathrm{Me_3Si})_2\mathrm{N}]_2\mathrm{P}$-*i*-Pr	$\mathrm{Me_3Si}$	0.20	1.2		6.16	7.9	116.6
		$\mathit{Me}_2\mathrm{CH}$	1.00	17.4	6.6	19.90	29.3	
		$\mathrm{Me}_2\mathit{CH}$	2.30	4.5	6.6	28.94	28.7	
11		$\mathrm{Me_3Si}$	0.15	0.8		4.83	6.7	57.7
		$\mathit{Me}_2\mathrm{CH}$[c]	1.30	13.2	7.2	19.57	8.6	
			1.10	22.2	6.6	21.22	34.8	
		$\mathrm{Me}_2\mathit{CH}$	2.35[d]			26.84	19.5	
		Ph	7.3[d]			129		
12		$\mathrm{Me_3Si}$	0.15	1.2		4.04	4.3	33.4
		$\mathit{Me}_3\mathrm{C}$	0.90	12.5		28.09	15.9	
		$\mathrm{Me}_3\mathit{C}$				30.00	18.9	
		PH	4.70	209				
13		$\mathrm{Me_3SiN}$	0.25	0.5		6.46	5.5	−3.2
		$\mathrm{Me_3SiC}$	0.10	0.7		−0.32	4.9	
		$\mathrm{PCH_2}$	0.90	13.2	13.5	19.80	38.5	
					2.3			
			1.50	13.2	6.0			
					2.3			
		PH	5.31	210	6.0			
					13.5			
14	$[(\mathrm{Me_3Si})_2\mathrm{N}]_2\mathrm{PH}$	$\mathrm{Me_3Si}$	0.30	0.9		4.33	5.5	58.8
		PH	6.61	210				
15		$\mathrm{Me_3Si}$	0.40	1.4		3.15	5.5	9.0
		Ph	7.3[d]			128		
		PH	6.20	215				

[a] Chemical shifts are downfield from $\mathrm{Me_4Si}$ for ^{1}H and ^{13}C spectra and from $\mathrm{H_3PO_4}$ for ^{31}P spectra; coupling constants are in hertz. Solvents: ^{1}H, $\mathrm{CH_2Cl_2}$; ^{13}C and ^{31}P, $\mathrm{CDCl_3}$. [b] Nonequivalent $\mathrm{Me_3Si}$ groups due to hindered P–N bond rotation. [c] Diastereotopic methyl groups observed in ^{1}H and ^{13}C spectra due to phosphorus chirality. [d] Complex multiplet with unresolved coupling constants and/or overlapping signals.

The relative amount of P–H product obtained increases generally with the steric bulk of the phosphorus substituents (i.e., $(\mathrm{Me_3Si})_2\mathrm{N} \approx$ *t*-Bu > $\mathrm{CH_2SiMe_3}$ > *i*-Pr > Ph). Thus, the most sterically hindered chlorophosphines **5** and **7** give the best yields of the P–H products **12** and **14**,[17] respectively. The phenyl derivative **8**, however, yields only the *i*-Pr substitution product **11**. An alternate synthesis of these P–H phosphines including the phenylphosphine **15** is described below. With the exception of **10**, all of these compounds are colorless, air-sensitive liquids that were purified by distillation under reduced pressure and characterized by NMR spectroscopy and elemental analysis (Tables I and II). The [bis(silylamino)]isopropylphosphine **10**, a low-melting solid, was obtained only in low yield and was not of sufficient purity for elemental analysis. Its characterization is therefore based on NMR data.

Some interesting trends in the ^{31}P chemical shifts (Table I) of these compounds are noted. For example, the P–H phosphines have shifts that are usually 50–60 ppm upfield of those signals for the corresponding isopropylphosphines. Within each of these series, there is a definite movement of ^{31}P shifts to lower field with increasing steric bulk of the R group on phosphorus. In addition, the rather low-field resonance (116.6 ppm) found for compound **10** falls well in line with those of other bis(silylamino)phosphines $[(\mathrm{Me_3Si})_2\mathrm{N}]_2\mathrm{PR}$

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(17) The compound $[(\mathrm{Me_3Si})_2\mathrm{N}]_2\mathrm{PH}$ has been independently prepared by A. H. Cowley and co-workers. We thank Professor Cowley for informing us of his work prior to publication.

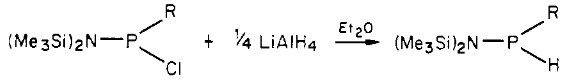
Table II. Preparative and Analytical Data

compd	prep		anal.[a]	
	% yield[b]	bp, °C (mm)	% C	% H
1	19	54–57 (0.25)	51.89 (51.93)	12.13 (11.62)
2	25 (65)	57–60 (0.85)	46.40 (45.90)	11.32 (11.13)
3	87	56–57 (0.45)	40.15 (40.04)	9.00 (9.34)
4	65	65–67 (0.02)	53.53 (53.55)	12.04 (11.75)
9	11	60–61 (0.02)	48.26 (48.54)	11.22 (11.28)
10	3	80–85 (0.05)[c]		
11	40	54–55 (0.13)	58.45 (57.84)	9.91 (9.71)
12	52 (63)	54–55 (0.4)	48.27 (48.14)	11.23 (11.31)
13	41 (37)	57–59 (0.3)	42.83 (42.96)	10.65 (10.82)
14	63 (57)	58–60 (0.02)	41.09 (40.86)	10.93 (10.57)
15	(72)	55–57 (0.04)	53.25 (53.47)	9.16 (8.98)

[a] Calculated values in parentheses. [b] Values in parentheses were obtained from $LiAlH_4$ reduction of chlorophosphines. [c] Solid, mp 30–35 °C; insufficient quantity and purity for elemental analysis.

(R = Me, Et, CH_2SiMe_3), which are described elsewhere.[18]

In order to verify the identification of the P–H substituted (silylamino)phosphines and also to obtain larger quantities for further studies, we were interested in developing a more straightforward method for their preparation. This was readily accomplished by treating the (silylamino)chlorophosphines with lithium aluminum hydride in ether solution (eq 8).


(8)

3, R = *i*-Pr
5, R = *t*-Bu
6, R = CH_2SiMe_3
7, R = $N(SiMe_3)_2$
8, R = Ph

2, R = *i*-Pr
12, R = *t*-Bu
13, R = CH_2SiMe_3
14, R = $N(SiMe_3)_2$
15, R = Ph

Generally, the P–H products are obtained in good yields (Table II) and high purities after a single distillation. Although the reactions occur exothermically at 0 °C, improved yields of the products result if the final mixtures are stirred at room temperature for at least 12 h. In all cases, the NMR spectral data for these products were identical with those observed for the same compounds prepared by the *i*-PrMgCl route. The $LiAlH_4$ method, however, is a much more efficient synthesis of these novel P–H phosphines, whose derivative chemistry is under active investigation in our laboratory.

Experimental Section

Materials and General Procedures. The following reagents were obtained from commercial sources and used without purification: $(Me_3Si)_2NH$, PCl_3, $PhPCl_2$, $MgSO_4$, *n*-BuLi (hexane solution), *t*-BuLi (pentane solution), *i*-PrMgCl (ether solution), and $LiAlH_4$ (ether solution). Ether was distilled from CaH_2 prior to use; other solvents were dried over molecular sieves. Proton NMR spectra were recorded on a Varian EM-390 spectrometer; ^{13}C and ^{31}P NMR, both with ^1H decoupling, were obtained in the FT mode on a JEOL FX-60 instrument. For the P–H compounds, ^{31}P spectra were also recorded without ^1H decoupling so that the $^1J_{PH}$ values could be measured. Infrared spectra were obtained on a Beckman 4250 spectrophotometer with samples as neat liquids. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. The procedures described herein are typical of those used for the preparation of the new compounds in this study.

Reaction of $(Me_3Si)_2NPCl_2$ with *i*-PrMgCl (1:2 Ratio). The general procedure of Wilburn[12,13] was used to prepare the intermediate species $(Me_3Si)_2NPCl_2$, which was not isolated. In a typical preparation, a 2-L, three-necked flask, equipped with a paddle stirrer, N_2 inlet, and an addition funnel, was charged with Et_2O (500 mL) and $(Me_3Si)_2NH$ (104 mL, 0.50 mol). After the solution was cooled to 0 °C, *n*-BuLi (313 mL, 1.6 M in hexane) was added with stirring. The mixture was warmed to room temperature, stirred for 1 h, and then cooled to −78 °C. Phosphorus trichloride (43.6 mL, 0.50 mol) was added quickly, and the mixture was allowed to warm to room temperature and was stirred for 30 min. The mixture, now containing $(Me_3Si)_2NPCl_2$, was cooled to 0 °C, and *i*-PrMgCl (334 mL of 3.0 M ether solution, 1.0 mol) was added dropwise with rapid stirring. After warming to room temperature, the mixture was stirred for 1 h and then filtered under N_2. Most of the solvent was removed under reduced pressure, and hexane (500 mL) was added to wash the products free of remaining solids. The mixture was filtered again, and solvents were removed under vacuum. Distillation under vacuum (≤1 mm) gave a colorless liquid, which was shown by NMR to be a mixture of the substitution product **1** and the P–H phosphine **2**. Redistillation through a 10-cm column afforded pure samples of both compounds (Table II).

Reaction of $(Me_3Si)_2NPCl_2$ with *i*-PrMgCl (1:1 Ratio). With use of the same procedure, $(Me_3Si)_2NPCl_2$ (0.20 mol) was treated with 1 equiv of *i*-PrMgCl (91 mL, 2.2 M ether solution, 0.20 mol). After filtration and solvent removal as described above, compound **3** (Table II) was isolated as a colorless liquid by vacuum distillation.

Reaction of Chlorophosphine 3 with *i*-PrMgCl. On a 0.036-mol scale, phosphine **3** was treated with 1 equiv of *i*-PrMgCl. After stirring at room temperature for 2 h, a ^1H NMR spectrum indicated that no reaction had taken place. A small amount of anhydrous $MgSO_4$ (ca. 8 mmol) was added to the mixture. An exothermic reaction occurred, and it was necessary to cool the mixture in an ice bath. After 30 min of stirring, workup as described above and fractional distillation gave compounds **1** (27% yield) and **2** (43% yield).

Reaction of Chlorophosphine 3 with *t*-BuLi. (a) With Purified 3. A freshly distilled sample of **3** (7.6 g, 0.028 mol) was dissolved in Et_2O (50 mL) and cooled to 0 °C. *tert*-Butyllithium (13.3 mL, 2.0 M in pentane, 0.028 mol) was added with stirring, and the mixture was then warmed to room temperature. After 1 h of stirring, the mixture was filtered and solvents were removed. Distillation afforded the substitution product **4** as a colorless liquid (Table II).

(b) With Unpurified 3. On a 0.10-mol scale, $(Me_3Si)_2NPCl_2$ was treated with *i*-PrMgCl as described above to give a solution containing **3**. The solid byproducts (LiCl and $MgCl_2$) were not removed. At 0 °C, *t*-BuLi was added with stirring, and the mixture was then warmed to room temperature. After 1 h of stirring, workup as above afforded the P–H phosphine **2** in 52% yield as the only distillable product.

Reactions of Chlorophosphines $(Me_3Si)_2NP(R)Cl$ with *i*-PrMgCl. 5, R = *t*-Bu. A solution of $(Me_3Si)_2NPCl_2$ (ca. 0.50 mol, prepared as described above) was cooled to 0 °C, while *t*-BuLi (467 mL, 2.1 M in pentane, 0.50 mol) was added with stirring. After 1 h of stirring, *i*-PrMgCl (167 mL, 3.0 M in Et_2O, 0.50 mol) was added and the mixture was then warmed to room temperature and stirred for an additional 30 min. When the usual workup procedure was followed, fractional distillation afforded only the P–H phosphine **12** as a colorless liquid (Table II). Essentially the same results were obtained when a freshly distilled sample of **5** (identified by its ^1H NMR spectrum[19]) was treated with *i*-PrMgCl. None of the substitution product **4** could be isolated by either procedure.

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6, R = CH_2SiMe_3. The chlorophosphine **6** was prepared and purified as described earlier.[4] A solution of **6** (0.025 mol) in Et_2O (50 mL) was treated with *i*-PrMgCl (0.025 mol) with stirring at 0 °C. Fractional distillation of the product mixture gave both the isopropylphosphine **9** and the P–H phosphine **13** (Table II).

7, R = $N(SiMe_3)_2$. A solution of the bis(silylamino)chlorophosphine **7**[20] (ca. 0.10 mol) was prepared by the reaction of 2 equiv of $(Me_3Si)_2NLi$ with PCl_3. Addition of *i*-PrMgCl (0.10 mol) at 0 °C, followed by the usual workup procedure, gave the P–H phosphine **14** and the isopropylphosphine **10** as the major and minor products, respectively (Table II).

8, R = Ph. A solution of the chlorophosphine **8** was prepared on a 0.50-mol scale from $(Me_3Si)_2NLi$ and $PhPCl_2$, with use of the procedure described above for the preparation of $(Me_3Si)_2NPCl_2$. Reaction with *i*-PrMgCl (0.50 mol) in the usual manner gave only the isopropylphosphine **11** (Table II).

Reactions of Chlorophosphines $(Me_3Si)_2NP(R)Cl$ with $LiAlH_4$. Generally, the chlorophosphine **3** and **5–8** were prepared as described above and, in the same reaction flask, were treated with an ether solution of $LiAlH_4$ at 0 °C. For example, a solution of unpurified **3** (prepared on a 0.10-mol scale from $(Me_3Si)_2NPCl_2$ and *i*-PrMgCl) was stirred at 0 °C and $LiAlH_4$ (25 mL, 1.0 M in ether, 0.025 mol) was added dropwise. The mixture was then warmed to room temperature and stirred overnight. After filtration and solvent removal, distillation afforded the P–H phosphine **2** in good yield (Table II).

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Registry No. **1**, 73270-07-2; **2**, 81072-83-5; **3**, 81072-82-4; **4**, 78614-55-8; **5**, 70009-04-0; **6**, 76946-89-9; **7**, 53327-45-0; **8**, 84174-75-4; **9**, 81072-87-9; **10**, 81072-88-0; **11**, 84174-76-5; **12**, 81072-84-6; **13**, 81072-85-7; **14**, 81072-86-8; **15**, 84174-77-6; *i*-PrCl, 75-29-6; $(Me_3Si)_2NPCl_2$, 54036-90-7; *t*-BuLi, 594-19-4.

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$Ti_2W_{10}PO_{40}^{7-}$ and $[CpFe(CO)_2Sn]_2W_{10}PO_{38}^{5-}$. Preparation, Properties, and Structure Determination by Tungsten-183 NMR

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Single isomers of $Ti_2W_{10}PO_{40}^{7-}$ and $[CpFe(CO)_2Sn]_2W_{10}PO_{38}^{5-}$ have been prepared and their structures determined by ^{183}W NMR. $Ti_2W_{10}PO_{40}^{7-}$ forms isolable complexes with divalent manganese, iron, cobalt, nickel, copper, and zinc.

Introduction

Keggin-structure heteropolyanions containing more than one peripheral heteroatom have generally been restricted to those containing molybdenum and tungsten, vanadium and tungsten, or vanadium and molybdenum as the peripheral atoms. Although such heteropolyanions can exist as more than one isomer, depending on the positioning of the peripheral heteroatoms,[1] few determinations of isomer composition have been made. Among the Keggin anions containing two peripheral heteroatoms, $V_2Mo_{10}PO_{40}^{5-}$ and $V_2W_{10}PO_{40}^{5-}$ have been shown to contain all five possible isomers,[2] and we recently described preparations of $(CH_3Sn)_2W_{10}PO_{38}^{5-}$ and $(C_6H_5Sn)_2W_{10}PO_{38}^{5-}$, which lead to mixtures containing at least four of the possible five isomers.[3] No structural characterization or isolation of a single isomer of a disubstituted Keggin anion has been reported.

We are interested in di- or polysubstituted Keggin anions, particularly those containing peripheral heteroatoms with an oxidation state less than 6, because such anions should have more surface negative charge than normal Keggin anions and exhibit enhanced basicity.

Increasing negative charge on a Keggin anion results in increased resistance to nucleophilic degradation. We therefore explored the preparation of tungstophosphates from tungstate, phosphate, and potential substitutent precursors in basic solution, rather than the acid media normally used to prepare heteropolyanions. Only those with substantial negative charge, i.e. di- or polysubstituted, should be stable and therefore able to form under such conditions.

Results and Discussion

Preparations. Reactions of $TiCl_4$ and $CpFe(CO)_2SnCl_3$ with aqueous solutions of sodium tungstate and sodium dihydrogen phosphate at pH 8–8.6 form $Ti_2W_{10}PO_{40}^{7-}$ and $[CpFe(CO)_2Sn]_2W_{10}PO_{38}^{5-}$, respectively. The reactions are pH dependent; in acidic solution $CpFe(CO)_2SnCl_3$ reacts with sodium tungstate and sodium dihydrogen phosphate to form $CpFe(CO)_2SnW_{11}PO_{39}^{4-}$, prepared earlier from $W_{11}PO_{39}^{7-}$ and $CpFe(CO)_2SnCl_3$.[4]

The ready availability of titanium tetrachloride and the simplicity of the reaction makes $Ti_2W_{10}PO_{40}^{7-}$ particularly easy to prepare. Over 100 g can be made at a time in a simple apparatus.

Characterization. ^{31}P NMR shows that, barring coincident chemical shifts, both $[CpFe(CO)_2Sn]_2W_{10}PO_{38}^{5-}$ and $Ti_2W_{10}PO_{40}^{7-}$ consist of essentially one isomer. ^{183}W NMR studies, detailed below, confirm this and further reveal that the isomers are isostructural with 1,4-substitution of the Keggin structure[1b] (Figure 1).

The ^{31}P NMR spectrum of $[(CH_3)_3NH]_5[CpFe(CO)_2Sn]_2W_{10}PO_{38}$ in aqueous dimethyl sulfoxide exhibits a single sharp resonance, at −9.58 ppm. The corresponding spectrum of one sample of $Li_5[CpFe(CO)_2Sn]_2W_{10}PO_{38}$ in water had, in addition to a major resonance at −9.67 ppm, several quite minor lines between −9.0 and −11.7 ppm, which may have represented other isomers. Similarly, the ^{31}P NMR spectrum of $Li_7Ti_2W_{10}PO_{40}$ (Figure 2) reveals that one isomer (δ −11.43) predominates but that small amounts of other isomers may be present, evidenced by the three smaller resonances at −10.96, −12.02, and −12.42 ppm. Attempted sep-

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