

Addition and Complexation Reactions of a Silylated Aminomethylenephosphine^{1,2}

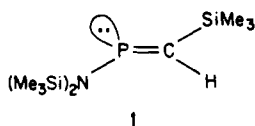
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Several new reactions, including a variety of 1,2-additions and complexation to $\text{Fe}(\text{CO})_4$, of the trisilylated aminomethylenephosphine $(\text{Me}_3\text{Si})_2\text{NP}=\text{CHSiMe}_3$ (**1**) are reported. The bromination of **1** appears to proceed via the intermediate addition product $(\text{Me}_3\text{Si})_2\text{NP}(\text{Br})\text{C}(\text{Br})\text{HSiMe}_3$ (**2a**), with further reaction affording the tribromophosphoranimine $\text{Me}_3\text{SiN}=\text{P}(\text{Br})_3\text{CHSiMe}_3$ (**2**) as the isolated product. The reactive silene $t\text{-BuCH}_2\text{CH}=\text{SiMe}_2$ reacts with **1** via a (2 + 2) cycloaddition reaction to give the 1-phospha-3-silacyclobutane derivative $(\text{Me}_3\text{Si})_2\text{NPCH}(\text{SiMe}_3)\text{SiMe}_2\text{CHCH}_2(\text{CMe}_3)$ (**3**). The addition of Ph_2PCl to the $\text{P}=\text{C}$ double bond of **1** produces the novel bis(phosphino)methane system $(\text{Me}_3\text{Si})_2\text{NP}(\text{Cl})\text{C}(\text{PPh}_2)\text{HSiMe}_3$ (**4**) in nearly quantitative yield. The chlorophosphine **4** is readily converted to the $\text{P}-\text{H}$ (**5**) and $\text{P}-\text{Me}$ (**6**) analogues by reactions with LiAlH_4 and MeMgBr , respectively. The sp^2 -hybridized phosphine center in **1** shows little nucleophilic character, being unreactive toward common organic electrophiles such as MeI , MeCHO , and $\text{PhC}(\text{O})\text{Cl}$. Compound **1** reacts with $t\text{-BuI}$ to form isobutylene and the iodophosphine $(\text{Me}_3\text{Si})_2\text{NP}(\text{I})\text{CH}_2\text{SiMe}_3$ (**7**) which, upon reaction with MeLi , yields the $\text{P}-\text{Me}$ derivative **8**. Treatment of **1** with $\text{Fe}_2(\text{CO})_9$ affords the η^1 complex $\text{LFe}(\text{CO})_4$ (**9**, $\text{L} = \text{1}$), which appears to involve axial coordination of the methylenephosphine ligand. Some significant differences between the chemistry of **1** and that of the isoelectronic iminophosphine $(\text{Me}_3\text{Si})_2\text{NP}=\text{NSiMe}_3$ are noted.

Introduction

The chemistry of phosphorus compounds containing $\text{Si}-\text{N}-\text{P}$ and/or $\text{Si}-\text{C}-\text{P}$ linkages is usually quite different from that of the nonsilylated analogues. On the one hand, the steric bulk and π -acceptor properties of silyl groups can be used to kinetically stabilize a variety of "low-coordinate" phosphorus systems. Alternatively, the $\text{Si}-\text{N}$ or $\text{Si}-\text{C}$ bonds may serve as reactive sites so that processes such as intramolecular silyl group rearrangements and condensation reactions due to silane elimination are commonly found. These points are particularly well illustrated by the synthesis and reactivity of silylated aminomethylenephosphines such as **1**, which have been under investigation in our laboratory.



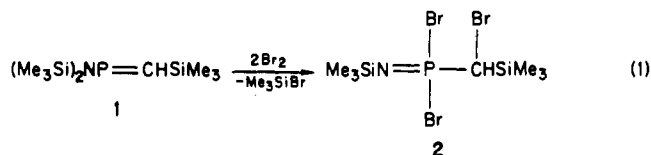
Compound **1**, a stable, distillable liquid, is readily prepared either by dehydrohalogenation³ or thermolysis⁴ of appropriate chlorophosphine precursors. The modes of reactivity of **1** and related compounds are quite varied but can be divided roughly into two general categories. Among the first type are relatively straightforward reactions in which the $\text{Si}_2\text{N}-\text{P}-\text{C}$ linkage remains intact. These include metal complexation via the phosphorus lone pair,¹ oxidation of the phosphorus center to give novel 3-coordinate phosphoranes,³⁻⁵ addition of polar reagents to the $\text{P}=\text{C}$ bond,³ and possible cycloaddition reactions involving the $\text{P}=\text{C}$ bond.^{1,6} Reactions of the second type are more complex processes in which cleavage of the $\text{Si}-\text{N}$ and/or $\text{P}-\text{N}$ bonds is involved. For example, the reaction of **1** with alkylolithium reagents occurs with both nucleophilic substitution and addition leading to trialkylphosphines or $\text{P}-\text{C}-\text{P}$ products depending on the size of the alkyl substituent.⁷

As a continuation of these studies, we report here several reactions of **1** that include some novel additions to the $\text{P}=\text{C}$ bond, metal complexation, and oxidative bromination. We were primarily interested in assessing the potential of compounds such as **1** as synthetic reagents in organophosphorus and organometallic

chemistry. As secondary objective of this study was to more closely compare the reactivity of **1** with its isoelectronic iminophosphine analogue, $(\text{Me}_3\text{Si})_2\text{NP}=\text{NSiMe}_3$,⁸

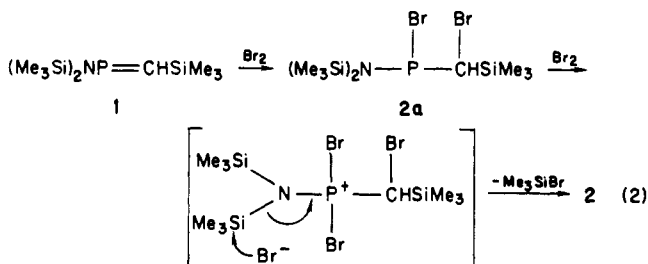
Results and Discussion

Addition Reactions of 1. Although methylenephosphines, in general, undergo a variety of simple 1,2-addition reactions with polar reagents (e.g., HCl , MeOH , etc.),⁹ their behavior toward reactive, nonpolar substances such as halogens has not been reported. We find that compound **1**, in benzene solution at 0°C , rapidly consumes 2 molar equiv of bromine (eq 1). Analysis of



the reaction mixture by ^1H and ^{31}P NMR indicates quantitative formation of Me_3SiBr and the novel tribromophosphoranimine **2**. Following solvent removal, product **2** is isolated in 80% yield by vacuum distillation as a yellow liquid that is characterized by NMR spectroscopy (Table I) and elemental analysis (Table II). Moreover, the mass spectrum of **2** exhibits peak clusters for M^+ and $(\text{M} - \text{CH}_3)^+$, with isotope patterns confirming the presence of three bromine substituents.

The formation of **2** might occur via the intermediacy of the 1,2-addition product **2a** (eq 2), which then reacts further with Br_2

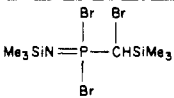
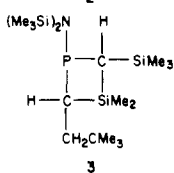
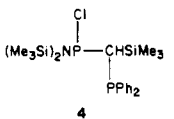
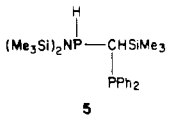
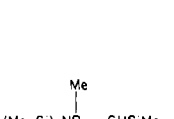
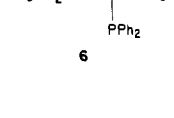
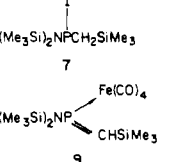


in the manner expected of a (silylamino)phosphine.¹⁰ When just 1 equiv of Br_2 is added to a solution of **1**, the NMR spectra of

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Table I. NMR Spectral Data^a for Derivatives of 1

compd	signal	¹ H NMR		¹³ C NMR		³¹ P NMR δ
		δ	J _{PH}	δ	J _{PC}	
	Me ₃ SiC	0.16		-0.18	3.1	-51.4
	Me ₃ SiN	0.38		1.61	7.9	
	CH	3.74	13.2	46.52	89.7	
	(Me ₃ Si) ₂ N	0.20		5.25	7.3	59.9
	Me ₃ SiC	0.03	2.9	2.12	4.9	61.9 ^b
	Me ₂ Si	c		0.59	5.5	
	SiCHSi	d		23.48	44.6	
	PCHSi	d		29.70	47.0	
	CH ₂	d		40.32	1.2	
	CMe ₃			29.60		
	CMe ₃	0.80		29.90	2.4	
	(Me ₃ Si) ₂ N	0.20	1.8	4.12	8.8	154.4
	Me ₃ SiC	-0.09	1.0	2.01	2.9	(-5.5) ^e
	CH	3.12	20.9, 2.7	34.05	79.1, 32.2	
	Ph	7.1-7.6 ^f		124-134 ^f		
	(Me ₃ Si) ₂ N	0.12	0.6	3.35	4.9	4.7
		0.11	0.6			(-10.4)
	Me ₃ SiC	-0.02	0.6	1.50	9.8	6.1
		-0.21	1.2	0.58	3.9	(9.8) ^{b,e}
	CH	2.4-2.7 ^f		20.37 ^b	44.0, 18.9	
				24.73 ^b	50.3, 32.0	
	PH	2.10	187.2, 56.3			
	Ph	7.1-7.9 ^f		127-136 ^f		
	(Me ₃ Si) ₂ N	0.18	1.3	4.92	6.1	49.6
	Me ₃ SiC	-0.20	0.9	2.24	3.7	(-3.4) ^e
	PMe	1.56	8.4	20.94	28.0	
			1.1		14.7	
	CH	2.46	9.1	26.52	53.7	
			1.5		29.3	
	Ph	7.1-7.7 ^f		127-140 ^f		
	(Me ₃ Si) ₂ N	0.37	1.8	3.63	9.2	173.9
	Me ₃ SiC	0.20	1.0	-0.06	5.5	
	CH ₂	2.25	10.3	30.76	67.8	
	(Me ₃ Si) ₂ N	0.29		2.79		305.5
	Me ₃ SiC	0.16	0.6	0.19	5.8	
	CH	6.82	36.6	160.7	8.8	
	CO			213.4	23.5	

^aChemical shifts downfield from Me₃Si for ¹H and ¹³C spectra and from H₃PO₄ for ³¹P spectra; coupling constants in Hz. Solvents: ¹H, CH₂Cl₂; ¹³C and ³¹P, CDCl₃. ^bDiastereomers. ^cObscured by Me₃Si signals. ^dComplex multiplet, δ 0.9-2.0. ^eChemical shifts for PPh₂ group in parentheses. ^fJ_{PP} values in Hz: 227.0 (4); 56.0 and 170.0 (5, diastereomers); 148.0 (6). ^gComplex multiplet.

Table II. Preparative and Analytical Data

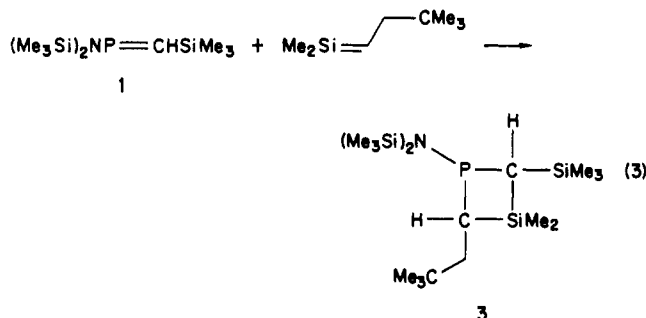
compd	preparative		analytical ^a	
	% yield	bp, °C (P, mm)	% C	% H
2	80	80-85 (0.1)	18.69 (18.93)	4.35 (4.31)
3	26	90-96 (0.01)	50.86 (51.49)	11.06 (11.04)
4 ^b	95		53.32 (53.04)	7.71 (7.63)
5	64	140-148 (0.03)	56.75 (56.97)	8.52 (8.48)
7	50 ^c	87-89 (0.07)		
9	42 ^d	125-130 (0.5)	37.91 (37.75)	6.61 (6.34)

^aCalculated values in parentheses. ^bNot distilled due to thermal instability. ^cConverted to known derivative 8 (see text). ^dYield ca. 95% before distillation.

the mixture provide evidence of the presence of 2a. In addition to signals for unreacted starting material 1 and product 2, the ³¹P (δ 175.8) and ¹H (CH: δ 1.98, J_{PCH} = 9.9 Hz) NMR spectra contain peaks that are assigned to the (disilylamino)bromophosphine 2a. Addition of the second equivalent of Br₂ results in complete conversion to phosphoranimine 2. In contrast, the bromination of the isoelectronic iminophosphine (Me₃Si)₂NP=NSiMe₃ proceeds via oxidative addition at phosphorus to the dibromophosphoranimine (Me₃Si)₂NPBr₂=NSiMe₃.¹¹

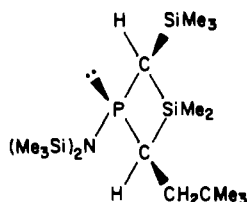
Several reactions of the methylenephosphine 1 with polar reagents were also investigated as part of this study. The reactive

silene species *t*-BuCH₂CH=SiMe₂ (generated from *t*-BuLi and CH₂=CHSiMe₂Cl by the method of Jones et al.¹²) undergoes a (2 + 2) cycloaddition reaction with 1 at -78 °C (eq 3). The

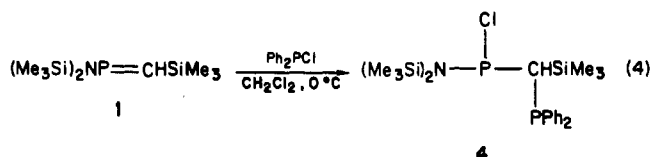


1-phospha-3-silacyclobutane 3 is located in moderate yield (ca. 25-40%) as a distillable liquid (Tables I and II). Phosphorus-31 NMR spectroscopy indicates that 3 is a mixture of two isomers in the ratio of ca. 8:1. The predominant isomer cannot be identified with certainty, but on the basis of examination of molecular models, it appears that the least congested structure is one in which the Me₃Si and neopentyl substituents on the ring are both trans

to the $(\text{Me}_3\text{Si})_2\text{N}$ group. The two isomers are not separable by GC-MS, although the mixture does give the correct molecular ion peak and a reasonable fragmentation pattern, as well as a satisfactory elemental analysis.

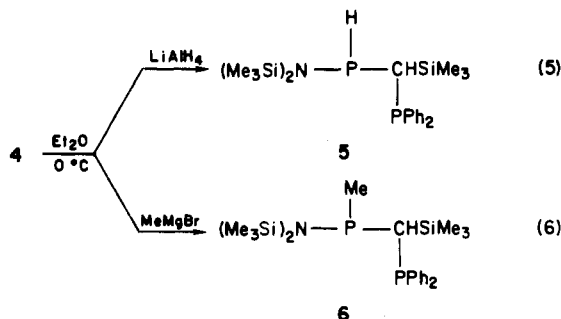


A process having greater synthetic potential is the reaction of **1** with chlorodiphenylphosphine, which results in the formation of the bis(phosphino)methane derivative **4** (eq 4). Compound



4 is obtained in ca. 95% yield as a viscous orange liquid that cannot be distilled without decomposition to Me_3SiCl and unidentified phosphorus-containing products. The undistilled product, however, is of sufficient purity to afford good NMR spectral data and elemental analysis. The ^{31}P spectrum of **4** consists of an AX pattern in which the chemical shifts of 154.4 and -5.5 ppm are indicative of the [bis(trimethylsilyl)amino]halophosphine^{3,13} and the diphenylalkylphosphine¹⁴ centers, respectively. The P-CH-P' linkage is further characterized by the doubled doublet patterns found for the CH group in both the ^1H and ^{13}C NMR spectra.

Although the steric crowding in compound **4** is rather severe, the P-Cl bond is still susceptible to nucleophilic substitution. Its reactions with LiAlH_4 (eq 5) and MeMgBr (eq 6) readily afford



the corresponding P-H (**5**) and P-Me (**6**) derivatives. The P-H phosphine **5** is a high-boiling liquid in which the P-H functionality is confirmed by IR ($\nu_{\text{PH}} = 2250 \text{ cm}^{-1}$) and NMR ($^1J_{\text{PH}} = 187.2$, $^3J_{\text{PH}} = 56.3 \text{ Hz}$) spectroscopy. The synthesis and purification of the P-Me compound **6**, however, were less straightforward since the product, a waxlike solid, could not be distilled without extensive decomposition. Attempts to purify **6** by recrystallization were unsuccessful, and an analytically pure sample could not be obtained. Nevertheless, the NMR and mass spectra of **6** readily confirmed the proposed structure, analogous to **4** and **5**.

The series of bis(phosphino)methanes **4-6** possess some interesting and, at this point, not readily explicable stereochemical features. Each of these compounds contains two chiral centers and, accordingly, may be expected to exist as a mixture of diastereomers. This seems to be the case only for the P-H derivative **5** since its ^{31}P spectrum consists of two AB patterns while the spectra of **4** and **6** show simple AX splitting. The formation of a single diastereomer of **4** would require the addition of Ph_2PCl to **1** to occur in a stereospecific fashion. To date, the mechanistic

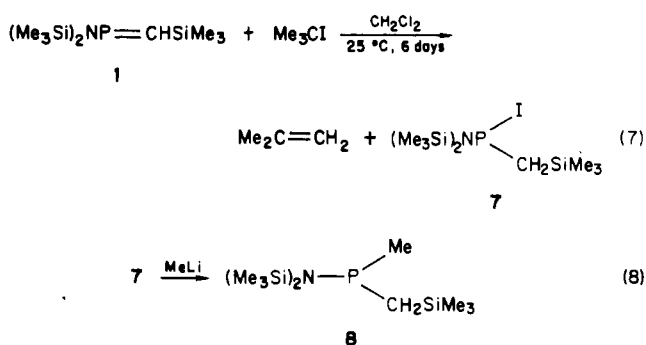
details of reactions involving P=C double bonds have not been systematically investigated. Compounds such as **1**, however, with their well-defined geometry about the double bond, should be excellent substrates for future studies of this type.

Another noteworthy point about compounds **4-6** is the large magnitude of their two-bond coupling constants $^2J_{\text{PCP}}$. The value for **4** ($^2J_{\text{PCP}} = 227 \text{ Hz}$), for example, is roughly twice that reported for simple bis(phosphino)methanes $\text{Ph}_2\text{PCH}_2\text{P}(\text{R})\text{Ph}$.¹⁵ In the analogous bis(phosphino)amines $\text{X}_2\text{PN}(\text{R})\text{PY}_2$, the $^2J_{\text{PNP}}$ values may vary widely (ca. -30 to $+700 \text{ Hz}$), with the highest values observed when bulky and/or electronegative groups are attached to phosphorus.¹⁶ There is also a strong conformational dependence of the coupling constant on the proximity of the two phosphorus lone pairs. The possibility that similar factors are operative in the P-C-P systems has, to our knowledge, not yet been investigated.

The successful preparation of **4** and its derivatives **5** and **6** suggests that the reaction of chlorophosphines with P=C double bonds can be a useful method for the synthesis of bis(phosphino)methanes. These compounds are important as "small-bite" chelate ligands in transition-metal chemistry.¹⁷ Since there are few routes to such ligands, particularly with unsymmetrical substitution patterns, the scope of the method illustrated by eq 4 is undergoing further study in our laboratory.

Nucleophilic Reactions of 1. Previous studies have shown that three-coordinate, sp^3 -hybridized phosphines bearing silylamino groups readily undergo many interesting and synthetically useful reactions with a wide variety of organic electrophiles.¹⁸ This is not generally the case, however, with the two-coordinate, sp^2 -hybridized phosphines such as **1**. We find, for example, that **1** does not react (at room temperature in CH_2Cl_2 solution) with several common electrophiles including MeI , acetone, acetaldehyde, and benzoyl chloride. A similar lack of nucleophilic character has been observed for other methylenephosphines⁹, especially those containing silyl substituents on carbon.¹⁹

Compound **1** does react slowly with *tert*-butyl iodide (eq 7) to afford the iodophosphine **7** accompanied by the elimination of isobutylene. For characterization purposes, **7** was readily con-



verted to the known methylphosphine **8**²⁰ (eq 8). Given that **1** does not react with typical electrophiles such as MeI , the formation of **7** probably does not result from nucleophilic attack of **1** on Me_3CI . A more plausible pathway might involve oxidative addition to **1**, giving an ylide intermediate (eq 9) that could then reductively eliminate $\text{Me}_2\text{C}=\text{CH}_2$. This suggestion is supported by the fact that the P-N analogue $(\text{Me}_3\text{Si})_2\text{NP}=\text{NSiMe}_3$ (also unreactive toward MeI) reacts with Me_3CI to give the *stable* oxidation product $(\text{Me}_3\text{Si})_2\text{NP}(t\text{-Bu})(\text{I})=\text{NSiMe}_3$.²¹

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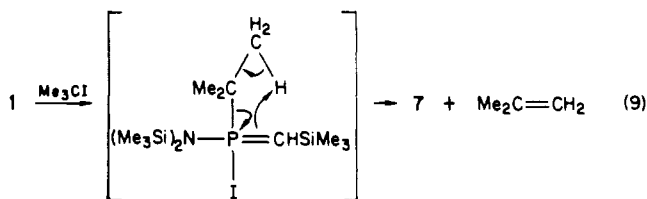
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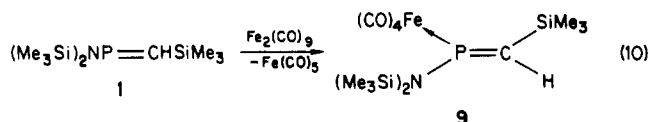
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Reaction of 1 with $\text{Fe}_2(\text{CO})_9$. Methylene phosphines have been found to form a variety of η^1 and η^2 complexes with transition-metal moieties.²² In a preliminary paper,²³ we recently reported the novel η^1 complex $[(\text{Me}_3\text{Si})_2\text{NP}=\text{C}(\text{SiMe}_3)_2]\text{Fe}(\text{CO})_4$ whose unusual structural features include (1) a short (1.657 Å), but severely twisted (30.3°), phosphorus-carbon double bond and (2) coordination of the phosphine ligand in an equatorial site of the trigonal-bipyramid structure. For comparative purposes, therefore, we were interested in preparing the $\text{Fe}(\text{CO})_4$ complex of the trisilylated ligand 1.

In fact, compound 1 reacts smoothly and quantitatively with 1 equiv of $\text{Fe}_2(\text{CO})_9$ (eq 10). After removal of solvent and $\text{Fe}(\text{CO})_5$,



the iron complex 9 is obtained as a viscous orange liquid that could not be crystallized. Complex 9 is, however, fully characterized by elemental analysis and NMR and IR spectroscopy. It undergoes partial decomposition upon vacuum distillation.

The ^{31}P chemical shift (δ 306) of 9 is very similar to that of the free ligand 1 (δ 310), thus showing little change in the electronic environment at the phosphorus center. In contrast, the ^{31}P signal of the tetrasilylated ligand $(\text{Me}_3\text{Si})_2\text{NP}=\text{C}(\text{SiMe}_3)_2$ (δ 383) shifts upfield by ca. 72 ppm upon complexation to $\text{Fe}(\text{CO})_4$. These differences might indicate that the less crowded $\text{P}=\text{C}$ double bond in 9 is not as distorted from planarity as in the bis(trimethylsilyl)methylene analogue. Furthermore, in complex 9, the phosphine ligand 1 appears to be coordinated in an *axial* rather than an equatorial site. This assignment is based on the IR spectrum of 9 (Figure 1b), which contains one strong (1951 cm^{-1}), two medium ($1984, 2056\text{ cm}^{-1}$), and one weak (2024 cm^{-1}) carbonyl stretching bands. This pattern is characteristic²⁴ of axial substitution and differs markedly from that observed for the confirmed equatorial complex (Figure 1a).

Conclusion. The results of this and earlier studies demonstrate that the silyl-substituted aminomethylene phosphines have a rich and varied derivative chemistry. Although the sp^2 -hybridized phosphorus center is weakly nucleophilic, it does complex with $\text{Fe}(\text{CO})_4$ and the $\text{P}=\text{C}$ double bond is susceptible to a wide range of 1,2-addition processes. Some of these reactions (e.g., with $\text{RLi}^{7,19}$ or Ph_2PCl) have considerable synthetic utility for the preparation of new bidentate phosphine ligands. Moreover, the fixed geometry about the double bond in 1^{3,4} makes it an attractive system for fundamental studies of the chemistry of the $\text{P}=\text{C}$ bond. Many of these synthetic and mechanistic implications are currently being explored in our laboratory.

Experimental Section

Materials and General Procedures. The following reagents were obtained from commercial sources and used without purification: MeMgBr , MeLi , $t\text{-BuLi}$, $\text{Fe}_2(\text{CO})_9$, Ph_2PCl , LiAlH_4 , Me_3SiCl , $\text{H}_2\text{C}=\text{CHSiMe}_2\text{Cl}$,

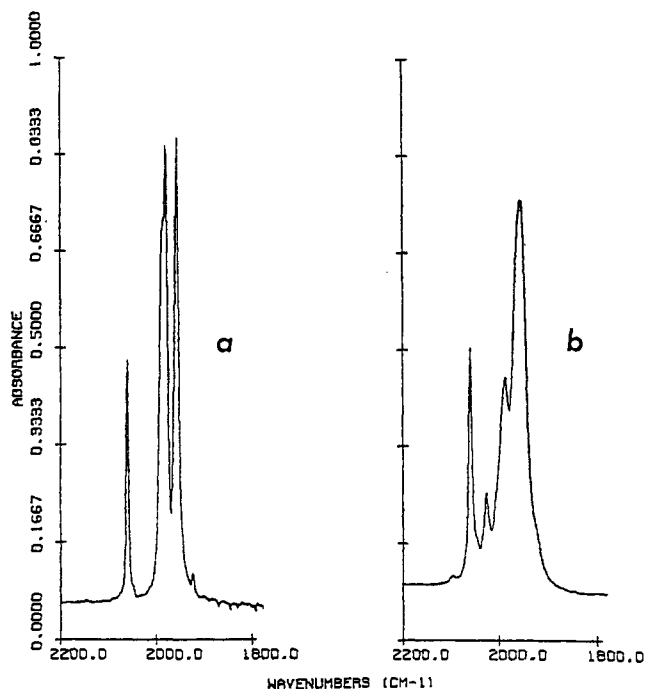


Figure 1. FT-IR spectra of [methylene phosphine]iron tetracarbonyl complexes $\text{LFe}(\text{CO})_4$: (a) equatorial substitution, $\text{L} = (\text{Me}_3\text{Si})_2\text{NP}=\text{C}(\text{SiMe}_3)_2$; (b) axial substitution, $\text{L} = (\text{Me}_3\text{Si})_2\text{NP}=\text{CHSiMe}_3$ (1).

$t\text{-BuLi}$, bromine. The solvents (C_6H_6 , CH_2Cl_2 , pentane, Et_2O) were distilled from CaH_2 prior to use. The starting methylenephosphine 1 was prepared according to the published procedure.³ 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. Infrared spectra (FT mode) were recorded on a Nicolet 5 DX FT-IR spectrophotometer using neat liquid or pressed KBr pellet samples. Mass spectra were obtained on a Finnigan OWA 1020 GC-MS system. 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.

***P,P*-Dibromo-*P*-[bromo(trimethylsilyl)methyl]-*N*-(trimethylsilyl)phosphoranimine (2).** A solution of bromine (8.8 g, 55 mmol) in benzene (30 mL) was added dropwise to a stirred solution of 1 (15.3 g, 55 mmol) in benzene (80 mL) at 0°C . The ^{31}P and ^1H NMR spectra of the mixture show the presence of 1, 2, and a third compound 2a (see above). After addition of a second equivalent of bromine by the same procedure, the NMR spectra indicated complete conversion to product 2. Benzene and Me_3SiBr (identified by ^1H NMR) were removed under reduced pressure. Distillation through a short-path apparatus afforded compound 2 (19.6 g) as a yellow liquid (Tables I and II). Mass spectrum, m/e (relative intensity): 443 (0.4) (M^+), 428 (7.1), 210 (19.3), 182 (11.0), 164 (3.0), 137 (51.6), 118 (13.3), 73 (100.0).

1-Phospha-3-silacyclobutane (3). The silene $\text{Me}_2\text{Si}=\text{CHCH}_2(t\text{-Bu})$ was prepared according to the literature procedure¹² by the addition of $t\text{-BuLi}$ (21 mL, 38 mmol, 1.8 M in pentane) to a solution of $\text{CH}_2=\text{CHSiMe}_2\text{Cl}$ (4.6 g, 38 mmol) in pentane (50 mL) at -78°C . After the mixture was stirred for 3 h at -78°C , compound 1 (10.7 g, 38.5 mmol) was added via syringe. The mixture was allowed to warm slowly to room temperature and was stirred overnight. After filtration and solvent removal, distillation through a 10-cm column afforded 3 (4.15 g) as a pale yellow liquid. Mass spectrum, m/e (relative intensity): 419 (11.7) (M^+), 404 (6.2), 364 (23.1), 363 (76.0), 274 (15.7), 262 (15.5), 218 (18.5), 202 (23.7), 130 (69.3), 129 (24.8), 116 (16.7), 100 (21.6), 99 (18.0), 85 (41.9), 73 (100.0).

[Bis(trimethylsilyl)amino]-(diphenylphosphino)(trimethylsilyl)methylchlorophosphine (4). Chlorodiphenylphosphine (5.52 g, 25 mmol) was added via syringe to a stirred solution of 1 (6.92 g, 25 mmol) in CH_2Cl_2 (50 mL) at 0°C . After warming to room temperature, the mixture was stirred overnight. The solvent and other volatile materials were removed at room temperature under vacuum (0.02 mm). Dichloromethane (25 mL) was then added, and a small amount of unidentified white solid was allowed to settle. The supernatant liquid was decanted from the solid, and the solvent was removed under vacuum,

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leaving **4** (11.8 g) as a viscous orange liquid. Attempted distillation caused elimination of volatile materials (Me_3SiCl and probably HCl) and formation of a complex mixture of unidentified, nonvolatile products.

[Bis(trimethylsilyl)amino] [(diphenylphosphino)(trimethylsilyl)methyl]phosphine (5). A freshly prepared sample of **4** (10.5 g, 21 mmol) was dissolved in Et_2O (50 mL). After the mixture was cooled to 0°C , LiAlH_4 (5.5 mL, 1.0 M in Et_2O , 22 mmol hydride) was added via syringe. The mixture was warmed to room temperature and stirred overnight. Following filtration and solvent removal, distillation through a short-path column gave a high-boiling fraction (bp $140\text{--}165^\circ\text{C}$ (0.03 mm)) that was redistilled through a 10-cm column to give **5** (6.2 g) as an analytically pure, colorless liquid.

[Bis(trimethylsilyl)amino] [(diphenylphosphino)(trimethylsilyl)methyl]methylphosphine (6). By the same procedure as described above for **5**, the P-Cl compound **4** (10.0 g, 20 mmol) in Et_2O (40 mL) was treated at 0°C with MeMgBr (10 mL, 28.5 mmol, 2.85 M in Et_2O). After the mixture was stirred overnight at room temperature, Me_3SiCl (ca. 2 mL) was added to consume the excess Grignard reagent. The solids were allowed to settle, and the supernatant solution was decanted. After solvent removal, CH_2Cl_2 (20 mL) was added, and the decantation process was repeated. Solvent removal left **6** (8.6 g, 90% yield) as a white wax that was identified by NMR spectroscopy, with only very minor impurities being detectable. Attempts to obtain an analytically pure sample of **6** by either recrystallization or distillation were unsuccessful. Mass spectrum, m/e (relative intensity): 478 (0.2) (M^+), 463 (2.6), 390 (4.2), 302 (16.0), 271 (24.2), 262 (11.8), 190 (26.6), 183 (12.4), 135 (51.4), 130 (30.5), 108 (9.9), 73 (100.0).

[Bis(trimethylsilyl)amino] [(trimethylsilyl)methyl]diphosphine (7) A mixture of *t*-BuI (0.80 mL, 6.7 mmol) and **1** (1.70 g, 6.12 mmol) in CH_2Cl_2 (3 mL) was stirred at room temperature with periodic monitoring by ^1H NMR spectroscopy. After 6 days, the signals due to **1** had disappeared and new peaks assignable to **7** and $\text{Me}_2\text{C}=\text{CH}_2$ (δ 1.70, 6 H; δ 4.60, 2 H; 4J = 1.4 Hz) were present. The solvent and other volatile materials were removed under vacuum, and **7** (0.85 g) was isolated by distillation as a yellow liquid. Treatment of **7** with an equimolar quantity of MeLi in Et_2O solution at 0°C gave the known P-Me derivative **8**²⁰ (quantitative yield by ^{31}P NMR; 44% distilled yield on 3 mmol scale reaction).

[Bis(trimethylsilyl)amino] [(trimethylsilyl)methylene]phosphineiron tetracarbonyl (9). Compound **1** (13.0 g, 46.7 mmol) was added to a slurry of $\text{Fe}_2(\text{CO})_9$ (17.0 g, 46.7 mmol) in pentane (200 mL). The mixture was stirred overnight and then filtered to remove a small amount of black solid. Solvent and $\text{Fe}(\text{CO})_5$ were removed under vacuum, leaving **9** as an orange liquid of good purity as indicated by NMR spectroscopy. Distillation resulted in partial decomposition, but an analytically pure sample of **9** (8.8 g, 42% yield) was obtained.

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Registry No. 1, 76173-65-4; 2, 89982-65-0; 2a, 96109-86-3; 3, 96192-48-2; 4, 89982-64-9; 5 (isomer 1), 96109-84-1; 5 (isomer 2), 96109-87-4; 6, 96109-85-2; 7, 89982-63-8; 8, 90413-57-3; 9, 89934-22-5; Ph_2PCL , 1079-66-9; $\text{Me}_2\text{Si}=\text{CHCH}_2$ (*t*-Bu), 79991-59-6.

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Preparation, Separation, and Characterization of Two New Series of Mixed-Ligand Eight-Coordinate Tungsten(IV) Complexes Containing the Pairs of Bidentate Ligands 2-Mercaptopyrimidine-5-*tert*-Butyl-2-mercaptopyrimidine and 5-Methylpicolinic Acid-5-*tert*-Butyl-2-mercaptopyrimidine

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Two new series of mixed-ligand eight-coordinate tungsten(IV) complexes have been prepared, isolated, and characterized. Six $\text{W}(\text{bmpd})_n(\text{mpd})_{4-n}$ complexes, where $\text{bmpd}^- = 5\text{-}tert\text{-butyl-2-mercaptopyrimidinato}$ and $\text{mpd}^- = 2\text{-mercaptopyrimidinato}$, and five $\text{W}(\text{bmpd})_n(\text{mpic})_{4-n}$ complexes, where $\text{mpic}^- = 5\text{-methylpicolinato}$, have been isolated by thin-layer chromatography on silica gel plates. The pair of bidentate ligands form four-membered chelate rings in the former series, while a four- and a five-membered chelate ring are formed by the pair of bidentate ligands in the latter series. In the $\text{W}(\text{bmpd})_n(\text{mpd})_{4-n}$ series a pair of stereoisomers (labeled α and β) are observed for $n = 2$, while in the $\text{W}(\text{bmpd})_n(\text{mpic})_{4-n}$ series only a single stereoisomer is observed for $n = 0\text{--}4$. ^1H NMR studies indicate these complexes are rigid on the NMR time frame. The stereochemistry of these complexes is discussed in terms of their NMR spectrum and Orgel's rule.

Introduction

The study of mixed-chelate complexes is potentially one of the best ways to explore the possibility of stereoisomers in early-transition-metal eight-coordinate complexes. The fruitfulness of this approach has been demonstrated by the study of the $\text{W}(\text{mpic})_n(\text{dcq})_{4-n}$ system, where $n = 0\text{--}4$ and $\text{mpic}^- = 5\text{-methylpicolinato}$ and $\text{dcq}^- = 5,7\text{-dichloro-8-quinolinolato}$.¹ Examination of these species revealed that the $\text{W}(\text{mpic})_2(\text{dcq})_2$ complex exists in two different stereoisomeric forms (labeled α and β). These two complexes are rigid enough to permit separation by column chromatography but in solution will equilibrate back to a mixture of the two forms in 24 h at 25°C . An activation energy of 114 kJ/mol was measured for the intramolecular rearrangement process that converts the β form to the α form. The ^1H NMR spectrum of the $\text{W}(\text{mpic})_3(\text{dcq})$ complex consists of two methyl signals in a 2:1 ratio and marked the first time rigid behavior was observed on a NMR time frame for an eight-coordinate tetrakis chelate complex at and above room temperature.

We have recently initiated a program to explore further the number and stereochemistry of eight-coordinate complexes that

arise when two or more different bidentate ligands are used to form tetrakis chelate complexes. In particular, we are interested in how the following three variables affect the number, stereochemistry, and rigid character of this class of eight-coordinate complexes: (1) the size of the chelate ring; (2) the nature of the donor atoms on the ligand; (3) the nature of the metal center. Because of the substitution inertness observed in the previously characterized tungsten(IV) eight-coordinate complexes $\text{W}(\text{q})_4$,² $\text{W}(\text{pic})_4$,³ and $\text{W}(\text{mpd})_4$ ⁴ and the molybdenum(IV) complex $\text{Mo}(\text{pic})_4$,⁵ our current efforts are directed toward the synthesis of new mixed-ligand eight-coordinate complexes of molybdenum(IV) and tungsten(IV).

The previously studied $\text{W}(\text{mpic})_n(\text{dcq})_{4-n}$ system employed two bidentate ligands both of which form five-membered chelate rings. Herein, we report the preparation, separation, and characterization of two new series of mixed-ligand eight-coordinate tungsten(IV) complexes. The first of these series contains the two bidentate

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