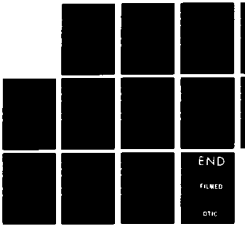
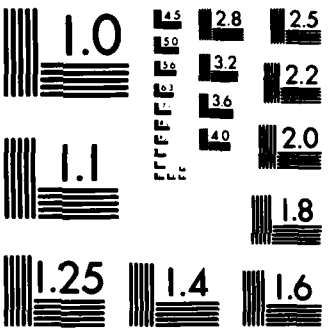
AD-A149 042 SOME ADDITION AND COMPLEXATION REACTIONS OF A SILYLATED AMINO(METHYLENE)P.. (U) TEXAS CHRISTIAN UNIV FORT WORTH DEPT OF CHEMISTRY R R FORD ET AL. 12 DEC 84 1/1

UNCLASSIFIED TCU/DC/TR-84-08 N00014-79-C-0632 F/G 7/3 NL





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OFFICE OF NAVAL RESEARCH

Contract No. N00014-79-C-0632

Task No. NR-053-720

TECHNICAL REPORT NO. TCU/DC/TR-84-08

AD-A149 042

Some Addition and Complexation Reactions of a Silylated Amino(methylene)phosphine

by

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Prepared for Publication

in

Inorganic Chemistry

Texas Christian University
Chemistry Department
Fort Worth, TX 76129

December 12, 1984

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER TCU/DC/TR-84-08	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Some Addition and Complexation Reactions of a Silylated Amino(methylene)-phosphine		5. TYPE OF REPORT & PERIOD COVERED Technical Report, 1984 6. PERFORMING ORG. REPORT NUMBER TR-84-08
7. AUTHOR(s) R. R. Ford, B.-L. Li, R. H. Neilson, and R. J. Thoma		8. CONTRACT OR GRANT NUMBER(s) N00014-79-C-0632
9. PERFORMING ORGANIZATION NAME AND ADDRESS Texas Christian University Fort Worth, TX 76129		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-053-720
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research		12. REPORT DATE December 12, 1984 13. NUMBER OF PAGES 27
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Prepared for publication in Inorganic Chemistry

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

(Methylene)phosphine
N-silylphosphoranimine
diphosphinomethane
Silylcyclobutane
Phosphacyclobutane
(silylamine)phosphine

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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S/N 0102-LF-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Contribution from the
Department of Chemistry
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Some Addition and Complexation Reactions of a Silylated Amino(methylene)phosphine[1,2]

RANDAL R. FORD, BEI-LI LI, ROBERT H. NEILSON,*
and RANDALL J. THOMA

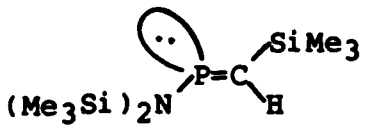
Abstract

Several new reactions, including a variety of 1,2-additions and complexation to $Fe(CO)_4$, of the trisilylated amino(methylene)phosphine $(Me_3Si)_2NP{=}CHSiMe_3$ (1) are reported. The bromination of 1 appears to proceed via the intermediate addition product $(Me_3Si)_2NP(Br)\text{-}C(Br)HSiMe_3$ (2a) with further reaction affording the tribromophosphoranimine $Me_3SiN{=}PBr_2\text{-}C(Br)HSiMe_3$ (2) as the isolated product. The reactive silene $t\text{-}BuCH_2CH{=}SiMe_2$ reacts with 1 via a (2+2)-cycloaddition reaction to give the 1-phospha-3-silacyclobutane derivative $(Me_3Si)_2NPCH(SiMe_3)SiMe_2CH(CMe_3)$ (3). The addition of Ph_2PCl to the P=C double bond of 1 produces the novel diphosphinomethane system $(Me_3Si)_2NP(Cl)C(PPh_2)HSiMe_3$ (4) in nearly quantitative yield. The chlorophosphine 4 is readily converted to the P-H (5) and P-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 PhC(O)Cl. Compound 1 reacts with t-BuI to form isobutylene and the P-iodo phosphine $(Me_3Si)_2NP(I)CH_2SiMe_3$ (7) which, upon reaction with MeLi, yields the P-Me derivative 8. Treatment of 1 with $Fe_2(CO)_9$ affords the η^1 complex $LFe(CO)_4$ (9, L = 1) which appears to involve axial coordination of the (methylene)phosphine ligand. Some significant differences between the chemistry of 1 and that of the isoelectronic iminophosphine $(Me_3Si)_2NP{=}NSiMe_3$ are noted.

Introduction

The chemistry of phosphorus compounds containing Si-N-P and/or Si-C-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 Si-N or Si-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 amino(methylene)phosphines, such as 1 which have been under investigation in our laboratory.



1

Compound 1, a stable, distillable liquid, is readily prepared either by dehydrohalogenation[3] or thermolysis[4] 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 Si_2N-P-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

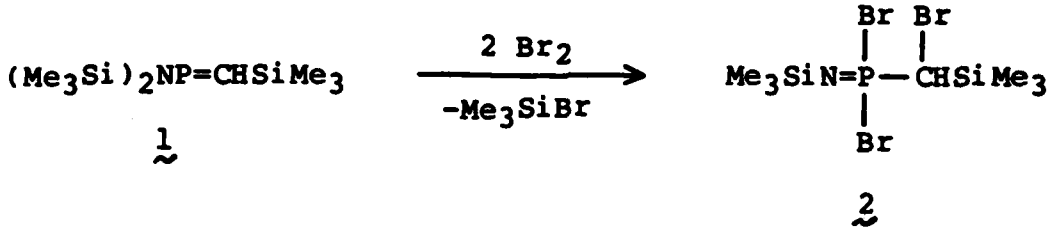
reagents to the P=C bond[3], and possible cycloaddition reactions involving the P=C bond.[1,6] Reactions of the second type are more complex processes in which cleavage of the Si-N and/or P-N bonds is involved. For example, the reaction of 1 with alkyllithium reagents occurs with both nucleophilic substitution and addition leading to trialkylphosphines or P-C-P products depending on the size of the alkyl substituent.[7]

As a continuation of these studies, we report here several reactions of 1 which include some novel additions to the P=C double 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. A secondary objective of this study was to more closely compare the reactivity of 1 with its isoelectronic iminophosphine analogue, $(Me_3Si)_2NP{=}NSiMe_3$.[8]

Results and Discussion

Addition reactions of 1. Although (methylene)phosphines, 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 two molar equivalents of bromine (eq 1). Analysis of the reaction mixture by ^1H and ^{31}P NMR indicates quantitative formation of Me_3SiBr and the novel tribromophos-

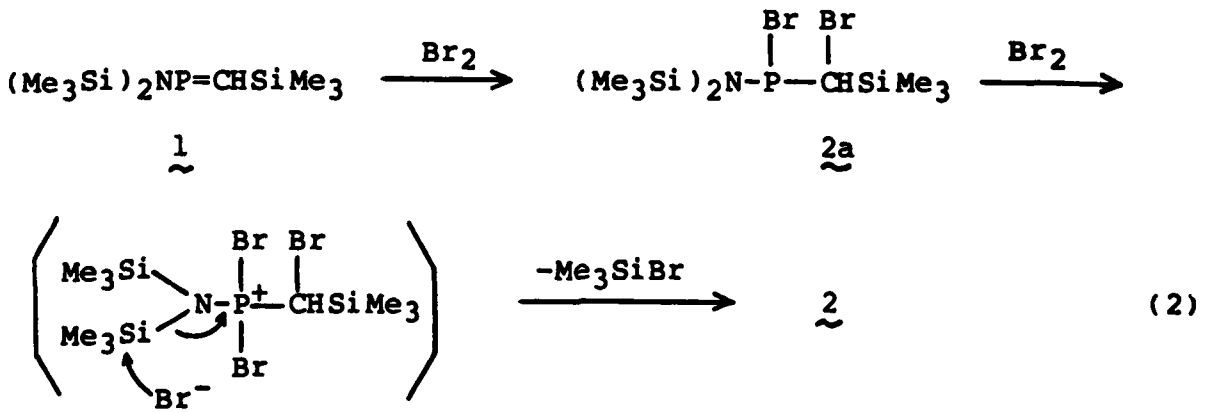
phoranimine 2. Following solvent removal, product 2 is isolated



(1)

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 $(M-CH_3)^+$ 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 one equivalent of Br_2 is added to a solution of 1, the NMR

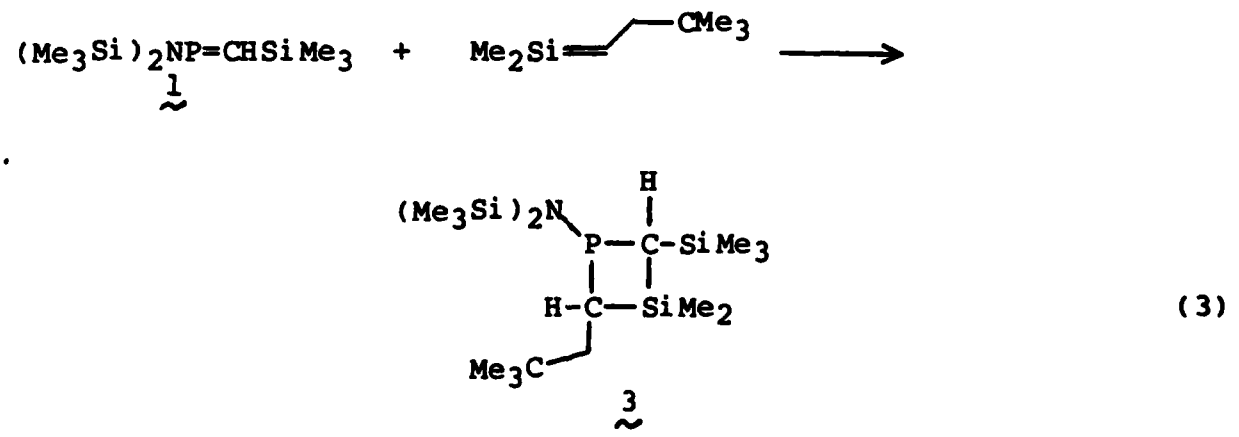


(2)

spectra of the mixture provide evidence of the presence of 2a. In addition to signals for unreacted starting material 1 and

product 2, the ^{31}P (δ 175.8) and ^{1}H (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 Br_2 results in complete conversion to phosphoranimine 2. In contrast, the bromination of the isoelectronic iminophosphine $(Me_3Si)_2NP{=}NSiMe_3$ proceeds via oxidative addition at phosphorus to the dibromophosphoranimine $(Me_3Si)_2NPBr_2{=}NSiMe_3$.[11]

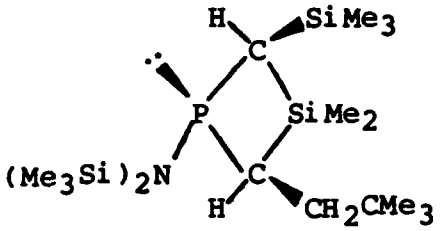
Several reactions of the (methylene)phosphine 1 with polar reagents were also investigated as part of this study. The reactive silene species t-$BuCH_2CH{=}SiMe_2$ (generated from t-BuLi and $CH_2{=}CHSiMe_2Cl$ by the method of Jones et al.[12]) undergoes a (2+2)-cycloaddition reaction with 1 at -78°C (eq 3). The 1-phospha-3-silacyclobutane 3 is isolated in moderate yield



(3)

(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, based on examination of

molecular models, it appears that the least congested structure is one in which the Me_3Si and neopentyl substituents on the ring are both trans to the $(Me_3Si)_2N$ 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.

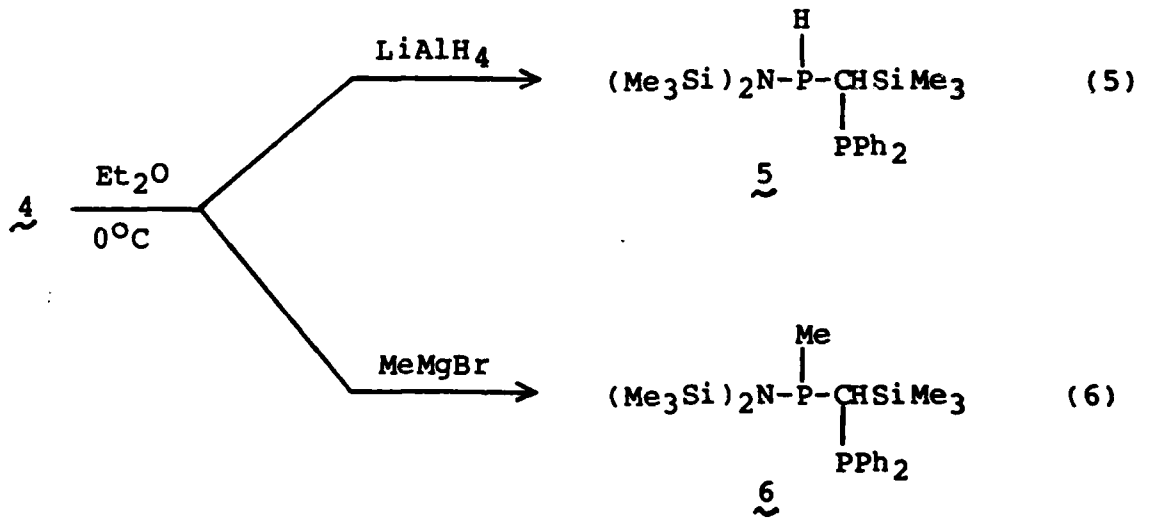
A process having greater synthetic potential is the reaction of 1 with chlorodiphenylphosphine which results in the formation of the diphosphinomethane derivative 4 (eq 4). Compound 4 is

$$(Me_3Si)_2NP{=}CHSiMe_3 \quad (\underset{\sim}{1}) \xrightarrow[CH_2Cl_2,\,0^oC]{Ph_2PCl} (Me_3Si)_2N{-}\overset{Cl}{\overset{|}{P}}{-}\overset{PPh_2}{\overset{|}{C}}HSiMe_3 \quad (\underset{\sim}{4}) \qquad (4)$$

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](halo)phosphine[3,13]

and the diphenyl(alkyl)phosphine[14] centers, respectively. The P-CH-P' linkage is further characterized by the doubled doublet patterns found for the CH group in both the ^{1}H 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



(5)

(6)

functionality is confirmed by IR (ν_{PH} = 2250 cm^{-1}, and NMR ($^{1}J_{PH}$ = 187.2, $^{3}J_{PH}$ = 56.3 Hz) spectroscopy. The synthesis and purification of the P-Me compound 6, however, were less straightforward since the product, a wax-like 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 diphosphinomethanes 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 $^2J_{PCP}$. The value for 4 ($^2J_{PP'}$ = 227 Hz), for example, is roughly twice that reported for simple diphosphinomethanes $Ph_2PCH_2P(R)Ph$.[15] In the analogous diphosphinoamines $X_2PN(R)PY_2$, the $^2J_{PNP}$ values may vary widely (ca. -30 to 700 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 diphosphinomethanes. 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 (methylene)phosphines[9], especially those containing silyl substituents on carbon.[19]

Compound 1 does react slowly with tert-butyl iodide (eq 7) to afford the P-iodo phosphine 7 accompanied by the elimination of isobutylene. For characterization purposes, 7 was readily converted to the known P-methyl phosphine 8[20] (eq 8). Given that

$$(Me_3Si)_2NP{=}CHSiMe_3 \quad \underset{\sim}{1} \quad + \quad Me_3CI \xrightarrow[25^{\circ}C,\ 6d]{CH_2Cl_2} Me_2C{=}CH_2 \quad +$$

$$(Me_3Si)_2NP(I)CH_2SiMe_3 \quad \underset{\sim}{7} \qquad (7)$$

$$\underset{\sim}{7} \xrightarrow{MeLi} (Me_3Si)_2N\text{-}P(Me)CH_2SiMe_3 \quad \underset{\sim}{8} \qquad (8)$$

$\underset{\sim}{1}$ does not react with typical electrophiles such as MeI, the formation of $\underset{\sim}{7}$ probably does not result from nucleophilic attack of $\underset{\sim}{1}$ on Me_3CI. A more plausible pathway might involve oxidative addition to $\underset{\sim}{1}$ giving an ylide intermediate (eq 9) which could then reductively eliminate $Me_2C{=}CH_2$. This suggestion is supported by the fact that the P-N analogue $(Me_3Si)_2NP{=}NSiMe_3$

$$\underset{\sim}{1} \xrightarrow{Me_3CI} \left[(Me_3Si)_2N\text{-}P(I)(CMe_2CH_2)=CHSiMe_3 \right] \longrightarrow \underset{\sim}{7} + Me_2C{=}CH_2 \qquad (9)$$

(also unreactive toward MeI) reacts with Me_3CI to give the stable oxidation product $(Me_3Si)_2NP(\underline{t}\text{-Bu})(I){=}NSiMe_3$.[21]

Reaction of 1 with $Fe_2(CO)_9$. (Methylene)phosphines have been found to form a variety of η^1 and η^2 complexes with transition metal moieties.[22] In a preliminary communication[23], we recently reported the novel η^1 complex $[(Me_3Si)_2NP=C(SiMe_3)_2]Fe(CO)_4$ 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 $Fe(CO)_4$ complex of the trisilylated ligand 1.

In fact, compound 1 reacts smoothly and quantitatively with one equivalent of $Fe_2(CO)_9$ (eq 10). After removal of solvent and $Fe(CO)_5$, 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.

$$(Me_3Si)_2NP=CHSiMe_3 \xrightarrow[-Fe(CO)_5]{Fe_2(CO)_9} \begin{matrix} (CO)_4Fe \\ \diagup \\ (Me_3Si)_2N \end{matrix} \!\!>\!\! P=C \!\!<\!\! \begin{matrix} SiMe_3 \\ \diagdown \\ H \end{matrix} \qquad (10)$$

1 → 9

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 $(Me_3Si)_2NP=C(SiMe_3)_2$ (δ 383) shifts upfield by ca. 72 ppm upon complexation to $Fe(CO)_4$. These differences might indicate that the less crowded P=C double bond in 9 is not as distorted from planarity as in the bis(trimethylsilyl)methylene analog. 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 cm^{-1}), and one weak (2024 cm^{-1}) carbonyl stretching bands. This pattern is characteristic[24] 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 amino(methylene)-phosphines have a rich and varied derivative chemistry. Although the sp^2-hybridized phosphorus center is weakly nucleophilic, it does complex with $Fe(CO)_4$ and the P=C double bond is susceptible to a wide range of 1,2-addition processes. Some of these reactions (e.g., with 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 P=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-BuLi, $Fe_2(CO)_9$, Ph_2PCl, $LiAlH_4$, Me_3SiCl, $H_2C{=}CHSiMe_2Cl$, t-BuI, and bromine. The solvents (C_6H_6, CH_2Cl_2, pentane, and Et_2O) were distilled from CaH_2 prior to use. The starting (methylene)phosphine 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 ^{1}H 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 ^{1}H NMR spectra of the mixture show the presence of 1, 2, and a third compound 2a (see above). After additon 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 $Me_2Si{=}CHCH_2$(t-Bu) was prepared according to the literature procedure[12] by the addition of t-BuLi (21 mL, 38 mmol, 1.8 M in pentane) to a solution of $CH_2{=}CHSiMe_2Cl$ (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)methyl](chloro)phosphine (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 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 cooling the mixture 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 140-165°C/0.03mm) which 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](methyl)phosphine (6). Using 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 stirring 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 which was identified by NMR spectroscopy, with only very minor impurities being detectable. Attempts to obtain an analytically pure sample of 6 either by 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](iodo)-phosphine (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 six days, the signals due to 1 had disappeared and new peaks assignable to 7 and $Me_2C{=}CH_2$ (δ 1.70, 6H; δ 4.60, 2H; ^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]phosphine}iron tetracarbonyl (9). Compound 1 (13.0 g, 46.7 mmol) was added to a slurry of $Fe_2(CO)_9$ (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 $Fe(CO)_5$ 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.

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

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Table I. NMR Spectral Data[a] for Derivatives of 1

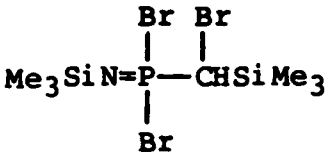
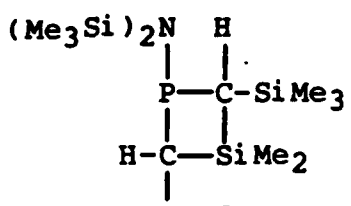
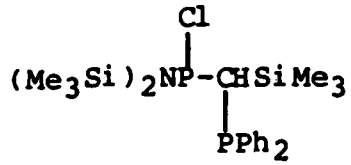
compd	signal	^{1}H NMR δ	^{1}H NMR J_{PH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
 2	Me_3SiC	0.16		-0.18	3.1	-51.4
	Me_3SiN	0.38		1.61	7.9	
	CH	3.74	13.2	46.52	89.7	
 3	$(Me_3Si)_2N$	0.20		5.25	7.3	59.9,
	Me_3SiC	0.03	2.9	2.12	4.9	61.9[b]
	Me_2Si	c		0.59	5.5	
	$SiCHSi$	d		23.48	44.6	
	$PCHSi$	d		29.70	47.0	
	CH_2	d		40.32	1.2	
	CMe_3	0.80		29.60		
	CMe_3			29.90	2.4	
 4	$(Me_3Si)_2N$	0.20	1.8	4.12	8.8	154.4
	Me_3SiC	-0.09	1.0	2.01	2.9	(-5.5)
	CH	3.12	20.9, 2.7	34.05	79.1, 32.2	
	Ph	7.1-7.6[f]		127-134[f]		

Table 1. 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
$(Me_3Si)_2NP(H)-CH(PPh_2)SiMe_3$	$(Me_3Si)_2N$	0.12	0.6	3.35	4.9	4.7
		0.11	0.6			(-10.4)
5	Me_3SiC	-0.02	0.6	1.50	9.8	6.1
		-0.21	1.2	0.58	3.9	(9.8)[b]
	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]		
$(Me_3Si)_2NP(Me)-CH(PPh_2)SiMe_3$	$(Me_3Si_2N$	0.18	1.3	4.92	6.1	49.6
	Me_3SiC	-0.20	0.9	2.24	3.7	(-3.4)
6	PMe	1.56	8.4 1.1	20.94	28.0 14.7	
	CH	2.46	9.1 1.5	26.52	53.7 29.3	
	Ph	7.1-7.7[f]		127-140[f]		
$(Me_3Si)_2NP(I)-CH_2SiMe_3$	$(Me_3Si)_2N$	0.37	1.8	3.63	9.2	173.9
	Me_3SiC	0.20	1.0	-0.06	5.5	
7	CH_2	2.25	10.3	30.76	67.8	

Table 1. 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
$(Me_3Si)_2NP$(→$Fe(CO)_4$)$CHSiMe_3$	$(Me_3Si)_2N$	0.29		2.79		305.5
	Me_3SiC	0.16	0.6	0.19	5.8	
9	CH	6.82	36.6	160.7	8.8	
	CO			213.4	23.5	

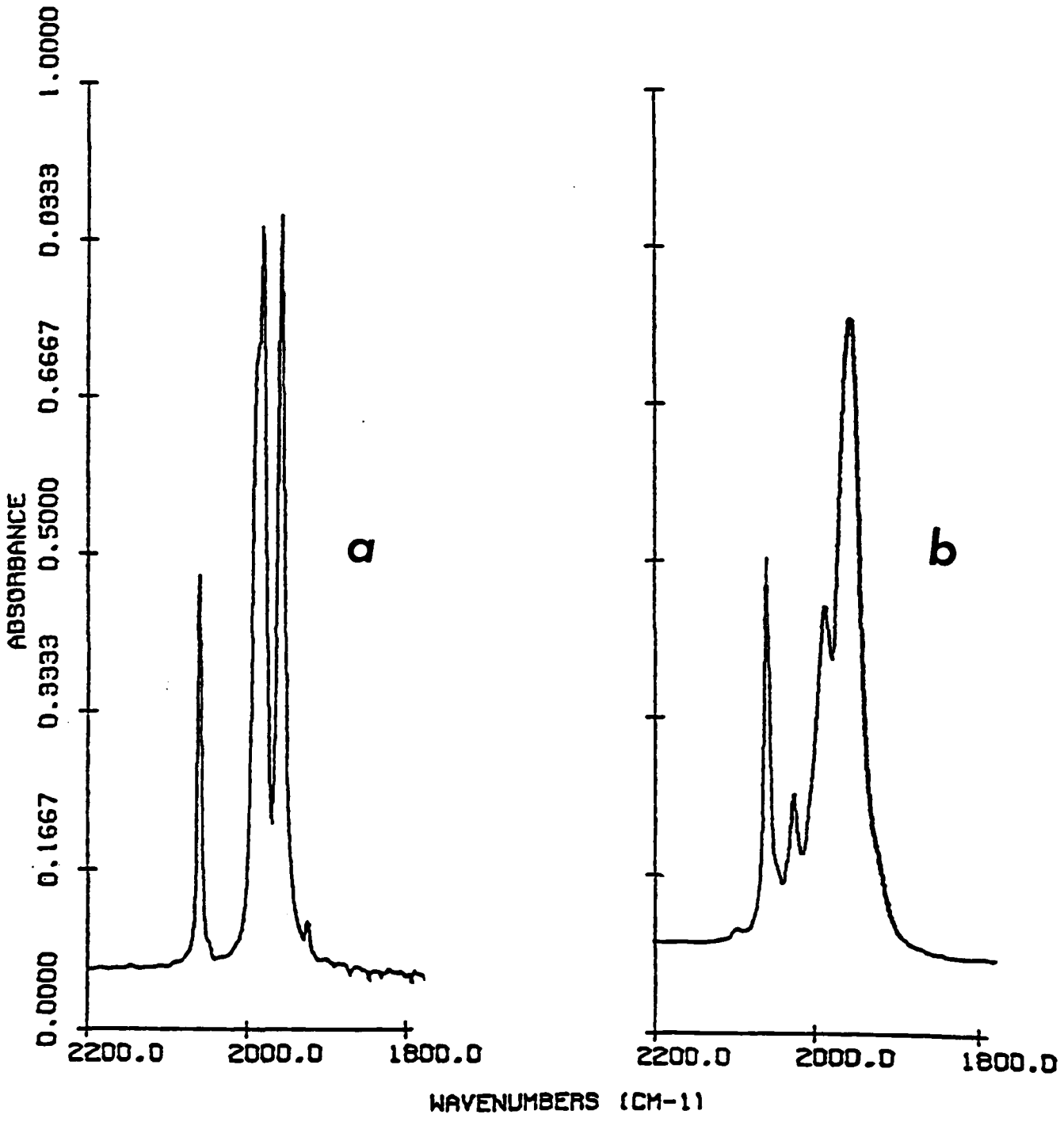
[a] Chemical shifts downfield from Me_4Si for ^{1}H and ^{13}C spectra and from H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvents: ^{1}H, CH_2Cl_2; ^{13}C and ^{31}P, $CDCl_3$. [b] Diastereomers. [c] Obscurred by Me_3Si signals. [d] Complex multiplet, δ 0.9-2.0. [e] Chemical shifts for PPh_2 group in parenthesis. $^2J_{PP}$ values in Hz: 227.0(4); 56.0 and 170.0 (5, diastereomers); 148.0(6). [f] Complex multiplet.

Table II. Preparative and Analytical Data

	preparative		analytical[a]	
Compd	% yield	bp, °C(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)

[a] Calcd values in parentheses. [b] Not distilled due to thermal instability. [c] Converted to known derivative 8 (see text). [d] Yield ca. 95% before distillation.

Figure 1. FT-IR spectra of [(methylene)phosphine]iron tetracarbonyl complexes $LFe(CO)_4$. (a) Equatorial substitution, $L = (Me_3Si)_2NP{=}C(SiMe_3)_2$. (b) Axial substitution, $L = (Me_3Si)_2NP{=}CHSiMe_3$ (1).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a
b
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2000.0
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2200.0
2000.0
1800.0
WAVENUMBERS (CM-1)

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