Synthesis and Reactivity of [Bis(trimethylsilyl)methylene]mesitylphosphine[1]

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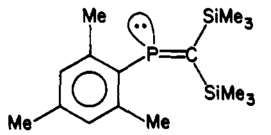
The title compound $MesP{=}C(SiMe_3)_2$ (2) is prepared by the dehydrohalogenation reaction of the chlorophosphine $MesP(Cl)CH(SiMe_3)_2$ (1) with DBU. The methylenephosphine 2 readily undergoes addition and oxidation reactions characteristic of a polar P=C double bond. Addition of methanol, for example, yields the methoxyphosphine $MesP(OMe)CH(SiMe_3)_2$ (4) while treatment with MeLi produces the reactive, ambident anion $[MesP(Me)C(SiMe_3)_2]^-$ (5). Reactions of 5 with MeOH and MeI afford the methylphosphine $MesP(Me)CH(SiMe_3)_2$ (6) and the stable ylide $MesPMe_2{=}C(SiMe_3)_2$ (7), respectively. Compound 6 is also obtained from 1 (by reaction with MeLi) or from the P–H phosphine $MesP(H)CH(SiMe_3)_2$ (3, prepared via 1 plus $LiAlH_4$) by treatment of its MeI salt with *n*-BuLi. A trisilylated iminomethylenephosphorane, $MesP({=}NSiMe_3){=}C(SiMe_3)_2$ (8), a methylenethioxophosphorane, $MesP({=}S){=}C(SiMe_3)_2$ (9), and a thiaphosphirane, $Mes\overline{P({=}S)SC}(SiMe_3)_2$ (10), result from the oxidation reactions of 2 with either Me_3SiN_3 or elemental sulfur. Compound 10 is smoothly desulfurized by $n\text{-}Bu_3P$ to yield 9. Proton, ^{13}C, and ^{31}P NMR data are reported for the new compounds, and the chemistry of 2 is contrasted and compared with that of other methylenephosphines such as $MesP{=}CPh_2$.

Introduction

In two recent papers,[2,3] we have described the synthesis and characterization of a series of *P*-mesityl-substituted phosphorus compounds containing Si–N–P and/or Si–C–P linkages. These systems are of interest, in part, as precursors to new types of "low-coordinate" phosphorus compounds including methylenephosphines, $RP{=}CR_2$[4] and iminomethylenephosphoranes, $RP({=}NR){=}CR_2$.[3,5] As an extension of these studies, we report here the synthesis and some derivative reactions of [bis(trimethylsilyl)methylene]mesitylphosphine.[6]



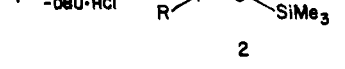
As well as imparting kinetic stability to such a compound, the silyl groups on carbon also serve to modify the reactivity of the P=C double bond. The π-acceptor ability of silicon should accentuate the polarity of the bond by stabilizing the dipolar form **b**. Thus, the chemistry of this

a b

(disilylmethylene)phosphine may be expected to be quite different, for example, from that of the diphenylmethylene analogue $MesP{=}CPh_2$ as prepared and studied by Bickelhaupt and co-workers.[7]

Results and Discussion

Synthesis of the Methylenephosphine. The new [bis(trimethylsilyl)methylene]phosphine 2 was prepared by the dehydrohalogenation of the appropriate chlorophosphine 1 (eq 1) using DBU (in 50% molar excess) as the HCl acceptor (eq 2). Similar dehydrohalogenation



$$RPCl_2 + (Me_3Si)_2CHMgCl \xrightarrow[THF]{-MgCl_2} R{-}P(Cl)CH(SiMe_3)_2 \quad (1)$$

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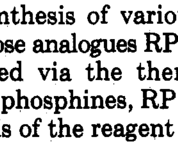

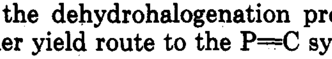

$$1 \xrightarrow[-DBU\cdot HCl]{DBU} RP{=}C(SiMe_3)_2 \quad (2)$$

2

procedures have been used in our laboratory[5a] and elsewhere[4,7] for the synthesis of various P=C derivatives. Alternatively, the close analogues $RP{=}C(SiMe_3)_2$ (R = Ph, *t*-Bu) were obtained via the thermolysis of [tris(trimethylsilyl)methyl]phosphines, $RP(Cl)C(SiMe_3)_3$.[8] The convenient synthesis of the reagent $(Me_3Si)_2CHCl$,[9] however, makes the dehydrohalogenation process a much simpler, higher yield route to the P=C system.

The methylenephosphine 2 was isolated by fractional distillation in ca. 65–70% yield as an air-sensitive yellow liquid that crystallized on standing. It was fully characterized by NMR spectroscopy (^1H, ^{13}C, and ^{31}P) and by elemental analysis (Table I and II). Noteworthy features of the NMR spectra of 2 include the ^{31}P and ^{13}C chemical shifts of the P=C moiety that confirm sp^2 hybridization

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[1] Presented in part at the International Conference on Phosphorus Chemistry, Nice, France, 1983. See: Neilson, R. H. *Phosphorus Sulfur* 1983, *18*, 43.

[2] Xie, Z.-M.; Neilson, R. H. *Organometallics* 1983, *2*, 291.

[3] Xie, Z.-M.; Neilson, R. H. *Organometallics* 1983, *2*, 1406.

[4] For a review, see: Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* 1981, *20*, 731.

[5] See, for example: (a) Neilson, R. H. *Inorg. Chem.* 1981, *20*, 1679. (b) Niecke, E.; Wildbredt, D.-A. *Angew. Chem., Int. Ed. Engl.* 1978, *17*, 199. (c) Niecke, E.; Seyer, A.; Wildbredt, D.-A. *Angew. Chem., Int. Ed. Engl.* 1981, *20*, 675. (d) Markovskii, L. N.; Romanenko, V. D.; Ruban, A. V.; Polyachenko, L. K. *J. Gen. Chem. USSR* (Engl. Transl.) 1983, *53*, 603.

[6] For a preliminary communication, see: Caira, M.; Neilson, R. H.; Watson, W. H.; Wisian-Neilson, P.; Xie, Z.-M. *J. Chem. Soc., Chem. Commun.* 1984, 698.

[7] See, for example: (a) Klebach, Th. C.; Lourens, R.; Bickelhaupt, F. *J. Am. Chem. Soc.* 1978, *100*, 4886. (b) van der Knaap, Th. A.; Klebach, Th. C.; Lourens, R.; Vos, M.; Bickelhaupt, F. *J. Am. Chem. Soc.* 1983, *105*, 4026. (c) van der Knaap, Th. A.; Klebach, Th. C.; Visser, F.; Bickelhaupt, F.; Ros, P.; Baerends, E. J.; Stam, C. H.; Konijn, M. *Tetrahedron* 1984, *40*, 765.

[8] Issleib, K.; Schmidt, H.; Wirkner, Ch. *Z. Anorg. Allg. Chem.* 1981, *473*, 85.

[9] Cowley, A. H.; Kemp, R. A. *Synth. React. Inorg. Met.-Org. Chem.* 1981, *11*, 591.

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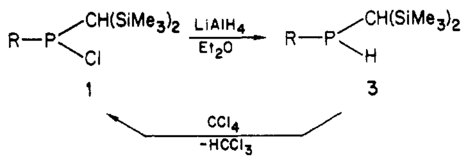
at these centers. In comparison to the related diphenylmethylene derivative,[7] the ^{31}P NMR signal is shifted to lower field by ca. 150 ppm. This is consistent with a more highly polarized P=C double bond having a greater degree of positive charge on phosphorus. Similar low-field shifts are known for other C-silylated methylenephosphines[5a,8] and for the isoelectronic disilylamino-substituted phosphenium ions, $R-P^+-N(SiMe_3)_2$.[10]

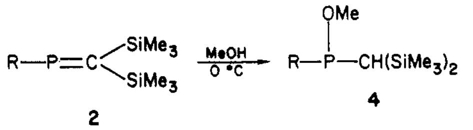
The NMR spectral data also shed light on some of the stereochemical features of **2**. In spite of the enhanced polarity, the degree of π-bonding is still sufficient to cause restricted rotation about the P=C double bond. This is clearly shown by the observation of nonequivalent Me_3Si groups in both the ^1H and ^{13}C NMR spectra (Table I). On the basis of other work,[5a,8,11,12] the signals having the larger couplings (J_{PH} and J_{PC}) to phosphorus can be reasonably assigned to the Me_3Si group that is in a cis relationship to the phosphorus lone pair (i.e., the *E* position in **2**). Rotation about the mesityl–P bond, on the other hand, is rapid on the NMR time scale as indicated by the simplicity of the signal patterns of the mesityl group in the ^{13}C spectrum.

In contrast to the methylenephosphine **2**, the chlorophosphine precursor **1** could not be completely purified and characterized due, in part, to its thermal instability. Nevertheless, **1** was routinely prepared (eq 1) in synthetically useful form as a viscous, orange liquid. It was characterized by ^1H and ^{31}P NMR spectroscopy in addition to its derivative chemistry. The reaction with $LiAlH_4$ (eq 3), for example, afforded the distillable P–H derivative **3** that upon treatment with CCl_4, was reconverted to **1**.



(3)

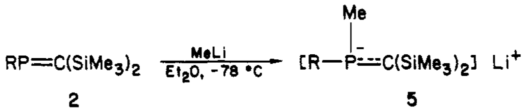
Reactions of the Methylenephosphine. Two general modes of reactivity of **2** were investigated: (1) addition of polar reagents to the P=C double bond and (2) oxidation of the phosphorus center to yield stable three-coordinate P(V) derivatives. In both cases, the silyl substituents on carbon help to greatly simplify the chemistry, first, by increasing the polarity of the double bond and, second, by kinetically stabilizing the products of many reactions.



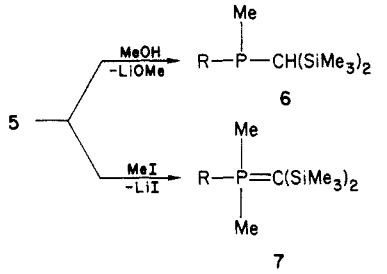
(4)

The first of these points is well illustrated by the addition of methanol to **2** that occurs rapidly and quantitatively at 0 °C (eq 4). In contrast, the diphenyl analogue MesP=CPh$_2$ is completely unreactive toward EtOH under similar conditions.[7b] Formation of the methoxyphosphine **4** clearly shows the polarity of the P=C double bond, and it parallels similar reactivity of some other methylenephosphines.[5a,12] The polarity can, however, be reversed by introducing π-donor substituents on carbon as demonstrated by recent MO calculations.[7c] Indeed, Becker[13] has obtained P–H products from the methanolysis of C–NMe$_2$ substituted methylenephosphines. The relatively high field ^{31}P shifts (ca. δ 10–90) of these latter compounds are also consistent with the reversed polarity P(δ–)–C(δ+) of their P=C double bonds.

A synthetically more useful reaction of the methylenephosphine **2** occurs with alkyllithium reagents. For example, treatment of **2** with 1 equiv of MeLi in Et$_2$O at –78 °C yields a solution of the reactive anion **5** (eq 5). Although it was not isolated, **5** appears to be stable in solution at room temperature (δ(^{31}P) –20.1). The ambident nature of anion **5** was demonstrated by its reactions with MeOH (eq 6) and MeI (eq 7) that gave the carbon- (**6**) and phosphorus-bonded (**7**) products, respectively. The identity of the methylphosphine **6** was confirmed by its preparation via two independent routes (eq 8 and 9) as well as NMR spectroscopy (Table I) and elemental analysis. The assignment of the ylide structure of **7**, a stable distillable liquid, was verified by NMR spectral data with two points being particularly diagnostic: (1) the equivalence of the *P*-methyl and *C*-silyl groups in both ^1H and ^{13}C spectra and (2) the dramatic upfield ^{13}C shift (δ –1.65) of the ylidic carbon.

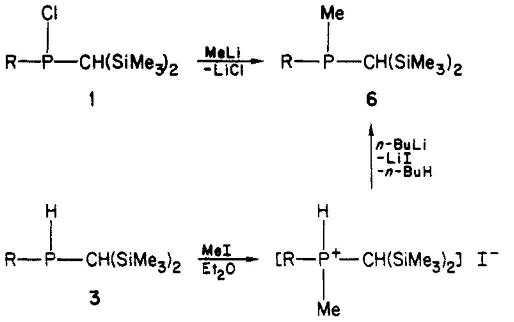


$$\underset{\mathbf{2}}{RP{=}C(SiMe_3)_2} \xrightarrow[Et_2O,\ -78\ ^\circ C]{MeLi} \underset{\mathbf{5}}{[R-\overset{Me}{\overset{|}{P}}{\overset{-}{\cdots}}C(SiMe_3)_2]}\ Li^+ \qquad (5)$$



$$\mathbf{5} \xrightarrow[-LiOMe]{MeOH} \underset{\mathbf{6}}{R-\overset{Me}{\overset{|}{P}}-CH(SiMe_3)_2} \qquad (6)$$

$$\mathbf{5} \xrightarrow[-LiI]{MeI} \underset{\mathbf{7}}{R-\overset{Me}{\overset{|}{\underset{Me}{\underset{|}{P}}}}{=}C(SiMe_3)_2} \qquad (7)$$



$$\underset{\mathbf{1}}{R-\overset{Cl}{\overset{|}{P}}-CH(SiMe_3)_2} \xrightarrow[-LiCl]{MeLi} \underset{\mathbf{6}}{R-\overset{Me}{\overset{|}{P}}-CH(SiMe_3)_2} \qquad (8)$$

$$\underset{\mathbf{3}}{R-\overset{H}{\overset{|}{P}}-CH(SiMe_3)_2} \xrightarrow[Et_2O]{MeI} [R-\overset{H}{\overset{|}{\underset{Me}{\underset{|}{P^+}}}}-CH(SiMe_3)_2]\ I^- \xrightarrow[-LiI,\ -n\text{-}BuH]{n\text{-}BuLi} \mathbf{6} \qquad (9)$$

The formation of anion **5** and its subsequent reactions provide good evidence that the reaction of methylenephosphines with organometallic reagents occurs by nucleophilic addition to the P=C double bond.[14] Other reactions of this type have involved two-coordinate phosphines bearing (Me$_3$Si)$_2$N[15] or Cl[4] groups on phosphorus in which nucleophilic substitution occurs. The first formed anionic intermediates, analogous to **5**, however, could not be detected in such cases.

The second general type of reaction; i.e., oxidation to the three-coordinate P(V) state is illustrated by the reaction of **2** with trimethylsilyl azide (eq 10) that gave the iminophosphorane **8**. Compound **8**, a thermally stable,

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[10] Cowley, A. H.; Kemp, R. A.; Wilburn, J. C. *Inorg. Chem.* **1981**, *20*, 4289 and references cited therein.

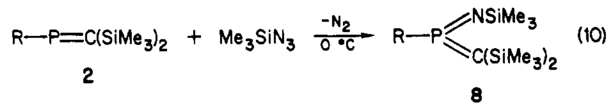
[11] Niecke, E.; Schoeller, W. W.; Wildbredt, D.-A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 131.

[12] Neilson, R. H.; Thoma, R. J.; Vickovic, I.; Watson, W. H. *Organometallics* **1984**, *3*, 1132.

[13] Becker, G.; Uhl, W.; Wessely, H.-J. *Z. Anorg. Allg. Chem.* **1981**, *479*, 41.

[14] van der Knaap, Th. A.; Bickelhaupt, F. *Tetrahedron Lett.* **1982**, *23*, 2037.

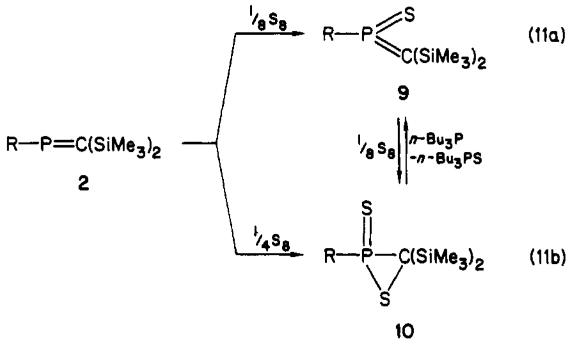
[15] (a) Li, B.-L.; Neilson, R. H. *Inorg. Chem.*, in press. (b) Romanenko, V. D.; Ruban, A. V.; Markovski, L. N. *J. Gen. Chem. USSR (Engl. Transl.)* **1983**, *53*, 679.



(10)

distillable product, was readily characterized by its ^{31}P (δ 120.0) and ^{13}C [δ 75.12 (J_{PC} = 81.8 Hz] NMR spectra and elemental analysis. The NMR data preclude the possibility of the isomeric cyclic structure $\overline{\mathrm{RPN(SiMe_3)C}}\mathrm{(SiMe_3)_2}$ for **8** since such strained ring systems normally have very high-field ^{31}P shifts.[5c] The observation of three distinct Me$_3$Si signals in both the ^{1}H and ^{13}C spectra show that there is restricted rotation, as in **2**, about the P=C double bond. The stabilizing influence of the Me$_3$Si groups is clearly evident here since the related disilylated compound MesP(=NSiMe$_3$)=CHSiMe$_3$[3] is stable for only a few hours at room temperature.

The oxidation of methylenephosphine **2** by elemental sulfur (eq 11) was also studied as part of this project.[6]



Treatment of **2** with 1 equiv of sulfur resulted in an inseparable mixture of the methylene thioxophosphorane **9**, the thiaphosphirane **10**, and starting material **2**. Addition of a second equivalent of sulfur afforded complete conversion of the mixture to **10**. A pure sample of **9** was then obtained by the desulfurization reaction of **10** with n-Bu$_3$P. Both **9** and **10** are fully characterized, crystalline solids that have been studied by X-ray crystallography.[6] The methylenethioxophosphorane **9** represents a stable analogue to the intermediate proposed by Bickelhaupt[7b] for the oxidation of MesP=CPh$_2$ by sulfur. Earlier, Niecke and Wildbredt[16] had reported stable, but noncrystalline, analogues of both **9** and **10** from the sulfur oxidation of (Me$_3$Si)$_2$NP=CHSiMe$_3$.

The ^{13}C and ^{31}P NMR spectra of **9** (Table I) show the expected low-field signals for the sp^2-hybridized carbon and phosphorus atoms. The trigonal-planar geometry at both centers and the short P=C double bond (1.65 Å) were confirmed by the X-ray structural analysis.[6] Moreover, the two widely separated signals for the Me$_3$Si groups in the ^{13}C and ^{1}H NMR spectra of **9** indicate that, even in solution, the Me$_3$Si groups are locked into different environments by the restricted rotation about the P=C double bond.

In the three-membered ring system **10**, both the P–C carbon and phosphorus resonances occur at significantly higher field than in **9**, reflecting the hybridization change.[6] The value of J_{PC} (8.6 Hz) in **10** is exceptionally low in comparison to the already small coupling constant (J_{PC} = 28.2 Hz)[16] in $\mathrm{(Me_3Si)_2N}\overline{\mathrm{P(=S)SC}}\mathrm{HSiMe_3}$. The additional ring strain in **10** caused by the two bulky Me$_3$Si substitutents on the ring is probably responsible for this difference. The steric congestion in **10** is also apparent in the ^{13}C NMR spectrum that shows a doubling of all of the mesityl signals due to hindered rotation about the mesityl-P bond.

As a final point of interest, the facile conversion of **9** to **10** by the second equivalent of sulfur may be viewed as the formation of a π-complex between the P=C bond of **9** and the sulfur atom. The extension of this concept to the possible preparation of π^2-complexes of **9**, and the related compound **8**, with transition metals is under investigation.

Experimental Section

Materials and General Procedures. The following reagents were obtained from commercial sources and used without purification: LiAlH$_4$, MeLi, n-BuLi, MeI, Me$_3$SiN$_3$, sulfur, n-Bu$_3$P, and MeOH. Tetrahydrofuran (THF) was distilled from Na/benzophenone immediately prior to use. Other solvents were distilled from CaH$_2$. Moisture was removed from DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) as the azeotrope with benzene. The DBU was then distilled [bp 80–83 °C (0.6 mm)] and stored over molecular sieves. The published procedure[9] was used to prepare (Me$_3$Si)$_2$CHCl on a 0.5–0.7-mol scale from Me$_3$SiCl, CH$_2$Cl$_2$, and n-BuLi. Mesityldichlorophosphine, MesPCl$_2$, was prepared as before[2] from PCl$_3$ and MesMgBr. When prepared in this manner, MesPCl$_2$ usually contains small amounts (ca. 10–20%) of the P–Br analogues due to halide exchange. This does not interfere with its subsequent derivative reactions. 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. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. All reactions and other manipulations were carried out under an atmosphere of dry nitrogen and/or under vacuum. The procedures described herein are typical of those used for the preparation of the new compounds in this study.

[Bis(trimethylsilyl)methyl]magnesium Chloride. A few milliliters of a solution of (Me$_3$Si)$_2$CHCl (9.73 g, 0.050 mol) in THF (25 mL) was added to a preheated flask (ca. 90 °C) containing Mg turnings (1.15 g, 0.050 mol). After the reaction started, the remaining solution was added continuously at a rate sufficient to maintain reflux. The mixture was then refluxed for 3 h (or stirred overnight at room temperature), cooled, and diluted with THF (25 mL) to afford an approximately 1 M solution of the Grignard reagent. When the use of larger quantities (ca. 0.1–0.5 mol) was required, the following procedure[17] was found to be more convenient. A 500-mL round-bottom flask was equipped with a magnetic stir bar, an addition funnel, and a reflux condenser. The flask was charged with Mg turnings (6.60 g, 0.272 mol) and THF (70 mL). The Mg was activated with 1,2-dibromoethane (2.0 mL, 0.023 mol). When the evolution of ethylene had subsided, a solution of (Me$_3$Si)$_2$CHCl (46.3 g, 0.238 mol) in THF (170 mL) was added dropwise at a rate sufficient to maintain steady reflux of the THF. After the addition was complete, the solution was allowed to stir for ca. 2 h. The mixture was usually then transferred via a double-ended syringe needle to an addition funnel for use in subsequent reactions.

[Bis(trimethylsilyl)methyl]chloromesitylphosphine (1). A solution of (Me$_3$Si)$_2$CHMgCl (50 mL, ca. 1 M in THF) was added dropwise to a stirred solution of MesPCl$_2$ (11.0 g, 0.050 mol) in THF (50 mL) at 0 °C. The mixture was stirred overnight at room temperature, THF was removed under reduced pressure, and hexane (100 mL) was added. After filtration and solvent removal, the viscous orange liquid that remained was identified as **1** by ^{1}H and ^{31}P NMR spectral data (Table I). Attempted purification by distillation resulted in decomposition to unidentified products. The ^{31}P spectrum of **1** indicates the presence of an impurity (ca. 10%), believed to be the bromophosphine analogue (δ(^{31}P) 110.5) due to bromide contamination in the MesPCl$_2$. Nevertheless, this crude product **1** gave satisfactory yields of pure derivatives **2** and **3**.

[Bis(trimethylsilyl)methylene]mesitylphosphine (2). A stirred solution of **1** (27.6 g, 0.080 mol), prepared as above, in Et$_2$O (200 mL) was treated with DBU (19.4 mL, 0.13 mol) at room temperature. A white solid formed while the mixture was stirred

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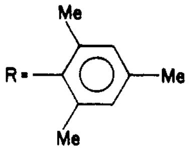
(16) Niecke, E.; Wildbredt, D.-A. *J. Chem. Soc., Chem. Commun.* 1981, 72.

(17) Ford, R. R. Ph.D. Dissertation, Texas Christian University, Fort Worth, TX, 1984.

Table I. NMR Spectroscopic Data[a] for Mesityl (R)-Phosphorus Compounds



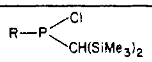
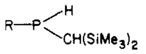
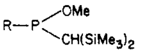
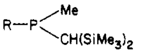
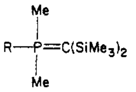
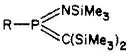
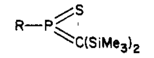
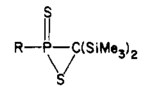
compd	signal	^{1}H NMR δ	^{1}H NMR J_{PH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
 1	Me_3Si	−0.08				104.9
		0.32	1.5			
	CH	2.27	12.0			
	o-Me	2.67				
	p-Me	2.26				
	C_6H_2	6.90	3.2			
$R{-}P{=}C(SiMe_3)_2$ 2	Me_3Si	−0.20		1.76	3.0	381.0
		0.27	1.9	2.35	17.7	
	P=C			204.18	86.9	
	o-Me	2.19		21.78	8.2	
	p-Me	2.19		21.11		
	C_6H_2	6.79				
	C_1			143.12	64.1	
	$C_{2,6}$			138.23	1.2	
	$C_{3,5}$			128.36		
	C_4			137.82		
 3	Me_3Si	0.07		0.73		−88.56
		0.10		1.03	4.3	
	CH	0.78	0.0[b]	5.68	37.2	
	PH	4.67	218[b]			
	o-Me	2.53		23.02	12.2	
	p-Me	2.12		20.83		
	C_6H_2	7.00	2.3			
	C_1			131.63	23.8	
	$C_{2,6}$			142.13	13.4	
	$C_{3,5}$			128.93	2.4	
	C_4			137.70		
 4	Me_3Si	−0.11		1.32	4.9	139.9
		0.24		2.39	4.9	
	CH	1.84	5.3	19.90	51.9	
	OMe	3.59	15.1	54.96	22.6	
	o-Me	2.62		21.91	20.1	
	p-Me	2.23		20.99		
	C_6H_2	6.83	1.2			
	C_1			134.94	47.3	
	$C_{2,6}$			143.00	17.7	
	$C_{3,5}$			129.80	3.0	
	C_4			139.25	1.2	
 6	Me_3Si	−0.17		1.40	4.3	−42.9
		0.19		2.53	5.5	
	CH	1.26	3.1	15.02	19.5	
	PMe	1.43	6.6	11.95	53.3	
	o-Me	2.53		23.29	20.1	
	p-Me	2.19		20.83		
	C_6H_2	6.81	2.4			
	C_1			135.04	25.0	
	$C_{2,6}$			143.45	15.3	
	$C_{3,5}$			129.71	3.7	
	C_4			138.31	1.2	
 $R{-}P(Me)_2{=}C(SiMe_3)_2$ 7[c]	Me_3Si	−0.07		5.98	4.0	6.6
	PMe_2	1.80	11.5	26.26	54.7	
	P=C			−1.65	61.5	
	o-Me	2.58		24.76	2.0	
	p-Me	2.21		21.05		
	C_6H_2	6.87	3.3			
	C_1			131.87	81.1	
	$C_{2,6}$			141.93	8.8	
	$C_{3,5}$			131.67	10.7	
	C_4			140.18	2.9	
 8	*Me*$_3$SiC	−0.21		2.56	1.2	120.0
		0.28		2.96	2.4	
	Me_3SiN	−0.25		1.96	4.3	
	P=C			75.12	81.8	
	o-Me	2.52	1.8	22.51	6.7	
	p-Me	2.04		21.44		
	C_6H_2	6.91	2.8			
	C_1			136.66	80.0	

Table I (*Continued*)

compd	signal	^{1}H NMR δ	^{1}H NMR J_{PH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
	$C_{2,6}$			137.84	9.2	
	$C_{3,5}$			128.18	10.4	
	C_4			140.97	3.0	
 9	Me_3Si	−0.22		2.11		190.9
		0.39		2.56		
	P=C			126.00	34.2	
	o-Me	2.51	1.5	22.50	7.3	
	p-Me	2.23		21.48		
	C_6H_2	6.91	4.8			
	C_1			131.74	78.7	
	$C_{2,6}$			137.99	8.5	
	$C_{3,5}$			128.79	11.6	
	C_4			141.78	3.1	
 10[d]	Me_3Si	−0.26		−0.14	3.1	2.60
		0.38		1.66	3.4	
	P=C			26.39	8.6	
	o-Me	2.66	1.5	22.76	4.3	
		2.57	1.1	22.19	5.5	
	p-Me	2.20		21.15	1.2	
	C_6H_2	6.83				
		6.89				
	C_1			133.09	97.1	
	$C_{2,6}$			139.08	7.3	
				138.29	12.8	
	$C_{3,5}$			129.91	13.4	
				128.99	14.0	
	C_4			141.58	3.0	

[a] Chemical shifts downfield from Me_4Si for ^{1}H and ^{13}C and from H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvents: ^{1}H, CH_2Cl_2; ^{13}C and ^{31}P, $CDCl_3$ except where noted. [b] J_{HCPH} = 7.5 Hz. [c] Solvent: CD_2Cl_2. [d] Hindered rotation about R-P bond.

Table II. Preparative and Analytical Data

compd	preparative % yield	preparative bp, °C (mm)	analytical[a] % C	analytical[a] % H
2	66	77-75 (0.01)	61.88 (62.33)	9.68 (9.41)
3	47	89 (0.03)	61.31 (61.91)	9.64 (9.99)
4	87	84-85 (0.03)	59.65 (60.17)	9.75 (9.72)
6	82	92-93 (0.02)	62.32 (62.91)	10.22 (10.25)
7	80	114-115 (0.03)	63.26 (63.85)	10.25 (10.42)
8	80	89-90 (0.02)	57.56 (57.71)	9.67 (9.61)
9	49	90 (0.01)	56.32 (56.42)	8.56 (8.58)
10	70	mp 139-141	51.75 (51.56)	7.98 (7.84)

[a] Calculated values in parentheses.

overnight. The Et_2O was removed, and hexane (200 mL) was added. After filtration and solvent removal, fractional distillation through a 10-cm Vigreux column afforded **2** as a yellow liquid that solidified upon standing (mp 32–33 °C).

[Bis(trimethylsilyl)methyl]mesitylphosphine (3). A solution of $LiAlH_4$ (30 mL, 1.0 M in Et_2O, 0.12 mol of hydride) was added dropwise to a stirred solution of **1** (34.5 g, 0.10 mol) in Et_2O (100 mL) at 0 °C. After being stirred overnight at room temperature, the mixture was filtered and the solvent was removed under vacuum. Distillation afforded **3** as a colorless liquid.

Reaction of 3 with CCl_4. Carbon tetrachloride (1.5 g) was added to a solution of **3** (3.0 g) in CH_2Cl_2 (15 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 72 h. Solvent removal left **1** as a viscous liquid that was spectroscopically identical with that prepared as described above.

[Bis(trimethylsilyl)methyl]mesitylmethoxyphosphine (4). Anhydrous methanol (0.54 g, 17 mmol) was added at 0 °C to a neat sample of **2** (5.4 g, 17 mmol). After the mixture was stirred 4 h at room temperature, distillation gave **4** as a colorless liquid.

[Bis(trimethylsilyl)methyl]mesitylmethylphosphine (6). (a) From Anion 5. Methyllithium (24 mL, 1.4 M in Et_2O, 34 mmol) was added via syringe to a stirred solution of methylenephosphine **2** (10.5 g, 34 mmol) in Et_2O (70 mL) at −78 °C. The mixture was warmed to room temperature and was stirred for 30 min. Quantitative formation of the anion **5** (δ(^{31}P) −20.1) was shown by ^{31}P NMR. The mixture was recooled to −78 °C, and MeOH (1.1 g, 34 mmol) was added. The mixture was warmed to room temperature, stirred overnight, and freed of solvent. Following addition of hexane (100 mL), filtration, and solvent removal, distillation afforded **6** as a colorless liquid. **(b) From Chlorophosphine 1.** In a 10-mm NMR tube, **1** (*ca.* 1 mmol in 1 mL of Et_2O) was treated with an equivalent of MeLi in Et_2O. Complete conversion to **6** was indicated by ^{31}P and ^{1}H NMR spectroscopy (the ^{1}H NMR signals of **6** were not obscurred by those of the Et_2O solvent). **(c) From P-H Phosphine 3.** In a similar manner, **3** was allowed to react with 1 equiv of MeI in Et_2O solution. Formation of the intermediate phosphonium salt $[MesP^+(Me)(H)CH(SiMe_3)_2]I^-$ was shown by ^{31}P NMR [δ 114.15 (J_{PH} = 476 Hz)]. Addition of an equimolar quantity of *n*-BuLi resulted in an exothermic reaction with complete conversion to **6**. Presumably, less reactive bases could also be used to dehydrohalogenate the phosphonium salt.

[Bis(trimethylsilyl)methylene]dimethylmesitylphosphorane (7). Iodomethane (1.4 g, 10 mmol) was added via syringe to a stirred solution of anion **5** (8.4 mmol) in Et_2O (15 mL) at −78 °C. With the same workup procedure as described above for **6**, compound **7** was isolated by distillation as a colorless liquid. The product reacted with $CDCl_3$ to give a mixture of two products (δ(^{31}P) 23.3 and 20.0) that were not identified. The ^{13}C and ^{31}P NMR spectra of **7** were, therefore, recorded by using CD_2Cl_2 as the solvent.

[Bis(trimethylsilyl)methylene]mesityl[(trimethylsilyl)imino]phosphorane (8). A neat sample of compound **2** (12.0 g, 39 mmol) was treated at 0 °C with an excess of Me_3SiN_3 (7.5

g, 65 mmol). An exothermic reaction occurred with evolution of a gas, presumably N_2. Distillation afforded **8** as a colorless liquid that solidified on standing (mp 49–50 °C).

[Bis(trimethylsilyl)methylene]mesitylthioxophosphorane (9). Tri-*n*-butylphosphine (2.1 mL, 8.4 mmol) was added via syringe to a stirred solution of **10** (3.12 g, 8.4 mmol, prepared as described below) in benzene (10 mL) at 0 °C. After the mixture was warmed to room temperature, ^{31}P NMR showed the formation of **9** and $n\text{-}Bu_3P{=}S$ (δ 46.50). The solvent was removed and distillation through a short-path column gave a yellow liquid that solidified in the receiving flask and the condenser. The solids were combined and recrystallized from hexane to give **9** as white crystals (mp 95–100 °C).

Thiaphosphirane (10). Sulfur (0.9 g, 28 mmol) was added to a stirred solution of **2** (4.4 g, 14 mmol) in benzene (80 mL) at room temperature. After the mixture was stirred overnight, the solvent was removed and the solid product was recrystallized from hexane (25 mL) to give **10** as white crystals (mp 139–141 °C). Preliminary experiments showed that the reaction of **2** with 1 equiv of sulfur gave an inseparable mixture of **9**, **10**, and unreacted **2**.

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

Registry No. **1**, 92270-32-1; **2**, 89982-70-7; **3**, 92270-33-2; **4**, 89982-71-8; **5**, 92284-16-7; **6**, 89982-77-4; **7**, 89982-76-3; **8**, 89982-72-9; **9**, 89982-73-0; **10**, 89982-74-1; $(Me_3Si)_2CHMgCl$, 86509-05-9; $MesPCl_2$, 6781-96-0.

Synthesis of the First Carbodiarsorane and Related Arsenic Ylides

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Bis(diphenylarsino)methane (**1**) gives only a monoquaternization product, **2**, with methyl iodide but is converted into the bis(arsonium) salt **4** when methyl fluorosulfate is employed. **2** is the precursor for the monoylide $MePh_2As{=}CHAsPh_2$ (**3**) while **4** yields the first bis(ylide) ("carbodiarsorane") $MePh_2As{=}C{=}AsPh_2Me$ (**5**) on treatment with sodium amide in liquid ammonia at −40 °C. **5** is thermally unstable at room temperature but can be reprotonated with acid to give the corresponding dication of salts **4**.

Introduction

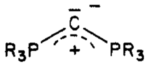
Carbodiphosphoranes,[1-3] $R_3P{=}C{=}PR_3$, have attracted considerable interest as versatile reagents in organic synthesis,[4] as ligands for both main-group and transition metals,[5] and as materials with intriguing physical properties.[6]

A large variety of open-chain and cyclic compounds containing the P=C=P moiety has been prepared as summarized in a recent publication from this laboratory.[7] Results of structural studies of several prototypes have indicated that the PCP bond angle is quite flexible and can vary between 180° and at least 116°.[8,9] The thermal stability of the compounds is quite satisfactory even for strained cyclic species.[10]

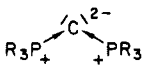
Formulas Ia–c are used for a general description of structure and bonding in carbodiphosphoranes, with the main emphasis on the semiylidic formula Ib. It has been pointed out, however, that according to Ic, pertinent compounds may also be considered as phosphine complexes of elemental carbon,[3] in line with a description of simple phosphorus monoylides as phosphine complexes of methylene, CH_2 (IIb).

$R_3P{=}C{=}PR_3$

Ia



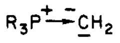
Ib



Ic

$R_3P{=}CH_2$

IIa



$R_3\overset{+}{P}\rightarrow\overset{-}{\underline{C}}H_2$

IIb

Analogous carbodiarsoranes, $R_3As{=}C{=}AsR_3$, have not yet been reported,[11] and even monoylides of arsenic of the type $R_3As{=}CH_2$[12-15] are thermally quite unstable materials. The mode of decomposition of the latter is best understood if a dissociation into tertiary arsines and carbenes is assumed. Therefore, carbodiarsoranes could be expected to be carriers or transfer reagents for carbon atoms, and a study was initiated to follow this idea, if suitable precursors could be generated. We report here the synthesis of the title compounds, whose reactivity is presently under investigation.

Experimental Section

General Data. All experiments were carried out under an atmosphere of pure and dry nitrogen. Glassware was dried at 140 °C and filled with nitrogen. Solvents were dried over sodium/benzophenone (diethyl ether, tetrahydrofuran), calcium hydride (benzene, toluene, pentane), or phosphorus pentoxide (dichloromethane, chloroform) and kept under nitrogen after distillation.

Bis(diphenylarsino)methane, **1**, was prepared from triphenylarsine following a literature procedure.[16]

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