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A New Synthesis and the Molecular Structure of Trimethyl(silylmethylene)phosphorane in the Gas Phase, Determined by Electron Diffraction

E. A. V. Ebsworth[a], *David W. H. Rankin*[a]*, *Beate Zimmer-Gasser*[b] and *Hubert Schmidbaur*[b]*

Department of Chemistry, University of Edinburgh[a],
West Mains Road, Edinburgh EH9 3JJ, Scotland, and
Anorganisch-Chemisches Institut der Technischen Universität München[b],
Lichtenbergstr. 4, D-8046 Garching

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Trimethyl(silylmethylene)phosphorane (**1**) has been prepared in a reaction of $H_3SiCH_2CH_2Cl$ and $(CH_3)_3P=CH_2$ in a molar ratio 1 : 2. C_2H_4 is evolved in a β-elimination process, followed by formation of $[(CH_3)_4P]^+Cl^-$ in a transylidation step. – The molecular structure of $(CH_3)_3P=CHSiH_3$ in the gas phase has been determined by electron diffraction. Principal bond lengths (r_a) are: P – C = 180.7(8), P = C = 165.3(11), Si – C = 185.2(20) pm. The angles between the P – C(methyl) bonds are 103.4(13)° and the Si – C = P angle is 123.4(8)°, consistent with a planar configuration of the methylene carbon atom. The molecule adopts a conformation in which the Si – C bond is twisted 25° from a position in which it eclipses one P – C bond, but there is a large amplitude torsional vibration about the P – C bond.

Eine neue Synthese und die Molekülstruktur von Trimethyl(silylmethylen)phosphoran durch Elektronenbeugung in der Gasphase

Trimethyl(silylmethylen)phosphoran (**1**) entsteht in der Reaktion von $H_3SiCH_2CH_2Cl$ mit $(CH_3)_3P=CH_2$ im Molverhältnis 1 : 2, wobei in einer β-Eliminierung C_2H_4 entwickelt und in einer Umylidierungsstufe $[(CH_3)_4P]^+Cl^-$ gebildet wird. Die Molekülstruktur von $(CH_3)_3P=CHSiH_3$ in der Gasphase wurde durch Elektronenbeugung bestimmt. Wichtigste Bindungslängen r_a sind P – C = 180.7(8), P = C = 165.3(11) und Si – C = 185.2(20) pm. Die Winkel CPC der Trimethylphosphangruppe betragen 103.4(13)°, der Si – C = P-Winkel 123.4(8)°, in Einklang mit einer planaren Konfiguration am Ylid-C-Atom. Das Molekül besitzt eine Konformation, in der die Si – C-Bindung um 25° von der Position weggedreht ist, in der sie mit einer P – C-Bindung eclipsed steht. Die Amplitude der Drehschwingungen um die P – C-Bindung ist jedoch beträchtlich hoch.

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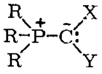
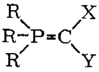
Introduction

Silicon has a pronounced stabilizing effect on neighbouring carbanions[1]. This effect renders CH_3-Si groups more acidic than CH_3-C groups and makes $R_3SiCH_2^-M^+$ compounds readily accessible[2]. In the light of these general phenomena it is surprising that no organometallic compound of the type $H_3SiCH_2^-M^+$ has ever been reported. Attempts to synthesize H_3SiCH_2Li or H_3SiCH_2MgX reagents in this laboratory have failed[3], and in contrast to the plethora of $[(CH_3)_3SiCH_2]_nM$ species, e.g.,[4] no complexes with either terminal or bridging $H_3Si-CH_{(2)}$ groups are available.

The mono- and disilylated phosphorus ylides $(CH_3)_3P^+-CH^--SiH_3$ and $(CH_3)_3P^+-C^-(SiH_3)_2$, first prepared in 1970, are therefore at present the only model compounds for a study of bonding and reactivity of silylated carbanions[1]. In previous investigations it has been demonstrated that $(CH_3)_3P^+-CH^--SiH_3$ is thermally unstable and undergoes elimination of molecular hydrogen to form a cyclic tris-ylide $[(CH_3)_3PCSiH_2]_3$[5]. This instability made a new method of synthesis desirable, which would allow the preparation at low temperature and with a minimum of workup and purification procedures. Such a method is now described and from the pure product obtained the molecular structure could be determined by electron diffraction. This structural work is an extension of the earlier study on the ylides $(CH_3)_3PCH_2$[6] and $(CH_3)_3PCP(CH_3)_3$[7]. In ylides of this type there is considerable interest in the nature of the phosphorus-carbon bond. The carbanion formulation I gives the $P-C$ bond the formal order 1. However, formulation II is also consistent with simple rules of valence-theory, and here the $P-C$ bond is of formal order 2.



I



II

In a recent study[6] of the molecular structure of trimethyl(methylene)phosphorane in the gas phase a phosphorus-carbon bond length of 164.0(6) pm, corresponding to a bond order of 2.0, was found, and thus provided evidence in support of the ylene formulation, II. However in the electron diffraction radial distribution curve for this compound, the peaks due to atom pairs involving the methylene hydrogen atoms overlapped with those involving the more numerous methyl hydrogen atoms, and it was not possible to establish whether the methylene carbon atom had a trigonal planar or a pyramidal configuration.

It was therefore desirable that a study should be made of the structure of a compound in which heavy atoms defined the configuration of the methylene carbon atom. In hexamethylcarbodiphosphorane a linear $P=C=P$ unit would be expected for the ylene form, but although the evidence from a study of the vapour by electron diffraction[7] did indicate that the average structure was linear, the situation was confused by a large amplitude bending vibration which gave rise to a large shrinkage effect.

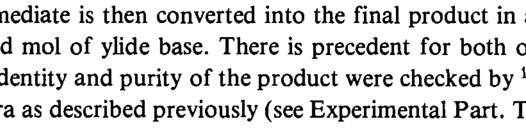
The ideal candidate for study would be isopropylidenetrimethylphosphorane, but in such compounds hydrogen shifts take place, and in this case rearrangement to isopropyldimethylmethylenephosphorane occurs[8]. The simplest compound available was therefore trimethyl(silylmethylene)phosphorane (**1**); a wide Si – C = P angle in this would provide support for the ylene representation. There is, of course, the possibility that a planar arrangement of the bonds at carbon could arise by delocalisation of the lone pair of electrons on carbon in the ylide form, I, into vacant silicon 3d orbitals. However, it would be expected that such delocalisation would also lead to a considerable shortening of the silicon-carbon bond.

In this paper we describe a new method of synthesis of **1** and present the results of our study of its gas phase structure.

Synthesis of $(CH_3)_3PCHSiH_3$ (1) in a β-Elimination Process

The previously used preparation of the title compound used H_3SiCH_2Cl as a starting material[1,8]. This (unstable) precursor was quaternized by $(CH_3)_3P$ and the resulting phosphonium salt treated with $(CH_3)_3PCH_2$ as a strong base[1], to yield the transylidation products $[(CH_3)_4P]Cl$ and $(CH_3)_3PCHSiH_3$[5]. Following earlier observations with β-haloethylsilicon compounds[9], a new one-step procedure starting from $H_3SiCH_2CH_2Cl$ was developed. The reaction of this β-chloroethylsilane with two equivalents of the ylide $(CH_3)_3PCH_2$, which can act both as an nucleophile and as a base, leads directly to the same transylidation products with concomitant evolution of ethylene. After filtration of the phosphonium salt and removal of the solvent **1** remains in a very pure form, as the synthesis can easily be carried out at low temperature.

$$2\ (CH_3)_3P{=}CH_2 + H_3SiCH_2CH_2Cl \xrightarrow[-C_2H_4]{} \underset{\mathbf{1}}{(CH_3)_3P{=}CH{-}SiH_3} + [(CH_3)_4P]Cl$$



In the proposed mechanism, initial attack of the ylidic carbanion is believed to occur at silicon, followed by elimination of ethylene and chloride ion. The phosphonium salt intermediate is then converted into the final product in a transylidation step with the second mol of ylide base. There is precedent for both of the assumed reactions[1,5,9]. The identity and purity of the product were checked by ^1H-, ^{13}C-, ^{29}Si-, and ^{31}P NMR spectra as described previously (see Experimental Part. The spectra of $H_3SiCH_2CH_2Cl$ are also included therein).

Molecular Model, Refinement, and Results

For least-squares refinements of the structure of trimethyl(silylmethylene)phosphorane (**1**) it was assumed that the $C-SiH_3$ and the three $P-CH_3$ groups had local C_{3v} symmetry, and that the $C-P(CH_3)_3$ unit had C_{3v} symmetry, with a methyl twist angle defined to be zero when one CH bond of each group was *trans* to the P – C(methylene) bond. It was also assumed that the single methylene hydrogen lay in the P = C – Si plane, with the CH bond making equal angles with the P = C and Si – C bonds, that all C – H bond lengths were equal, and that the conformation of the silyl group was such that one Si – H bond was *trans* to one P – C bond. With these assump-

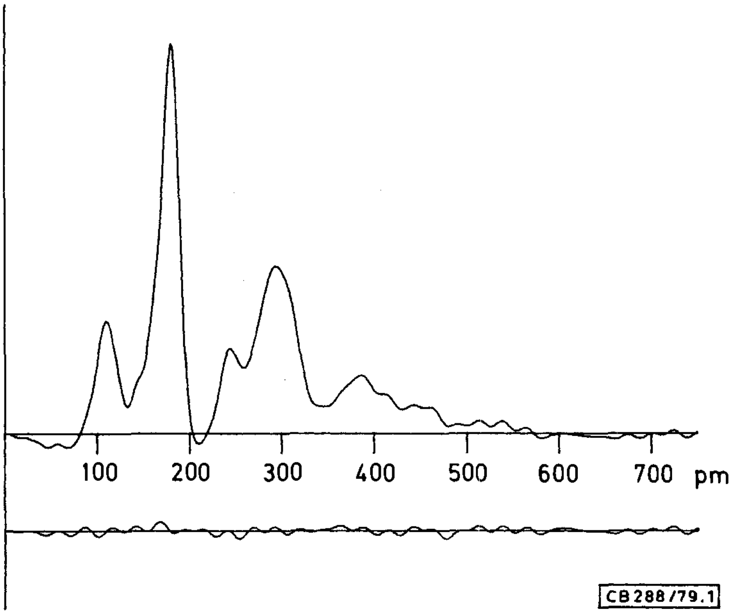


Figure 1. Electron diffraction radial distribution curve, $P(r)/r$, and difference curve for $(CH_3)_3P=CHSiH_3$ (**1**). Before Fourier inversion the data were multiplied by $s \cdot \exp[-0.000015\, s^2/(z_{Si}-f_{Si})(z_C-f_C)]$

Table 1. Electron diffraction of **1**. Least squares correlation matrix, multiplied by 100

r1	r2	r4	r5	<1	<2	<3	<5	<6	u5	u6	u7	u10	u12	u13	k1	k2	
100	-56	-9	20	-93	48	14	23	33	8	-8	-7	70	-7	30	47	49	r1
	100	39	26	77	-20	-4	-7	-59	-19	-1	-7	-78	-6	-14	-84	-73	r2
		100	4	24	42	36	-16	-55	-13	-27	-4	-47	0	-1	-40	-36	r4
			100	-9	-11	-4	11	5	26	0	0	1	-18	10	-12	-25	r5
				100	-36	-13	-21	-50	-15	6	-7	-82	5	-26	-65	-61	<1
					100	20	-2	-31	-10	-41	1	0	12	13	6	19	<2
						100	-13	-21	-2	-33	-6	-14	-12	16	6	-9	<3
							100	-39	3	-3	0	23	-28	4	8	21	<5
								100	21	27	8	63	11	7	56	38	<6
									100	5	2	18	-3	9	35	13	u5
										100	3	37	5	-8	6	15	u6
											100	9	1	2	7	8	u7
												100	-1	14	68	69	u10
													100	-5	2	7	u12
														100	28	12	u13
															100	62	k1
																100	k2

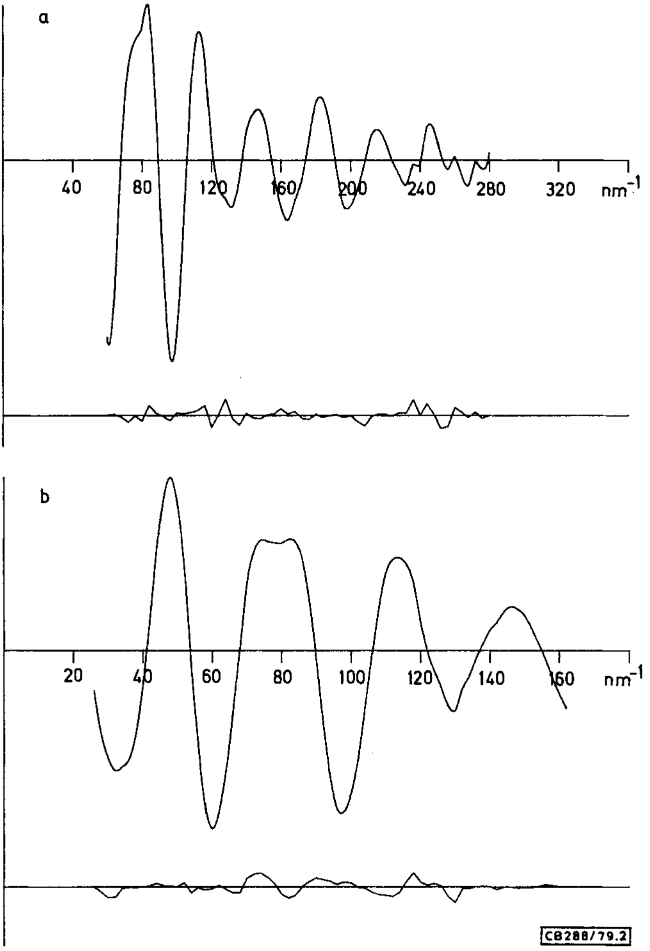


Figure 2. Observed and final weighted difference molecular scattering intensities of **1**, obtained with nozzle-to-plate distances of a) 128 and b) 285 mm

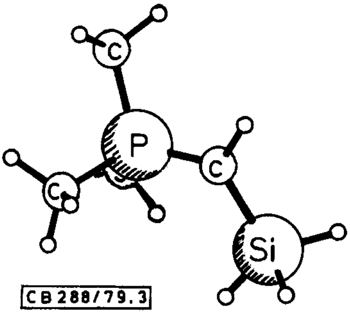


Figure 3. Molecular model of $(CH_3)_3P=CH-SiH_3$ (**1**)

tions, the geometry could be defined by the P – C, P = C, Si – C, C – H, and Si – H distances, the angles C = P – C, Si – C = P, P – C – H(methyl) and C – Si – H, the twist angle of the methyl groups, and a twist angle about the P = C bond, defined to be zero when the Si – C bond was *trans* to one P – C bond. The possibility of free rotation about the P = C bond was also considered, but this was soon discounted.

The principal features of the radial distribution curve for **1** (fig. 1) are two strong peaks at ca. 180 and 290 pm arising from pairs of heavy atoms separated by one and two bonds, respectively. As each of these peaks includes contributions from three different distances, there are several strong correlations between refining bond lengths and angles, and the amplitudes of vibration associated with these distances (table 1). In practice, it was found that the P – C and P = C distances and the Si – C = P angles all refined satisfactorily, but that no stable refinements were possible when the Si – C distance was included. From a comparison of *R* factors obtained with this parameter fixed at values between 170 and 190 pm, it was deduced that the optimum value was 185.2(20) pm. As this distance was varied, small changes in other refining parameters were noted, and allowances for these changes have been included in the quoted errors, which are otherwise estimated standard deviations derived from the least squares analysis, increased to allow for systematic errors.

Other significant peaks in the radial distribution curve arise from atom pairs including hydrogen, and so it proved possible to refine the mean C – H distance, the Si – H distance, the P – C – H(methyl) angle and the methyl twist angle. The remaining large peaks, above 350 pm, arise from the three Si···C distances, which define the conformation about the P = C bond. The possibility of free rotation about this bond was considered, but the best fit was obtained with a fixed conformation, with large amplitudes of vibration for the two shortest distances, and a much smaller one for the longest distance. By consideration of the rates of change of these distances with respect of the twist angle, it can be seen that these probably arise from a torsional vibration with an amplitude of about 15°.

In the final refinement, for which the *R* factors were 0.10 (R_G) and 0.07 (R_D), all geometrical parameters except the Si – C distance and the C – Si – H angle were included, together with six amplitudes of vibration. The final parameters are listed in table 2, the experimental and difference intensity curves are shown in figure 2, and a molecular model is drawn in figure 3.

Discussion

The geometry of trimethyl(silylmethylene)phosphorane (**1**) is extremely similar to that of unsubstituted trimethylmethylenephosphorane[6]. It has a slightly longer P = C bond, 165.3(11) pm compared with 164.0(6) pm, and a narrower C = P – C angle, 115.0(13)° compared with 116.5(6)°, but otherwise interatomic distances and amplitudes of vibration are essentially the same in the two molecules. The silyl substitution therefore has little effect on the phosphorane, and there is no evidence for any extended P = C – Si electron delocalisation, which would be expected to lead to a substantial lengthening of the P = C bond and to a shortening of the Si – C bond. The length of the latter is 185(2) pm, very slightly shorter than the Si – C bonds in methylsilane

[186.7(1) pm][10], but the difference is no greater than would be expected for a change from sp^3 to sp^2 hybridised carbon.

Table 2. Molecular parameters of $(CH_3)_3P=CHSiH_3$ (**1**)

		Distance (pm)	Amplitude (pm)
Independent distances (r_a)			
$r1$	(P – C)	180.7(8)	5.3(fixed)[a]
$r2$	(P = C)	165.3(11)	4.8(fixed)[a]
$r3$	(Si – C)	185.2(20)[b]	5.3(fixed)[a]
$r4$	(C – H)	110.7(7)	9.2(9)
$r5$	(Si – H)	149.4(12)	7.0(fixed)
Dependent distances[c]			
$d6$	(Si···P)	308.7(11)	9.5(9)
$d7$	(Si···C)	463.4(22)	16.2(30)
$d8$	(Si···C)	356.8(42)	29.4(fixed)[a]
$d9$	(Si···C)	405.4(46)	
$d10$	(C···C)	292.0(29)	10.5(21)
$d11$	(C···C)	283.5(32)	
$d12$	(C···H)	377 – 386	11.9(18)
$d13$	(P···H)	243.0(21)	11.5(9)
Independent angles (degrees)			
<1	(C = P – C)	115.0(13)	
<2	(Si – C = P)	123.4(8)	
<3	(P – C – H) (methyl)	110.7(7)	
<4	(C – Si – H)	110.5(fixed)	
<5	(P = C twist)[d]	25.0(14)	
<6	(methyl twist)[d]	27.7(21)	

[a] Value obtained by refinement, but not included in final refinement.

[b] See text.

[c] Other C···H, Si···H, P···H, and H···H distances were included in refinements but are not listed here. No other amplitudes of vibration were refined.

[d] For definition, see text.

The most important parameter is the Si – C = P angle. Given that the possibility of extensive delocalisation of a lone pair of electrons from carbon to silicon is ruled out by the length of the silicon-carbon bond, one would expect the ylide structure I to have an Si – C = P angle close to the tetrahedral angle, 109.5°, whereas the ylene structure, II, would have an angle somewhat greater than 120°. The experimental angle is 123.4(8)°, and this therefore reinforces the view, based on the P = C bond length, that insofar as the geometry of the molecule is concerned, the ylene representation is the more acceptable. It should be pointed out, that this result is not conflicting with the high polarity of ylides and their strong basicity and nucleophilicity in chemical reactions.

An alternative approach to the interpretation of bond angles is to use the concept of "hard sphere radii"[11], and to consider the distances between atoms separated by two bonds. Typical Si···Si distances in simple disilyl compounds are 306 – 301[12,13], but are as small as 300 pm in trisilylamine[14], and P···P distances are usually around 295 pm[15–17]. Thus it should easily be possible to get Si···P contacts down to about 300 pm, and indeed this distance is 303 pm in difluoro(silylamino)phosphane[18]. In the present case, however, the Si···P distance is 308.7(11) pm, and in the closely related compound trimethyl(trimethylsilylimino)phosphorane the equivalent distance is 307.2(10) pm[19]. It would therefore appear that in these cases the nonbonded contact approach does not adequately account for the observed structures.

The conformation adopted by the silylmethylene group is such that neither the C – H nor the C – Si bond eclipses a P – C bond, but there is evidence from Si···C amplitudes of vibration that the torsional vibration about the P = C bond has a large amplitude.

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Experimental Part

(2-Chloroethyl)silane: 40 g Trichloro(2-chloroethyl)silane (0.2 mol) is diluted with 25 ml di-n-butyl ether and added rapidly to a suspension of excess $LiAlH_4$ in 500 ml of the same solvent held at –10 °C. The product is condensed into a trap at –78 °C *in vacuo,* the condensate redistilled over a Vigreux column and the fraction at b.p. 25 °C/120 Torr collected (10 g, 50% yield). – ^{1}H-NMR ([D$_6$]benzene): δ = 1.06 [tq, 2H; ^3J(HH) = 8.6; ^3J(HH) = 3.9 Hz], 3.44 (t, 3H); 3.50 (t, 2H). – ^{13}C-NMR ([D$_6$]benzene): δ = 11.93 [t, ^1J(CH) = 126.8 Hz]; 42.7 [t, ^1J(CH) = 153.8 Hz]. – ^{29}Si-NMR ([D$_6$]benzene, rel. TMS ext.): δ = –55.2 [q, ^1J(SiH) = 198.5 Hz].

Trimethyl(silylmethylene)phosphorane (**1**) (Trimethylphosphonium-silylmethylide): 1.8 g $(CH_3)_3PCH_2$ (20 mmol) and 0.95 g $H_3SiCH_2CH_2Cl$ (10 mmol) are reacted in 25 ml diethyl ether at –78 °C. A white precipitate is formed immediately. It is filtered at –20 °C and volatiles are evaporated from the filtrate at this temperature *in vacuo*. The clear liquid residue (1.2 g, 95% yield) consists of pure product, provided that the starting materials were pure and in exactly the correct molar ratio. The precipitate is shown to be $[(CH_3)_4P]Cl$ by IR and NMR spectra. The properties and spectra of the ylide have been reported previously[5].

Electron diffraction: Scattering intensities were recorded photographically on Kodak Electron Image plates, using the Cornell/Edinburgh diffraction apparatus[17,20]. The sample and nozzle were maintained at room temperature (293 K) during exposures. Two camera distances were used, 128 mm (1 plate) and 285 mm (4 plates), giving useful data over a range of 26 to 280 mm^{-1} in the scattering variable, s. Intensities were measured and digitised using a Jarrell-Ash double-beam microphotometer[21] with spinning plates. The electron wavelength, 5.117 ± 0.002 pm, was determined from the diffraction pattern of gaseous benzene.

Table 3. Weighting functions, correlation parameters, and scale factors

Camera Height mm	Δs nm^{-1}	$s_{\min}$ nm^{-1}	s_{w_1} nm^{-1}	s_{w_2} nm^{-1}	$s_{\max}$ nm^{-1}	correlation parameter	scale factor
128.4	4	60	100	220	280	0.026	0.870(26)
284.9	2	26	43	135	162	0.461	0.947(24)

Calculations were carried out on an ICL 2970 computer, using established data reduction[17] and least-squares refinement[22] programmes. Weighting points used in setting up the off-diagonal weight matrix are given in table 3, together with scale factors and correlation parameters. In all calculations the complex scattering factors of *Schäfer, Yates,* and *Bonham*[23] were used.

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