

^{29}Si , ^{13}C AND ^{31}P NMR SPECTRA OF SILICON-SUBSTITUTED
 ω -DIPHENYLPHOSPHINOALKYL SILANES,
 $(\text{CH}_3)_{3-n}(\text{OC}_2\text{H}_5)_n\text{Si}(\text{CH}_2)_m\text{P}(\text{C}_6\text{H}_5)_2^*$

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^{29}Si , ^{13}C , and ^{31}P NMR spectra of a series of compounds of the structure $(\text{CH}_3)_{3-n}(\text{C}_2\text{H}_5\text{O})_n\text{Si}(\text{CH}_2)_m\text{P}(\text{C}_6\text{H}_5)_2$ ($m = 1-6$, $n = 0-3$) are reported and assigned. Using monodeutero derivative of the compound with $m = 3$ and $n = 0$ an earlier assignment of ^{13}C NMR spectrum is confirmed, but the assignment in the compounds with $m = 4$ is reversed. Introduction of ethoxy groups leads to violation of additivity rule for the ^{13}C chemical shifts in the derivatives with $m = 1$. In all derivatives presence of one ethoxy group in the molecule has a profound effect on ^{31}P chemical shift which is not changed by any further increase in the number of ethoxy groups in the molecule. The changes in ^{29}Si chemical shifts follow the pattern known from other series of compounds. The observed trends in NMR parameters with changing n and m values can be explained by an interaction between phosphorus and oxygen atoms. Possible connections between the spectral parameters and catalysis employing the studied compounds are discussed.

In connection with our extensive study¹⁻⁸ of NMR spectra of carbonfunctional compounds of the type I



and in relation to the technical importance of ω -(diphenylphosphino)alkyl substituted silanes we studied⁹ the spectra of a series of compounds of the structure II

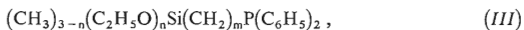


with $m = 1-4$. Since the effects of trimethylsilyl group on ^{31}P chemical shifts were small, we could conclude⁹, that this substituent does not adversely affect the complexing power of the phosphino part of the molecule. Similarly motivated

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studies of other systems have been published shortly afterwards by other research groups¹⁰⁻¹³.

In real situations, if the ω -diphenylphosphinoalkylsilane is used as an anchoring agent for a heterogenized homogenous catalyst, the trimethylsilyl group must be modified to provide binding to a supporting medium. One possible modification includes partial or full replacement of the methyl groups on the silicon atom by ethoxy groups. The resulting compounds



which have been proved to be useful in catalysis^{14,15} are also of spectroscopic interest since it has been shown¹⁻⁸ that the effects of substituent Y on ²⁹Si chemical shifts in *I* depend on the nature and number of substituents X (for a fixed number *m*). Results of such an extension of our earlier work⁹ are reported here.

RESULTS AND DISCUSSION

¹³C NMR Spectra

Assignment. The two methods of methylene carbon line assignment (*i.e.* either according to their chemical shifts or according to their ¹²C-³¹P coupling) led⁹ to the identical assignments for the compounds of the type *II* (*m* = 1-4). The only exception was the compound with *m* = 3 for which the assignment based on the chemical shifts was accepted⁹. In the series studied here discrepancies in the assignments occur also in compounds with *m* = 5 and 6. That prompted us to attempt specific deuterium labeling of one methylene group near the phosphorus atom. Unfortunately (see Experimental), we were successful only in preparation of 3-(diphenylphosphino)-2-deuteropropyltrimethylsilane the spectrum of which confirmed the earlier assignment⁹ with ²*J*(P-C) > ¹*J*(P-C) ~ ³*J*(P-C). Confirmation of this order of coupling constants makes the earlier assignment for the compound with *m* = 4 questionable. Using data of Gray and coworkers¹⁶ for *n*-butyldiphenylphosphine and the SCS values of (CH₃)₃Si and (C₂H₅O)₃Si groups⁷ additivity rule for substituent effects gives the following predictions for chemical shifts in compounds with *m* = 4:

Compound	Si*CH ₂	SiC*CH ₂	SiC ₂ *CH ₂	SiC ₃ *CH ₂
(CH ₃) ₃ Si(CH ₂) ₄ P(C ₆ H ₅) ₂	16.8	25.1	29.1	27.9
(C ₂ H ₅ O) ₃ Si(CH ₂) ₄ P(C ₆ H ₅) ₂	10.0	23.4	28.1	27.9

These predictions are in perfect agreement with the shifts observed for α and β carbon atoms (relative to the silicon atom) and if the original assignment⁹ for the remaining carbons is reversed, similarly good agreement holds for all the shifts and also the above relationship for the coupling constants is maintained (Table I). Accordingly,

we have assigned the shifts in compounds with $m = 5$ and 6 on the basis of this relationship for the coupling constants. Since the coupling constants and chemical shifts of α and γ carbons relative to phosphorus atom are similar, the assignment of these two chemical shifts is uncertain. Assignment of aromatic carbon chemical shifts was straightforward⁹ as well as that of methyl and ethoxy group carbons.

Methylene carbon chemical shifts and coupling constants. The chemical shifts fit the dependence on the Del Re total charges (Table II) described earlier^{2,3,9}, notable deviations occur only for the carbons directly attached to the phosphorus atom. These deviations are due to a very inadequate approximation in which the diphenylphosphino group had to be treated as a dimethylphosphino group.

Comparison of the present data with the chemical shifts in the corresponding alkylmethylethoxysilanes⁷ on one side and in alkyl-diphenylphosphines^{16,17} on the other shows that the substituent effects (SCS in Table III) of the two groups are additive in compounds with $m = 2, 3, 4$. In the derivatives with $m = 1$ the additivity rule is violated as can be demonstrated *e.g.* by the trend in SCS values of $P(C_6H_5)_2$ group. Apparently in these compounds some interaction between oxygenous substituents and phosphorus is taking place, in other compounds, with longer methylene chain, the substituents are too remote to interact and the SCS take also their usual values^{9,16,17}.

The phosphorus-carbon coupling constants show no sensitivity to the substitution on the silicon atom. This is especially surprising in compounds with $m = 1$ in which the coupling retains the same value and additivity of the chemical shifts is violated.

Aromatic carbon chemical shifts and coupling constants. As it is apparent from Table I the chemical shifts are not only independent of the alkyl chain length m but also of the nature of silicon substituents. Even in the series of compounds with $m = 1$ the chemical shifts are within the experimental error identical. Similarly, the variations in the carbon-phosphorus coupling constants exceed the experimental error only in the case of meta carbon. Therefore, the conclusions reached earlier⁹ for the compounds of the type II hold for the whole series of the studied compound III.

Methyl and ethoxy carbon chemical shifts. The chemical shifts of the methyl-on-silicon carbons do not reflect any influence of the diphenylphosphino group. They are practically the same as the corresponding chemical shifts in compounds of the type I with $Y = H$ (ref.⁷). The few available values of $^3J(^{13}C-^{31}P)$ couplings do not show any remarkable dependence on the substitution at the silicon atom. The chemical shifts of carbon atoms of the ethoxy group have their usual values⁷.

³¹P NMR Spectra

The dependence of ³¹P chemical shifts on alkyl chain length in compounds with $n = 0$ was described and discussed in detail⁹, the nonmonotonous trend is also paral-

TABLE I
 ^{13}C NMR Chemical shifts and carbon-phosphorus coupling constants in $(\text{CH}_3)_3\text{-}_n(\text{C}_2\text{H}_5\text{O})_n\text{Si}(\text{CH}_2)_m\text{P}(\text{C}_6\text{H}_5)_2$ compounds^a

<i>m</i>	<i>n</i>	Si^*CH_3		Si^*CH_2		SiC^*CH_2		$\text{SiC}_2^*\text{CH}_2$		$\text{SiC}_3^*\text{CH}_2$		$^{\text{H}}\text{C}^*\text{CH}_2$		$^{\text{H}}\text{C}^*\text{O}$		C_{ipso}^b		$\text{C}_{\text{ortho}}^b$		C_{meta}^b		C_{para}^b			
		δ	<i>J</i>	δ	<i>J</i>	δ	<i>J</i>	δ	<i>J</i>	δ	<i>J</i>	δ	<i>J</i>	δ	<i>J</i>	δ	<i>J</i>	δ	<i>J</i>	δ	<i>J</i>	δ	<i>J</i>	δ	<i>J</i>
1	0	-0.2 ^c	29.3	14.5	—	—	—	—	—	—	—	—	—	—	—	—	14.6	141.0	19.5	132.2	4.9	127.9	128.0		
1	1	-0.8 ^c	29.3	14.9	—	—	—	—	—	—	—	58.2	18.3	—	—	—	13.4	140.8	20.7	132.3	6.1	128.1 ^d	128.2 ^d		
2	2	-3.8 ^e	29.3	12.7	—	—	—	—	—	—	—	58.0	18.1	—	—	—	14.6	140.6	19.5	132.2	7.3	128.0	128.1 ^d		
3	3	—	29.3	9.4	—	—	—	—	—	—	—	58.3	17.9	—	—	—	14.6	140.6	19.5	132.2	7.3	127.9	128.1 ^d		
2	0	-1.9	11.0	12.0	14.6	21.6	—	—	—	—	—	—	—	—	—	—	14.6	138.9	18.3	132.5	6.1	128.1	128.1		
3	3	—	10.9	6.0	13.4	20.3	—	—	—	—	—	58.2	18.2	—	—	—	14.6	138.4	18.3	132.5	7.2	128.2	128.3		
3	0	-1.7	11.0	18.4	17.1	20.3	13.5	32.1	—	—	—	—	—	—	—	—	14.6	139.0	18.3	132.4	7.3	128.0	128.0		
2	2	-2.74	12.2	15.7	17.1	19.6	11.0	31.6	—	—	—	58.0	18.3	—	—	—	<i>f</i>	138.4 ^d	18.3	132.6	6.1	128.3	128.4		
3	3	—	12.2	12.1	18.3	19.4	11.0	31.3	—	—	—	58.1	18.1	—	—	—	13.4	138.7	18.3	132.4	4.9	128.0	128.0		
4	0	-1.6	0	16.3	12.2	25.5	15.9	29.6	12.2	27.8	—	—	—	—	—	—	13.4	139.1	18.3	132.5	6.1	128.1	128.1		
3	3	—	0	10.2	13.4	24.4	15.9	29.3	11.0	27.6	—	—	—	—	—	—	12.2	138.8	18.3	132.6	6.1	128.2	128.3		
5	3 ^g	—	0	10.3	0	22.4	13.4	34.6	15.9	25.6	—	—	—	—	—	—	13.4	138.8	18.3	132.6	6.1	128.2	128.4		
6	3 ^h	—	0	10.3	0	22.6	0	32.7	12.2	30.7 ⁱ	—	—	—	—	—	—	12.2	138.8	18.3	132.5	6.1	128.2	128.3		

^a The pertinent carbon is denoted by an upper left asterisk in the heading. The chemical shifts are in δ -scale, approximate error ± 0.05 ppm. Coupling constants are in Hz, their signs were not determined, approximate errors ± 1 Hz. ^b Aromatic carbon, the position relative to the substituent. ^c $J(^{13}\text{C}-^{31}\text{P}) = 3.7$ Hz. ^d Impurity in the vicinity of this line. ^e $J(^{13}\text{C}-^{31}\text{P}) = 2.4$ Hz. ^f Could not be determined because of impurity interference. ^g For $\text{SiC}_4^*\text{CH}_2$, $\delta = 27.9$ and $J(^{13}\text{C}-^{31}\text{P}) = 11.0$ Hz. ^h For $\text{SiC}_4^*\text{CH}_2$, $\delta = 24.3$ and $J(^{13}\text{C}-^{31}\text{P}) = 15.9$ Hz; for $\text{SiC}_5^*\text{CH}_2$, $\delta = 28.0$ and $J(^{13}\text{C}-^{31}\text{P}) = 11.0$ Hz. The assignment of the two doublets is uncertain.

TABLE II
The total net σ -electron charges in $(\text{CH}_3)_{3-n}(\text{C}_2\text{H}_5\text{O})_n\text{Si}(\text{CH}_2)_m\text{P}(\text{C}_6\text{H}_5)_2$ compounds, calculated by the Del Re method^a

<i>m</i>	<i>n</i>	Si*CH ₃	Si*CH ₂	SiC*CH ₂	SiC ₂ *CH ₂	SiC ₃ *CH ₂	SiC ₃ *CH ₂	SiC ₄ *CH ₂	SiC ₅ *CH ₂	O*CH ₂	OC*CH ₃	*P	*Si
1	0	-0.160	-0.154	-	-	-	-	-	-	-	-	0.119	0.141
	1	-0.146	-0.140	-	-	-	-	-	-	0.023	-0.106	0.114	0.232
	2	-0.147	-0.141	-	-	-	-	-	-	0.022	-0.106	0.114	0.442
	3	-	-0.142	-	-	-	-	-	-	0.022	-0.106	0.115	0.650
2	0	-0.145	-0.099	-0.107	-	-	-	-	-	-	-	0.117	0.021
	3	-	-0.103	-0.108	-	-	-	-	-	0.022	-0.106	0.117	0.651
3	0	-0.145	-0.099	-0.068	-0.112	-	-	-	-	-	-	0.118	0.021
	2	-0.148	-0.102	-0.070	-0.112	-	-	-	-	0.022	-0.106	0.118	0.443
	3	-	-0.103	-0.070	-0.112	-	-	-	-	0.022	-0.106	0.118	0.651
4	0	-0.145	-0.099	-0.068	-0.074	-0.113	-	-	-	-	-	0.118	0.021
	3	-	-0.103	-0.070	-0.074	-0.113	-	-	-	0.022	-0.106	0.118	0.651
5	3	-	-0.103	-0.070	-0.074	-0.075	-0.113	-	-	0.022	-0.106	0.118	0.651
6	3	-	-0.103	-0.070	-0.074	-0.075	-0.075	-0.113	-	0.022	-0.106	0.118	0.651

^a The pertinent atom is denoted by an upper left asterisk in the heading.

leled in the series of compounds with $n = 3$, for other series (Table IV) there is not enough data to permit comparisons.

The most surprising feature of the phosphorus chemical shifts in the studied series of compounds is their profound sensitivity to the presence of oxygenous substituent on the silicon atom. Independently of alkyl chain length, substitution of one methyl group on the silicon by ethoxy group causes considerable deshielding of the phosphorus, further substitution, however, has only negligible effect (*i.e.* in the studied cases with fixed m the shifts in compounds with $n = 1, 2$, and 3 are practically identical). This low-field shift even somewhat increases with increasing alkyl chain length, *e.g.* difference between the shifts in compounds with $n = 0$ and $n = 3$ increases from 7.0 ppm to 9.5 ppm to 8.8 ppm and to 9.0 ppm for m increasing gradually from 1 to 3, resp. The fact that this low-field shift is also observed in compounds with $m = 3$ in which the phosphorus atom is separated from oxygen by six bonds is suggestive that there is some direct interaction between phosphorus and the silicon substituent. Since this shift is not increased by an increase in n , it appears that only one of the substituents on the silicon can interact with the phosphorus atom by this

TABLE III

^{13}C Substituent chemical shifts of $\text{P}(\text{C}_6\text{H}_5)_2$ group (SCS-P) and of $(\text{CH}_3)_{3-n}(\text{C}_2\text{H}_5\text{O})_n\text{Si}$ group (SCS-Si) in $(\text{CH}_3)_{3-n}(\text{C}_2\text{H}_5\text{O})_n\text{Si}(\text{CH}_2)_m\text{P}(\text{C}_6\text{H}_5)_2$ compounds

m	n	SCS—P ^a			SCS—Si ^b		
		α	β	γ	α	β	γ
1	0	14.5			1.8		
	1	15.8			2.2		
	2	16.2			0.0		
	3	16.8			-3.3		
2	0	15.4	4.2		1.6	0.1	
	3	14.2	3.5		-4.4	-1.2	
3	0	13.9	2.7	-1.2			
	2	13.8	3.1	-0.8			
	3	13.9	2.8	-1.1			
4	0	14.4	3.9	-0.5	2.5	1.0	1.2
	3	15.2	4.3	0.1	-3.6	-0.1	0.9

^a Calculated from the present data and the shifts in the corresponding alkylsilanes⁷, in ppm ± 0.5 ppm. ^b Calculated from the present data and shifts in the corresponding alkyl-diphenylphosphines^{16,17}, in ppm, ± 0.5 ppm.

way. Of course, it is also possible that phosphorus atom enters an interaction with the silicon atom when that is substituted by an electronegative substituent like oxygen. Such interaction, however, should be discernable from the ^{29}Si chemical shifts; as will be seen below, no such interaction was noticed.

^{29}Si NMR Spectra

The trends in ^{29}Si chemical shifts of Table IV agree with the trends described for other series of similar compounds¹⁻⁸, the dependence on the number of substituents follows the "sagging pattern"¹⁸, the effect of diphenylphosphino group (SCS values) is small and decreases with alkyl chain length. The SCS values exceed appreciably the experimental errors only in compounds with $m = 1$. In that case the effect of diphenylphosphino group increases in magnitude with increasing number of ethoxy

TABLE IV
 ^{29}Si and ^{31}P chemical shifts and coupling constants in $(\text{CH}_3)_{3-n}(\text{C}_2\text{H}_5\text{O})_n\text{Si}(\text{CH}_2)_m\text{P}(\text{C}_6\text{H}_5)_2$ compounds^a

<i>m</i>	<i>n</i>	^{29}Si			^{31}P	
		<i>J</i>	δ	SCS—P ^b	δ	SCS—Si ^c
1	0	15.0	1.31	1.31	-30.7	-4
	1	17.09	15.26	1.76	-23.2	+3
	2	17.58	-9.70	-3.6	-23.6	+2
	3	15.14	-50.56	-6.06	-23.7	+2
2	0	20.89	2.54	0.9	-18.6	-6
	3	31.25	-47.10	-1.2	(-9.1)	+3
3	0	0	1.13	0.4	-26.1	-9
	2	0	-6.24	+1.36	-17.1	0
	3	1.47	-46.50	+0.5	-17.3	0
4	0	0	1.46	0.9	-24.9	-8
	3	0	-46.17	+1.2	-15.9	+1
5	3	0	-45.73	0	-15.8	0
6	3	0	-45.50	0	-16.0	0

^a The chemical shifts are in δ scale. ^{31}P shifts are relative to external 85% H_3PO_4 . Estimated error ± 0.1 ppm. Coupling constants *J* are ^{29}Si — ^{31}P couplings determined from ^{29}Si NMR spectra. They are in Hz with approximate error ± 1 Hz. ^b SCS—P = $\delta(\text{Si}(\text{CH}_2)_m\text{P}(\text{C}_6\text{H}_5)_2) - \delta(\text{Si}(\text{CH}_2)_m\text{H})$ in ^{29}Si NMR spectra, data of ref.⁷. ^c SCS—Si = $\delta(\text{Si}(\text{CH}_2)_m\text{P}(\text{C}_6\text{H}_5)_2) - \delta(\text{H}(\text{CH}_2)_m\text{P}(\text{C}_6\text{H}_5)_2)$ in ^{31}P NMR spectra, data of ref.^{16,17}.

groups bonded to the silicon atom. The trend in the SCS values closely parallels that in other compounds⁷ of the type *I* with $Y = \text{CH}_3$ or C_2H_5 . There is no indication of any special interaction between the silicon atom and any other part of the molecule in the ²⁹Si NMR spectra of the studied molecules.

Structural Conclusions

It has been shown⁹ that in trimethylsilyl derivatives *II* the two substituents of the alkyl chain are independent and exercise also their effects on the other parts of the molecules independently. The present work has shown that substitution of methyl groups on the silicon atom by ethoxy group brings about some special interactions which are reflected in the NMR spectra: additivity rule is violated in compounds with $m = 1$, and profound changes in phosphorus chemical shifts are observed even if $m = 4$. Absence of any anomaly in ²⁹Si spectra can be taken as an indication that this interaction does not involve silicon atom. It seems most likely that a direct interaction between phosphorus atom and oxygen is taking place.

This interaction apparently involves only one of the oxygen atoms present in the molecule, its averaged effect on chemical shifts of the carbons of the ethoxy group is negligible. It can be anticipated that this interaction should not affect adversely the support-binding ability of triethoxysilyl group.

On the other hand, the noticed interaction leads to a low-field shift of ³¹P resonance. If the chemical shift can be straightforwardly interpreted in the terms of electron density, the above shift should indicate a decrease in the electron density and hence some decrease in the complexing power of diphenylphosphino group in a free solution.

Comparison of these findings with the found activity of catalysts employing the studied ligands supports our earlier conclusion that the catalytic activity is controlled by steric factors^{14,19} in a homogenous catalysis and by the mobility of the anchoring ligands in the heterogenized case^{14,15,20}.

EXPERIMENTAL

Preparation of ω -diphenylphosphinoalkylsilanes was described before¹⁴. 3-Diphenylphosphino-2-deuteropropyltrimethylsilane was prepared by an addition of deuterodiphenylphosphine on allyltrimethylsilane. The addition was carried out at 60°C under a continuous UV irradiation for 100 hours. Attempts for an analogous addition of deuterodiphenylphosphine on 5-(trimethylsilyl)-1-pentene were not successful.

The spectra were measured under the identical conditions as described earlier⁹, details of Del Re calculations were also given elsewhere².

REFERENCES

1. Schraml J., Chvalovský V., Mägi M., Lippmaa E.: This Journal 40, 897 (1975).
2. Schraml J., Nguyen-Duc-Chuy, Chvalovský V., Mägi M., Lippmaa E.: Org. Magn. Resonance 7, 379 (1975).

3. Schraml J., Včelák J., Engelhardt G., Chvalovský V.: *This Journal* **41**, 3758 (1976).
4. Schraml J., Chvalovský V., Mägi M., Lippmaa E.: *This Journal* **42**, 306 (1977).
5. Schraml J., Chvalovský V., Mägi M., Lippmaa E.: *This Journal* **43**, 3365 (1978).
6. Schraml J., Nguyen-Duc-Chuy, Novák P., Chvalovský V., Mägi M., Lippmaa E.: *This Journal* **43**, 3202 (1978).
7. Schraml J., Chvalovský V., Mägi M., Lippmaa E.: *This Journal* **44**, 854 (1979).
8. Schraml J., Ponec R., Chvalovský V., Engelhardt G., Jancke H., Kriegsmann H., Larin M. F., Pestunovich V. A., Voronkov M. G.: *J. Organometal. Chem.* **178**, 55 (1979).
9. Čapka M., Schraml J., Jancke H.: *This Journal* **43**, 3347 (1979).
10. Singh G., Reddy G. S.: *J. Org. Chem.* **44**, 1057 (1979).
11. Vincent E., Verdonck L., Van der Kelen G. P.: *Spectrochim. Acta* **36A**, 699 (1980).
12. Vincent E., Verdonck L., Van der Kelen G. P.: *J. Mol. Struct.* **65**, 239 (1980).
13. Naaktgeboren A., Nolte R. J. M., Drenth W.: *J. Amer. Chem. Soc.* **102**, 3350 (1980).
14. Czaková M., Čapka M.: *J. Mol. Catal.* **11**, 313 (1981).
15. Michalska Z. M., Čapka M., Stoch J.: *J. Mol. Catal.* **11**, 323 (1981).
16. Gray G. A., Cremer S. E., Marsi K. L.: *J. Amer. Chem. Soc.* **98**, 2109 (1976).
17. Mann B. E.: *J. Chem. Soc., Perkin Trans. 2*, 1972, 30.
18. Lauterbur P. C. in the book: *Determination of Organic Structure by Physical Methods* (F. C. Nachod, W. D. Phillips, Eds), Vol. 2, p. 465. Academic Press, New York 1962.
19. Jakoubková M., Čapka M.: *This Journal* **45**, 2219 (1980).
20. Kozák Z., Čapka M.: *This Journal* **44**, 2624 (1979).

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