has a maximum, which is characteristic of autocatalytic reactions and is obtained for the oxidation of H_2O_2 with xenon trioxide in 1 *M* H_2SO_4 (Fig. 3, curve *2*), and the good time correlation of curves *1* and *2* (curve *3*) attest to the validity of the assumptions made for explaining kinetic peculiarities of the CL-process observed in the interaction of U(IV), XeO_3, and H_2O_2 in aqueous solutions of sulfuric acid.

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Synthesis of diphenyl[alkyl(aryl)trimethylsiloxymethyl]phosphines

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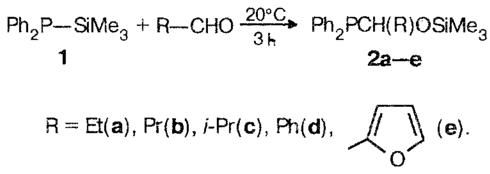
A series of previously unknown diphenyl[alkyl(aryl)trimethylsiloxymethyl]phosphines was prepared by the reaction of diphenyl(trimethylsilyl)phosphine with carbonyl compounds. The first complexes of these ligands with palladium chloride were prepared.

Key words: diphenyl(trimethylsilyl)phosphine, reactions with aldehydes and ketones.

It is known that functionally substituted tertiary phosphines behave as ligands of transition-metal complexes.[1] In the present work a general synthesis of diphenyl[alkyl(aryl)trimethylsiloxymethyl]phosphines has been proposed and complexes of these compounds with palladium chloride have been prepared.

It is known that diethyl(trimethylsilyl)phosphine reacts with formaldehyde to produce diethyl(trimethylsilylmethyl)phosphine[2] and with α,β-unsaturated aldehydes to give products of 1,4-addition .[2,3]

We have found that less active diphenyl(trimethylsilyl)phosphine (**1**) reacts with some aliphatic and aromatic aldehydes at room temperature to produce the corresponding diphenyl[alkyl(aryl)trimethylsiloxymethyl]phosphines (**2a—e**). Phosphine yields are 50—70 %.



$$\underset{\mathbf{1}}{Ph_2P{-}SiMe_3} + R{-}CHO \xrightarrow[3\,h]{20\,^{\circ}C} \underset{\mathbf{2a{-}e}}{Ph_2PCH(R)OSiMe_3}$$

R = Et(**a**), Pr(**b**), *i*-Pr(**c**), Ph(**d**), (**e**).

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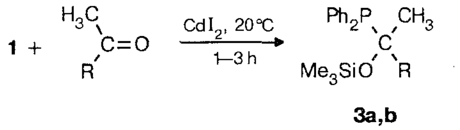
Table 1. Physicochemical characteristics, yields, and data of ^{31}P NMR and elemental analysis of compounds **2a—e**, **3a—e**

Compound	Yield (%)	B. p./°C (0.01 Torr)	n_D^{20}	NMR ^{31}P δ	Found/Calculated (%) C	H	P	Elemental formula
2a	50	98—100*	—	−6.5	68.04 68.35	7.12 7.91	9.68 9.81	$C_{18}H_{25}OPSi$
2b	65	126—127	1.5620	−8.0	68.67 69.09	7.52 8.18	9.22 9.39	$C_{19}H_{27}OPSi$
2c	70	125—126	1.5615	−8.4	68.86 69.09	6.94 8.18	9.47 9.39	$C_{19}H_{27}OPSi$
2d	70	169—171*	—	2.8	72.84 72.53	6.62 6.78	8.52 8.50	$C_{22}H_{25}OPSi$
2e	52	166—168	1.5624	−5.0	67.53 67.77	6.51 6.54	8.90 8.74	$C_{20}H_{23}O_2PSi$
3a	50	112—113	1.5651	13.0	68.30 68.35	8.54 7.91	9.69 9.81	$C_{18}H_{25}OPSi$
3b	52	170—171	1.5674	21.0	72.54 72.78	7.91 7.43	8.20 8.17	$C_{23}H_{28}OPSi$
3c	56	154—155	1.5680	6.0	70.57 70.85	7.90 8.14	8.55 8.71	$C_{21}H_{29}OPSi$

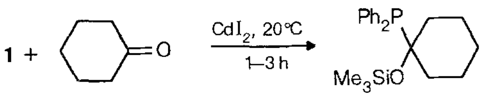
* M.p./°C: 61(**2a**); 68(**2d**).

The addition of diphenyl(trimethylsilyl)phosphine at the carbonyl group of ketones was successful only in the presence of a catalytic amount of cadmium iodide. The reaction proceeds for 3 hours, and the yields of the corresponding phosphines **3a, b** are 50—60 %.



3a,b

R = Me(**a**), Ph(**b**)



3c

Table 1 presents physicochemical characteristics, data of elemental analysis, yields and spectral parameters of the compounds synthesized. Phosphines **2** react with lithium tetrachloropalladate in methanol to form corresponding complexes **(4)**.

$$2\,Ph_2PCH(R)OSiMe_3 + Li_2PdCl_4 \xrightarrow[-2\,LiCl]{20°C}$$

2c,d

$$\longrightarrow [Ph_2PCH(R)OSiMe_3]_2PdCl_4$$

4a,b

R = *i*-Pr(**a**), Ph(**b**)

Compounds **4** were used as catalysts in cross-coupling reactions.

Experimental

All procedures were carried out in dry argon. ^{31}P NMR spectra were recorded using a Varian FT—80 A spectrometer. The external standard was H_3PO_4 (85 %).

Diphenyl[alkyl(aryl)trimethylsiloxymethyl]phosphines (2a-e, 3a-c). General procedure. Aldehyde or ketone (4 mmol) was added to 4 mmol (0.23 g) of (trimethylsilyl)diphenylphosphine (in the case of ketones 0.04 mmol (0.0146 g) of cadmium iodide was also added to the reaction mixture). After stirring for 1—3 h at ca. 20°C the mixture was distilled in *vacuo* to obtain phosphines **2a-e** or **3a-c**.

Bis[diphenyl(isopropyltrimethylsioxymethyl)phosphine]palladium(II)chloride (4a). A solution of lithium tetrachloropalladate (4 mmol) in methanol (2 mL) was added dropwise to a mixture of phosphine **2c** (0.8 mmol) dissolved in methanol (2 mL) to obtain **4a**, which was recrystallized from hexane. Yield 78 %, m. p. 90 °C. ^{31}P NMR (δ, ppm): 9.4. Found (%): (C) 54.39, (H) 6.23. C_{38} $H_{54}O_2C_{12}P_2PdSi$. Calculated (%): 54.51 (C), 6.45 (H).

Bis[diphenyl(phenyltrimethylsiloxy)methylphosphine]palladium(II)chloride (4b). Procedures for complexes **4b** and **4a** are the same. The yield is 94%, m. p. 104°C.^{31}P NMR (δ, ppm) 19.2. Found (%): 73.01 (C), 7.14 (H). $C_{46}H_{54}O_2C_{12}P_2PdSi_2$. Calculated (%): 72.83 (C), 7.02 (H)

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