

Letters to the Editor

Synthesis of (acylethynyl)triphenylphosphonium bromides

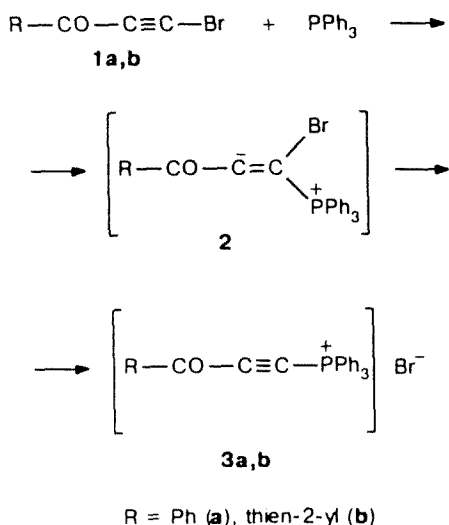
V. N. Yelokhina and A. S. Nakhmanovich*

*Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences,
1 ul. Favorskogo, 664033 Irkutsk, Russian Federation.
Fax: +7 (395 2) 46 6434*

It is known that reaction of 1-bromoacetylenes with sodium dialkyl phosphites or with trialkyl phosphites affords ethynylphosphinates.^{1,2}

Organylthioethynylphosphonates were obtained by the reaction of 1-chloro-2-alkylthioacetylenes with trialkyl phosphites, following the Arbuzov rearrangement pattern.³

We found that 1-bromo-3-benzoyl(thenoyl-2)acetylenes (**1a,b**) readily interact with triphenylphosphine in



ether at 20 °C to afford (acylethynyl)triphenylphosphonium bromides (**3a,b**) (in 79–88 % yields), which were not described previously. One may assume that this reaction proceeds by the mechanism of nucleophilic substitution of a bromine atom upon intermediate formation of carbanion **2**.

Compounds **3a,b** may be used as reagents for fine organic synthesis.

(Benzoylethynyl)triphenylphosphonium bromide (3a). A solution of triphenylphosphine (2.62 g, 0.01 mol) in abs. ether (15 mL) was slowly added to a solution of 1-bromo-2-benzoylacetylene (2.09 g, 0.01 mol) in abs. ether (20 mL), and the mixture was stirred for 0.5 h at 20 °C. The precipitate formed was filtered off and washed on a filter with cold (0 °C) ether to afford 3.72 g of **3a** (79 %), m.p. 99–100 °C. Found (%): C, 68.45; H, 4.32; Br, 16.75; P, 6.56. $\text{C}_{27}\text{H}_{20}\text{BrOP}$. Calculated (%): C, 68.79; H, 4.25; Br, 16.99; P, 6.58. IR, ν/cm^{-1} : 1445 (P–Ph); 1660 (C=O); 2085 (C≡C).

(2-Thenoylethynyl)triphenylphosphonium bromide (3b) was obtained by a similar procedure from 1-bromo-2-thenoylacetylene (2.15 g, 0.01 mol) and triphenylphosphine (2.62 g, 0.01 mol). The yield of **3b** was 4.20 g (88 %), m.p. 139–140 °C. Found (%): C, 63.05; H, 3.79; Br, 16.97; P, 6.52; S, 6.78. $\text{C}_{25}\text{H}_{18}\text{BrOPS}$. Calculated (%): C, 62.89; H, 3.77; Br, 16.77; P, 6.50; S, 6.71. IR, ν/cm^{-1} : 705 (C–S); 1440 (P–Ph); 1662 (C=O); 2105 (C≡C).

References

1. G. Sturtz, C. Charrier, and H. Normant, *Bull. Soc. Chim. Fr.*, 1966, 1707.
2. B. I. Ionin and A. A. Petrov, *Zh. Obshch. Khim.*, 1962, **32**, 2387 [*J. Gen. Chem.*, 1962, **32** (Engl. Transl.)].
3. A. N. Mirskova, N. V. Lutsкая, and M. G. Voronkov, *Zh. Obshch. Khim.*, 1979, **49**, 2668 [*J. Gen. Chem.*, 1979, **49** (Engl. Transl.)].

Received October 17, 1995

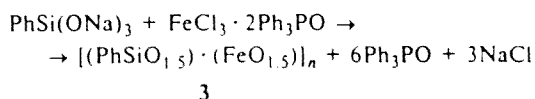
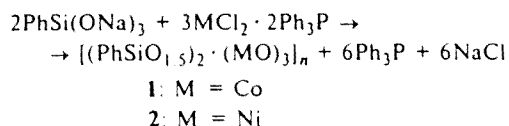
Peculiarities of the introduction of transition metal atoms with *n*-donor ligands into the siloxane framework

M. M. Levitsky,* N. V. Karpilovskaya, A. N. Gavrilova, B. G. Zavin, and E. S. Shubina

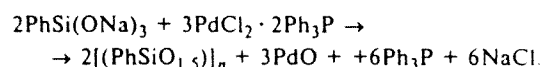
A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: dir@ineos.ac.ru

At the present time, various types of filling of the coordination sphere of a metal (M) in a siloxane chain are known: a metal atom can coordinate with the O atom of a metallosiloxane —M—O—(R)Si— fragment or of an aliphatic alcohol as well as with a siloxanolate anion RSiO^- ($\text{M} = \text{Co}$,^{1,2} Ni ³). In addition, variants involving π -bonded ($\text{M} = \text{Zr}$)⁴ and σ -bonded ($\text{M} = \text{Sn}$)⁵ organic ligands are described. Addition of an *n*-donor ligand to the metal atom in the siloxane chain is also possible ($\text{M} = \text{Ti}$, V).⁶

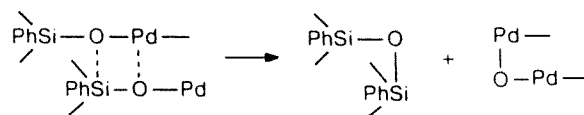
We studied the possibility of introduction of metal atoms already bonded to *n*-donor ligands into the siloxane chain. It is established⁷ that the reactions of butanol solutions of organosilanolate $\text{C}_6\text{H}_5\text{Si}(\text{ONa})_3 \cdot 6\text{Pr}^n\text{OH}$ with metal-complex compounds $\text{MCl}_n \cdot 2\text{L}$ ($\text{M} = \text{Co}$, Ni , $n = 2$, $\text{L} = \text{Ph}_3\text{P}$; $\text{M} = \text{Fe}$, $n = 3$, $\text{L} = \text{Ph}_3\text{PO}$) at an equimolar ratio of Na^+ and Cl^- results in the formation of metallosiloxane (MS) accompanied by substitution of the organophosphorus ligand. Oxygen atoms of the metallosiloxane fragment play the role of a substituting ligand. The exchange reaction occurs according to the scheme:



Found (%): 1, Si, 11.10; Co, 35.95; Si/Co, 0.65; 2, Si, 10.90; Ni, 35.81; Si/Ni, 0.64; 3, Si, 12.95; Fe, 26.10; Si/Fe, 0.99. The data of the UV spectra [CHCl_3 , $\lambda_{\text{max}}/\text{nm}$: 1 (555 (ϵ 28)) and 2 (390 (ϵ 45), 690 (ϵ 38))] are similar to those obtained for Co-MS^2 and Ni-MS^3 whose coordination metal spheres are filled with O atoms of M-O-Si(R) fragments. According to the elemental analysis data, none of the MS formed contains phosphorus. Colorless crystalline products whose composition corresponds to ligands of metal-containing compounds were isolated from the reaction mixture: Ph_3P , m.p. 78–80 °C (from benzene) (cf. Ref. 8: m.p. 79 °C), and Ph_3PO , m.p. 154–156 °C (from benzene) (cf. Ref. 8: m.p. 156 °C). In the case of $\text{M} = \text{Pd}$, the reaction occurs via a different scheme:



The formation of PdO is the result of the intermolecular rearrangement according to the scheme:



Reaction products: (1) colorless amorphous polysiloxane [found (%): C, 55.12; Si, 21.12; $(\text{PhSiO}_{1.5})_n$; calculated (%): C, 55.86; Si, 21.77]; (2) black amorphous precipitate [found (%): Pd, 86.2; PdO ; calculated (%):