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. Lutskaya, and M. G. Voronkov, *Zh. Obshch. Khim.*, 1979, **49**, 2668 [*J. Gen. Chem.*, 1979, **49** (Engl. Transl.)].

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

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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 $RSiO^-$ (M = Co,[1,2] Ni [3]). In addition, variants involving π-bonded (M = Zr)[4] and σ-bonded (M = Sn)[5] organic ligands are described. Addition of an *n*-donor ligand to the metal atom in the siloxane chain is also possible (M = Ti, V).[6]

We studied the possibility of introduction of metal atoms already bonded to *n*-donor ligands into the siloxane chain. It is established[7] that the reactions of butanol solutions of organosilanolate $C_6H_5Si(ONa)_3 \cdot 6Pr^nOH$ with metal-complex compounds $MCl_n \cdot 2L$ (M = Co, Ni, *n* = 2, L = Ph_3P; M = Fe, *n* = 3, L = Ph_3PO) 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:

$$2PhSi(ONa)_3 + 3MCl_2 \cdot 2Ph_3P \rightarrow \rightarrow [(PhSiO_{1.5})_2 \cdot (MO)_3]_n + 6Ph_3P + 6NaCl$$

1: M = Co
2: M = Ni

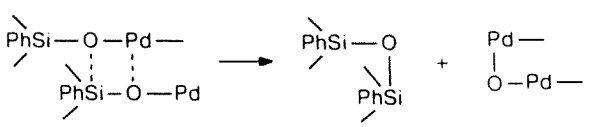
$$PhSi(ONa)_3 + FeCl_3 \cdot 2Ph_3PO \rightarrow \rightarrow [(PhSiO_{1.5}) \cdot (FeO_{1.5})]_n + 6Ph_3PO + 3NaCl$$

3

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 [$CHCl_3$, λ_{max}/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 M = Pd, the reaction occurs *via* a different scheme:

$$2PhSi(ONa)_3 + 3PdCl_2 \cdot 2Ph_3P \rightarrow \rightarrow 2[(PhSiO_{1.5})]_n + 3PdO + +6Ph_3P + 6NaCl$$

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; $(PhSiO_{1.5})_n$; calculated (%): C, 55.86; Si, 21.77]; (2) black amorphous precipitate [found (%): Pd, 86.2; PdO; calculated (%):

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Pd, 86.9]; and (3) crystalline product, m.p. 79—80 °C (from benzene), Ph_3P (*cf.* Ref. 8: m.p. 79 °C).

The results obtained show that the synthesis of metallosiloxanes involves the displacement of the *n*-donor ligand from the coordination sphere of metal by the highly basic oxygen atom of the metallosiloxane fragment.

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References

1. Yu. E. Ovchinnikov, A. A. Zhdanov, M. M. Levitsky, V. E. Shklover, and Yu. T. Struchkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1206 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 1098 (Engl. Transl.)].
2. V. A. Igonin, O. I. Shchegolikhina, S. V. Lindeman, M. M. Levitsky, Yu. T. Struchkov, and A. A. Zhdanov, *J. Organomet. Chem.*, 1992, **423**, 351.
3. M. M. Levitsky, O. I. Shchegolikhina, V. A. Igonin, Yu. E. Ovchinnikov, V. E. Shklover, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1991, **401**, 199.
4. F. J. Feher, *J. Am. Chem. Soc.*, 1986, **108**, 3850.
5. F. J. Feher, T. A. Badzichovski, R. L. Blanski, K. J. Weller, and W. Z. Joseph, *Organometallics*, 1991, **10**, 2526.
6. F. J. Feher and J. F. Walzer, *Inorg. Chem.*, 1990, **29**, 1604.
7. A. A. Zhdanov, M. M. Levitsky, and O. Yu. Shilkloper, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 958 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, 877 (Engl. Transl.)].
8. *Spravochnik khimika* [*Chemist's Manual*], Khimiya, Moscow, 1971, **2**, 1060 (in Russian).

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Perfluoroperhydro-7,10-diazaphenanthrene

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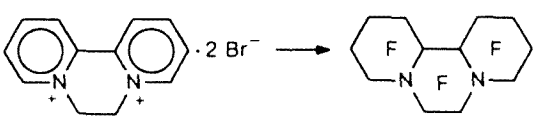
Perfluoroperhydro-7,10-diazaphenanthrene (**2**), the first representative of a new class of compounds, *viz.*, perfluorinated tricyclic amines with two bridged nitrogen atoms, was obtained in high yield by electrochemical fluorination of diquat dibromide (**1**) (product of quaternization of 2,2′-dipyridyl by 1,2-dibromoethane) in liquid hydrogen fluoride.



1 **2**

Conditions of electrolysis: concentration of **1** in HF 17 wt. %, current density 500—550 A/m^2, temperature 20 °C.

Fluorination products were separated from HF, washed with H_2O and $NaHCO_3$, and distilled. The preparative yield of compound **2** was 65 %, b.p. 173—175 °C. Found: C, 24.2; F, 70.6; N, 4.4. $C_{12}F_{22}N_2$. Calculated: C, 24.4; F, 70.8; N, 4.7.

Compound **2** is a mixture of six stereoisomers in a ratio of 1 : 0.2 : 0.03 : 0.02 : 0.015 : 0.01 (from the data of JC-MS). Mass spectrum of the main isomer: 590 M^+ (4.2 %); 571 [M^+—F] (14.6 %); 521 [M—CF_3] (2.5 %); 371 (1.0 %); 326 (1.3 %); 176 (2.8 %); 145 (1.7 %); 131 (17.1 %); 119 (7.8 %); 114 (4.9 %); 100 (100 %); 69 (17.5 %).

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